

Hans-Klaus Roth, Klaus Heinemann, Gerhard Gobsch

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and showed also remarkable patience in preparing this proceedings of TPE 10.

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Hans-Klaus Roth, Klaus Heinemann
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Part X:

Posters

NANOSCALE ULTRAVIOLET AND OZONE DEGRADATION OF P3OT THIN FILMS STUDIED BY SCANNING PROBE MICROSCOPY AND RELATED TECHNIQUES

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In the field of organic solar cells the power conversion efficiency and the durability are issues that have to be addressed before this technology could be competitive with traditional silicon solar cells. One of the research lines of our group is devoted to a better understanding of how the nanoscale properties determine the macroscopic behaviour of such devices [1-4]. In order to study the durability of plastic solar cells, we investigate in the present work the modification of thin P3OT films by ultraviolet (UV) radiation and ozone degradation. Films of 50-200 nm thickness have been prepared by spin-coating on conducting as well as insulating substrates. The morphology and electrostatic properties of the thin films were studied at room temperature and ambient conditions using scanning force microscopy (SFM). A commercial SFM system with a phase locked loop (PLL)/dynamic measurement board [5] was used with Olympus OMCL-AC-type cantilevers (nominal force constant: 2 N/m; resonance frequency: 70 kHz). Unless specified otherwise, imaging was performed in non-contact dynamic SFM (NC-DSFM) using the oscillation amplitude as feedback parameter. A special home build piezo and sample holder allowed us to perform a nanoscale studies of the same area of the sample in order to attribute the observed changes to the real effect of radiation as compared to possible statistical variations of surface properties. The prepared P3OT thin films were also characterized using macroscopic electronic transport techniques. Since the resistance of the samples is very high, the conventional four probe configuration can not be used and therefore the experimental set up has been a two probe system, where a controlled voltage is applied to the sample with a programmable voltage source acting as active load (Keithley Mod. 220) while the current is measured with an electrometer (Keithley Mod. 6514) which allows us to measure ultra-low currents [6]. All measurements were performed at room temperature and dark conditions. Tungsten probes with controlled contact pressure have been used. Therefore, we will present a detailed study of the correlation between nanoscale structure and macroscopic measurements, which ultimately will deliver important consequences on the final performance of the devices.

Results

Figure 1 show images ($20 \times 20 \mu\text{m}^2$) of a P3OT thin film (108 nm thickness) before A) and after UV irradiation B) 5 minutes, C) 7 minutes, D) 10 minutes, E) 15 minutes, and F) 30 minutes. It is important to note that always the images show the same zone of the sample. Figure 1 A) is a typical image of this kind of thin film, a flat surface with many balls, we think that these balls are polymer aggregates which have not been well dissolved during the preparation method. During the first 5 minutes of exposure no significant changes on the morphology of the samples are observed, figures 1 B), only some holes appear (marked in the image with an I) with a depth around 9 and 18 nm. After 7 minutes a new hole appears in the largest ball (lower part of the image) and the balls are surrounded by a fuzzy rim. These rims are clearly observed after 10 minutes of UV irradiation, figure 1D). However, the main changes are observed after 15 minutes, figure 1 E), where small grains like structures appear over the surface and in the case of the largest structure, the hole reaches all the way down to the glass substrate (depth about 100 nm). Finally after 30 minutes, figure 2 F), the small grains like structures coalesce to form larger features making the surface more blurred and the surface roughness has significantly increased, as it is analyzed in detail in figure 2.

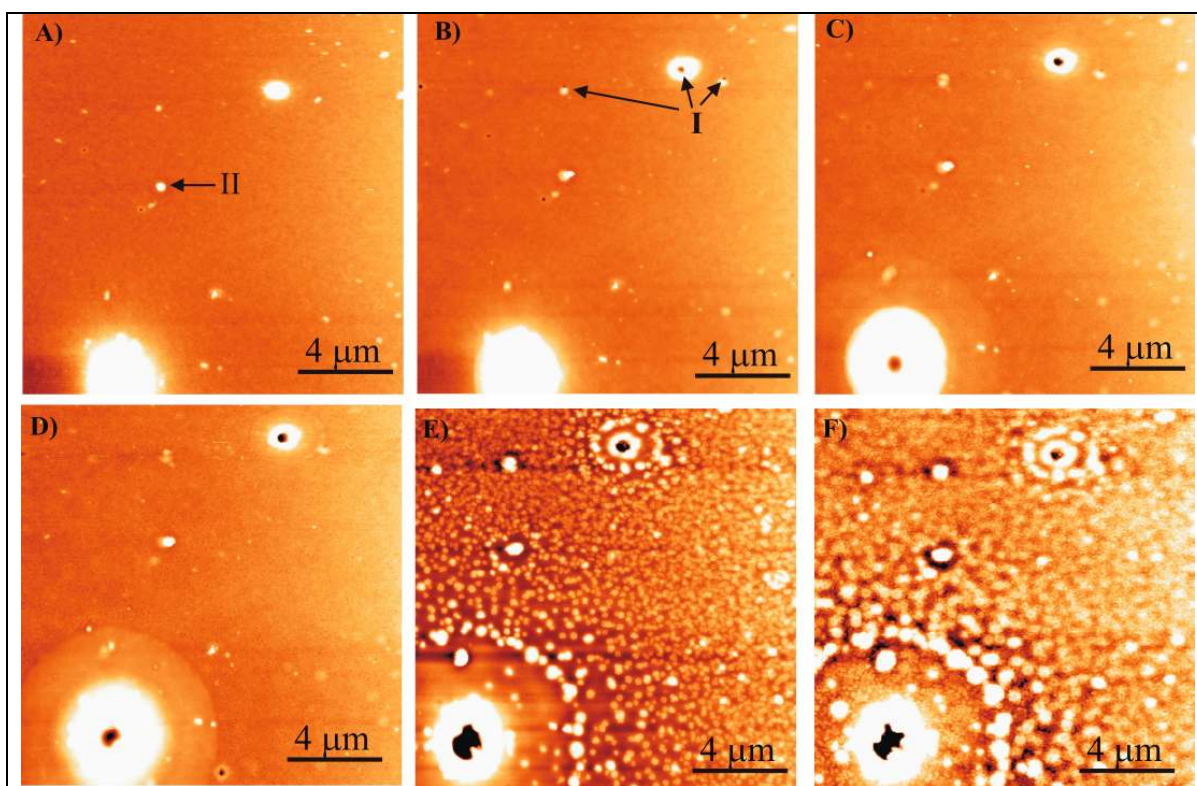


Figure 1: A series of SFM topographic images ($20 \times 20 \mu\text{m}^2$) showing the morphology of the P3OT thin film (a) pristine sample, (b) after 5 minutes, (c) 7 minutes, (d) 10 minutes, (e) 15 minutes and (f) 30 minutes of UV irradiation. In all images $\Delta z = 50 \text{ nm}$.

Figure 2 shows the root mean square (RMS) roughness evolution as function of the UV irradiation. In order to calculate the RMS roughness a rectangle of $10 \times 13 \mu\text{m}^2$ centered in the feature marked II has been analyzed for each image of figure 1, allowing to determine RMS roughness on the same area of the sample, thus we can attribute the observed roughness changes to the real effect of radiation as compared to possible statistical variations of surface properties. In the graph we observe that within the experimental error the roughness is almost constant in first 10 minutes of UV irradiation and increases after 10 minutes. Therefore in view of the figures 1 and 2 the main morphology changes are produced between 10 and 15 minutes of UV irradiation.

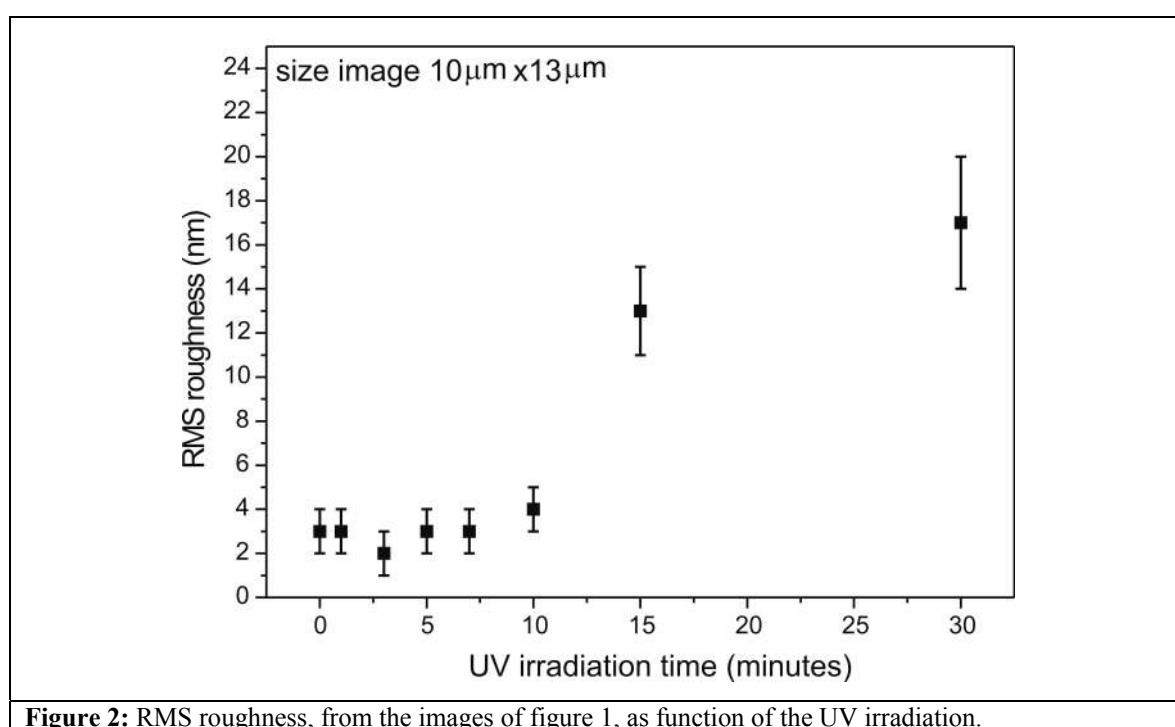


Figure 2: RMS roughness, from the images of figure 1, as function of the UV irradiation.

To estimate the height of the films, these were very carefully scratched off in order to expose the substrate. The corresponding trench was imaged by SFM to determine the film thickness after each cycle of UV irradiation to study the relationship between UV irradiation time and film thickness. We have found that in the first 10 minutes of irradiation the film thickness is almost constant (around 100 nm). However, after 10 minutes the thickness decreases linearly with the time exposure until a value of 25 nm for 60 minutes of irradiation. It is remarkable that the change in the thickness versus time exposure dependence coincide with the main changes observed in the morphology of the samples (roughness increase).

The observed nanoscale structural changes have been correlated with the macroscopic

transport properties. After each irradiation cycles following the SFM measurement I-V transport curves have been acquired. A summary of results is presented in figure 3. After every exposure, we applied a voltage sweep and recorded the current. From both values we obtain the resistance presented in the figure. With further analysis, correlated with the thickness obtained by SFM, and considering the probe configuration, the conductivity behaviour can be obtained. The trend is therefore clear: an exponential dependence of the conductance of the film against the UV time exposure is obtained: the conductance decreases exponentially with increasing time exposure. Only after more than 10 minutes of exposure a conductance increase is obtained and is related with the thickness decrease of the thin films. Further UV exposure reduces strongly the thickness of the sample and we can not perform macroscopic transport measurements.

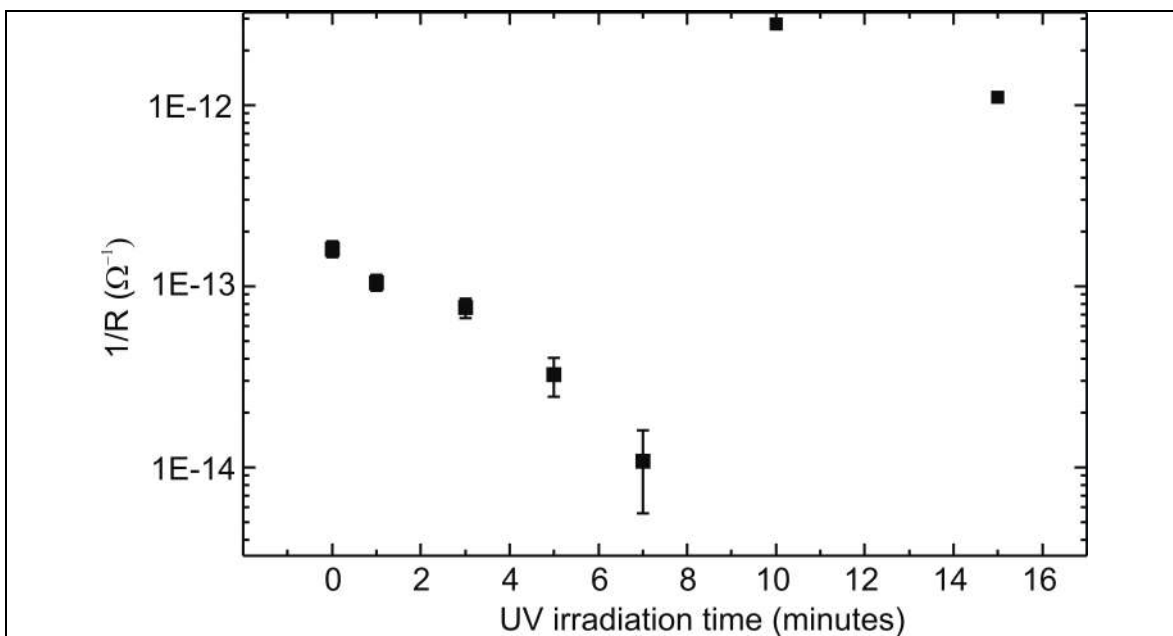


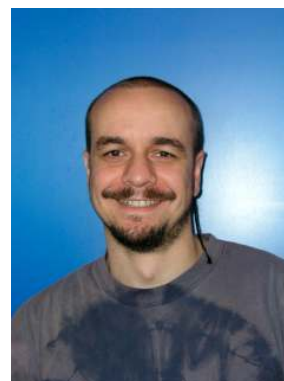
Figure 3: Macroscopic two-probe electronic transport measurements on P3OT thin films for different UV irradiation times in a low voltage linear regime (from -1 to 1 volts)

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- [4] J. Abad *et al.* *European Polymer Journal* **44**(2008) 2506.
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- [6] A. Urbina *et al.* *European Physical Journal: Appl. Phys.* **37** (2007) 283.

BIOGRAPHIC DATA OF DR JOSE ABAD

Jose Abad studied physics at the Complutense University in Madrid, Spain where he got his degree in Physics in 1999. After that period he obtains his Ph D. degree in Sciences at the Autonoma University of Madrid in 2005, as predoctoral student in The Institute of Materials Science of Madrid. The research theme developed in his doctoral thesis was the “Study of the crystalline and electronic structure of the $\text{SiO}_x\text{-TiO}_2$ (110) system and its reactivity with nitric oxide”. To complete his research formation the applicant made two predoctoral stays (7 months in total, years 2001 and 2002) at the Fritz Haber Institute of the Max Planck Society, Berlin.



In 2005 he moved to the Synchrotron Elettra, Trieste, Italy. For the construction of the experimental end station and testing the "Bad Elph" beamline.

In 2006 he moved to the University of Murcia to joint the group of Dr. Jaime Colchero, He was contracted to build up an ultra high vacuum (UHV) scanning force microscopy (SFM) On that period the applicant gained skill in atomic force microscopy and related techniques as electrostatic force microscopy (EFM), capacitance force microscopy (CFM), conducting force microscopy using jumping mode (CFM-JM) and Kelvin probe microscopy (KPM). Besides he has collaborated in the development of different SFM operating in air and variable temperature.

In 2007 May the applicant visited (2 months) the NanoSciences Group at the CEMES-CNRS, Toulouse (to upgrade the detection system of an UHV-SFM).

In the University of Murcia he also began to study different organic conducting materials with very high potential applications in optoelectronics devices, as organic solar cells and organic light emitting diodes. In this kind of devices the understanding of the relationship between the nanomorphology of the organic active layer and the electronic properties in the nano and macro scale is crucial to improve the performance of the final devices.

RESIDUE-FREE NIL STRUCTURING TECHNIQUES FOR SUBMICRON OTFTs

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In this study we report on innovative nanoimprinting processes for the fabrication of patterned submicron OTFTs in a bottom-gate configuration. The methods are based on UV-Nanoimprint Lithography (UV-NIL)¹ and thermally initiated radical polymerization based Nanoimprint Lithography (TIP-NIL)², respectively. These techniques are combined with a novel imprint resist whose outstanding chemical and physical properties are responsible for the excellent results in structure transfer on both rigid and flexible substrates.

.....

The UV-NIL core process implies no extra temperature budget, imprints residue-free thus making etching obsolete, is time saving due to short curing times, eco-friendly due to a water-based lift-off and completely r2r compatible. It is shown that the UV-NIL technique works perfectly even if ultra-thin organic and hybrid films are used as gate dielectrics. On this basis, entirely patterned functional submicron OTFTs with pentacene as the semiconductor are fabricated showing clear saturation, low switch-on voltage (~3V) and a sufficiently high on-off ratio (10^3). In Fig. 1 a SEM image of an UV-NIL imprint result is shown.

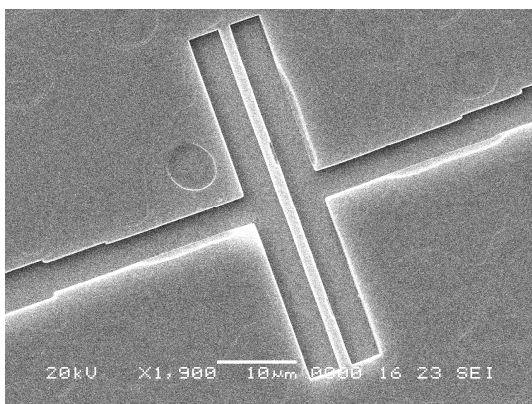


Figure 1: SEM image of the imprinted resist.

The principle of the UV-NIL process is illustrated in Fig. 2. The first step (A) is to align the silicon stamp, which contains the relief pattern of the source-drain electrodes, with respect to the gate electrode. Then the aligned stamp is pressed into the low-viscous resist, thus displacing the resist underneath the source-drain structures (B). Here, the innovation is an etch-free process enabled by residue-free displacement of the UV-NIL resist due to a high difference in polarity of resist and stamp.

Curing is performed by UV exposure for up to 2 min, depending on the initiator concentration, whereby the source-drain pattern is permanently transferred into the resist. After removing the stamp (C) the source-drain material - in our case gold - is evaporated onto the device (D). The subsequent lift-off is performed by dissolving the resist with deionized water, the evaporated gold layer on top of the resist is removed while the imprinted areas are preserved (E). Finally the active layer, which is pentacene here, is evaporated to complete the transistor structure (F).

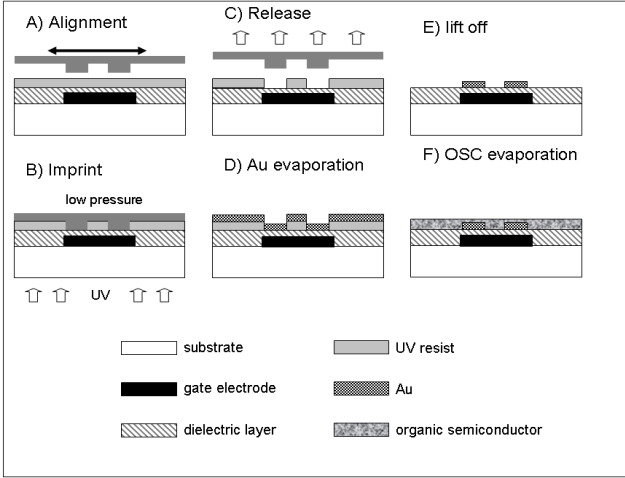


Figure 2: Scheme of the residue-free UV-NIL process

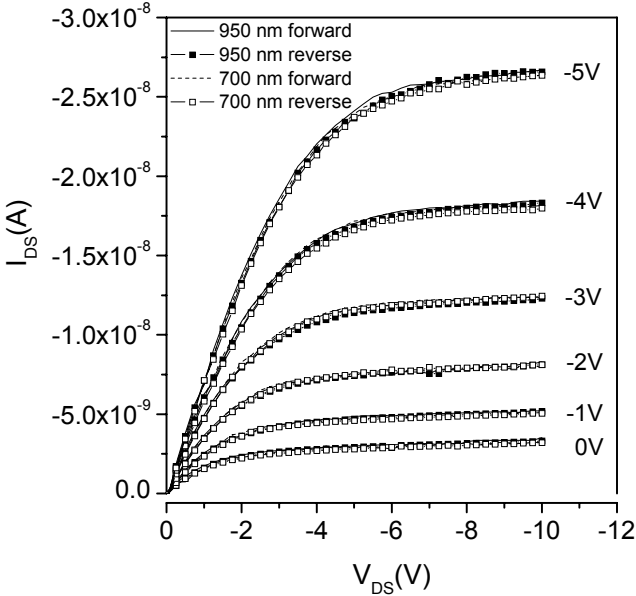


Figure 3: Output characteristics of an UV-NIL patterned OTFT

The effect of proper downscaling of device dimensions is illustrated in Fig. 3. The drain current at higher drain voltages fully saturates indicative of an insignificant influence of channel length modulation.

The electrical performance of submicron OTFTs fabricated by UV-NIL is very convincing. In this case the gate dielectric consists of a double layer of benzocyclobutene (BCB) and polyvinylene cinnamate (PVCi) both applied by spin coating. Due to the fact that gate dielectric layer thickness is smaller by more than a factor 5 than the channel length, an unbalanced increase of the lateral electric field with respect to the vertical one can be avoided, even for devices with channel lengths down to 500 nm.

In Figure 4 a scheme of the TIP-NIL process is shown: A silicon stamp containing the source–drain structures is aligned roughly onto the substrate (A). The stamp is pressed into the resist thus completely displacing the resist under the source–drain structures (B).

Subsequently, the resist is cured by thermal initiated polymerization. After the stamp removal (C) the source–drain material is evaporated onto the substrate (D).

The imprint resist is dissolved with water, which leaves the metal source–drain electrodes well preserved (E). Finally, the sample is covered by the organic active layer, pentacene (F).

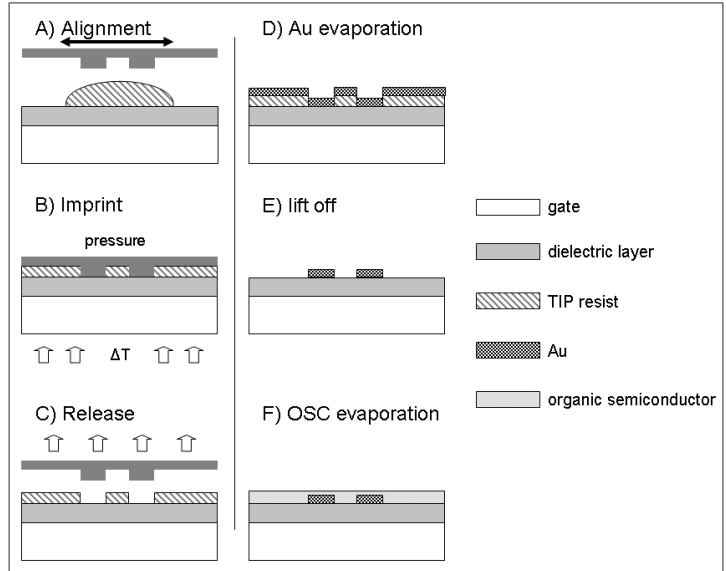


Figure 4: Scheme of the TIP-NIL process

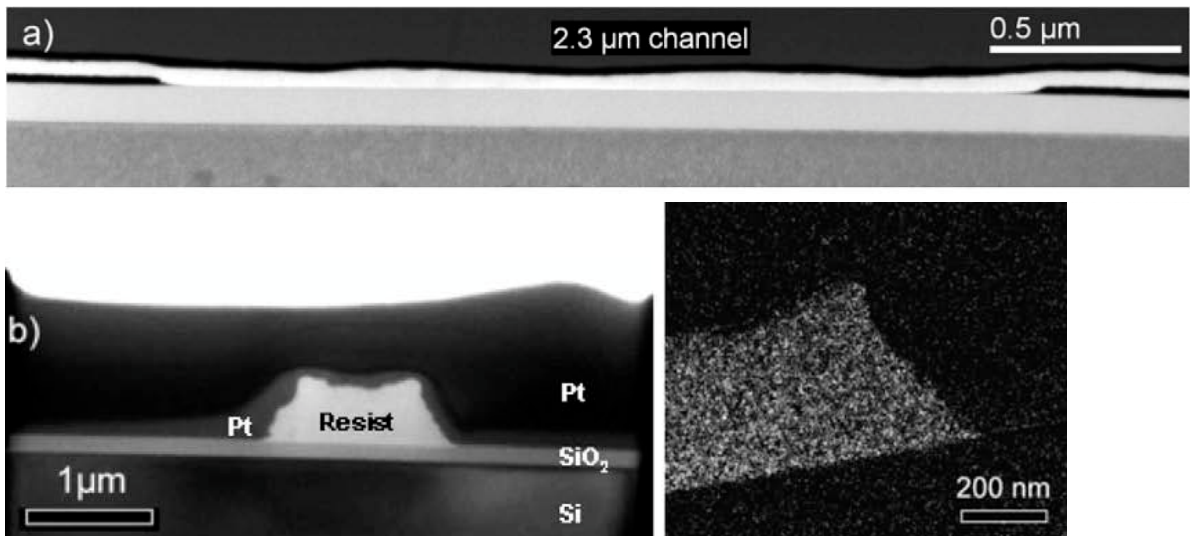


Figure 5: Imprint- and device characterisation (TIP NIL Process)

To characterize the imprint result, the specimens were investigated by transmission electron microscopy. Post column energy filters were used for zero-loss imaging and elemental mapping. The cross section lamellae of the samples were prepared using a focused ion beam instrument (FIB). A TEM bright field image of the lamella is displayed in Figure 5b, showing the troughs for the electrodes on the sides and the appearance of the resist (bright trapezoid) in the middle acting as place-holder for the channel. The organic

layer of the resist can clearly be distinguished from the Si/SiO₂ substrate. In order to investigate whether the imprint is residue-free or not, a close-up of the region near the resist edge was analyzed by energy filtered TEM, which enables the distinction of materials according to their elemental composition. Figure 5c represents an elemental map of the nitrogen distribution. Here, regions of materials containing nitrogen, such as TIP-NIL-ACMO, appear bright. It clearly reveals the limited spatial distribution of the imprinted TIP-NIL-ACMO layer in the channel region and its absence in the electrode areas. This is explicit evidence that the resist is displaced completely during the TIP-NIL process; no residue of the resist is observed in the imprinted areas. After lifting-off the gold layer on top of the TIP-NIL-ACMO resist by using deionized water, pentacene is thermally evaporated to finalize the transistor structure as shown in Figure 5a. Here, a cross section TEM image is presented. As expected, the gold electrode is perfectly preserved in the imprinted region (right and left parts of Fig. 5a), whereas it is gone in the channel where the TIP-NIL-ACMO was dissolved. Thereby, it is proven that the introduced TIP-NIL route gives excellent downscaled transistor structures.

In summary, we have fabricated well performing OTFTs with submicron channel lengths using an improved NIL processes. The UV-nanoimprinted OTFTs are comprised of pentacene as active semiconductor and an ultra-thin double layer gate dielectric composed of BCB and PVCi. With the novel UV-NIL process fully functional devices with channel lengths down to 700 nm could be fabricated showing complete drain current saturation and low switch-on voltages. The process is based on a special formulated UV-NIL resist optimally adapted to fast and precise nanoimprinting of organic electronic components. Since no heating step is involved in the process, thermal stress can be disregarded and, more importantly, thermally unstable materials can be used as substrates and gate dielectrics. Furthermore, the resist is cured by UV light which reduces the fabrication time decisively, thus enabling a high throughput. Remarkable is the absence of any residual layer after the imprint step, which makes etching obsolete. O₂-etching of organic dielectrics is known to increase the gate leakage and the number of OH-groups acting as traps at the interface. Furthermore, reactive ion etching is hard to implement in a standard printing line. Finally, the resist allows a lift-off with deionized water, which is a big advantage with respect to ubiquitous availability, the potential for immediate recycling and environmental sustainability, resulting in a decrease of the production costs and an increase of process safety. All in all UV-NIL has a huge potential as a high-resolution patterning

process for large-area fabrication of flexible organic electronics in a roll-to-roll manufacturing environment.

The TIP-NIL process also enables residue-free imprinting with the same advantages as described for the UV-NIL process. Furthermore, this process implies only moderate temperature budgets in comparison to Hot Embossing, is eco-friendly due to a water-based lift-off and provides complete r2r compatibility. To validate the process OTFTs with sub μm patterned source and drain contacts with pentacene as the semiconductor were fabricated showing excellent transistor behavior parameterized by a low switch-on voltage of $V_{\text{SO}} = -3\text{V}$, an on-off ratio of more than 10^5 and a charge carrier mobility of $\mu = 0,25 \text{ cm}^2/\text{Vs}$ (see Figure 6).

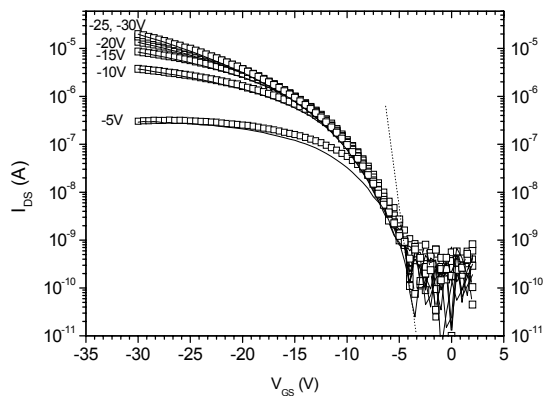


Figure 6: Transfer characteristics TIP-NIL OTFT with 950nm channel length.

¹ C. Auner et al.; *Organic Electronics*, Volume 10, Issue 8, December 2009, Pages 1466-1472

² C. Auner et al.; *Organic Electronics*, Volume 11, Issue 4, April 2010, Pages 552-557

REEL-TO-REEL WET COATING FOR THE FORMATION OF THIN FUNCTIONAL LAYERS IN BULK-HETEROJUNCTION POLYMER SOLAR CELLS

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Conjugated polymers and fullerene derivatives received attention for photovoltaic energy conversion. The primary step in the operation of such a polymer solar cell (PSC) is a fast photo-induced electron transfer from the conjugated polymer to the fullerene in a so-called “bulk heterojunction” (BHJ) architecture. With the realization of efficiencies (single layer) up to 7.9 %^[1] on glass and about 5 % on flexible substrates^[2] in lab and life times of about 2000 sun hours in the meantime the performance is close to that of amorphous silicon cells. The next step to a real production would be a test of large scale processing instead of discontinuous spin coating or doctor blading.

After the feasibility of BHJ-PSC on plastic foil using a reel-to-reel (R2R) slot die coating process^[3] could be demonstrated, the current focus is on search for alternative solvents, especially non-chlorinated because of environmental reasons to enable mass-production^[4]. For the R2R-preparation of the photoactive layers (P3HT:PCBM) we now tested xylene in comparison to chlorinated standard solvents. We reached in these first experiments with this solvent promising light power conversion efficiencies up to 1.17 % as maximum value (Fig. 1).

There is still much potential for further improvements to raise efficiency and processing speed. This will be part of the upcoming work.

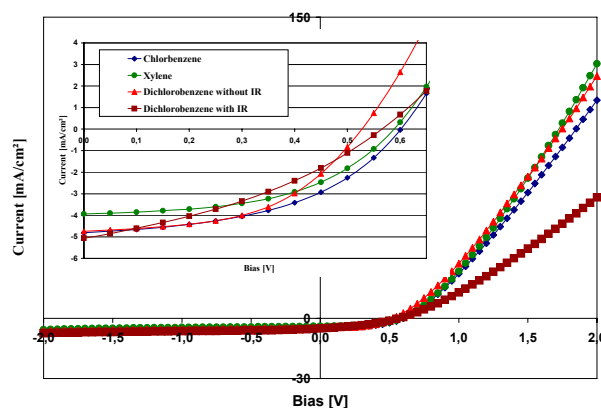


Figure 1: Slot die coating of low viscosity solution P3HT:PCBM (xylene, 1 m/min, 5 cm on PET/ITO foil with 2 m/min R2R coated PEDOT:PSS) at TITK e.V. coating machine LBA-200 (left) and I/V-characteristics of flexible solar cells; system: PET/ITO/ PEDOT:PSS-**R2R (2 m/min)**/P3HT:PCBM-**R2R (1 m/min; different solvents)**/Al; AM1.5, cell size 0.25 cm² (right)

- [1] Solarmer Energy, Inc. *press release* 3rd Dec 2009
- [2] TITK e.V. *press release* May 2010
- [3] L. Blankenburg, K. Schultheis, H. Schache, S. Sensfuss, M. Schrödner, *Solar Energy Materials & Solar Cells* 2009, 93, 476-483
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RECOMBINATION-LIMITED PHOTOCURRENT IN DITHIAPYRANNYLIDENE/PCBM BULK HETEROJUNCTIONS

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The Abstract of this poster is not available!

POLYANILINE–SILVER COMPOSITES

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Polyaniline is one of the most famous conducting polymers on account of high electrical conductivity, environmental stability, ease of preparation from common chemicals, good processibility and relatively low cost. In the last years, the interest in polyaniline–silver composite grew, because the presence of silver can still improve their conductivity. Such materials may also potentially be useful in applications, such as water treatment, noble-metal recovery, antibacterial substances, electrode materials, electrocatalysis, *etc.* [1,2].

Aniline was oxidized with silver nitrate in the solution of formic acid. The structure and properties of composites were characterized by Fourier-transform infrared (FTIR), Raman, and UV–visible spectroscopies, transmission electron microscopy (TEM), scanning electron microscopy, thermogravimetric analysis, density, and conductivity measurement.

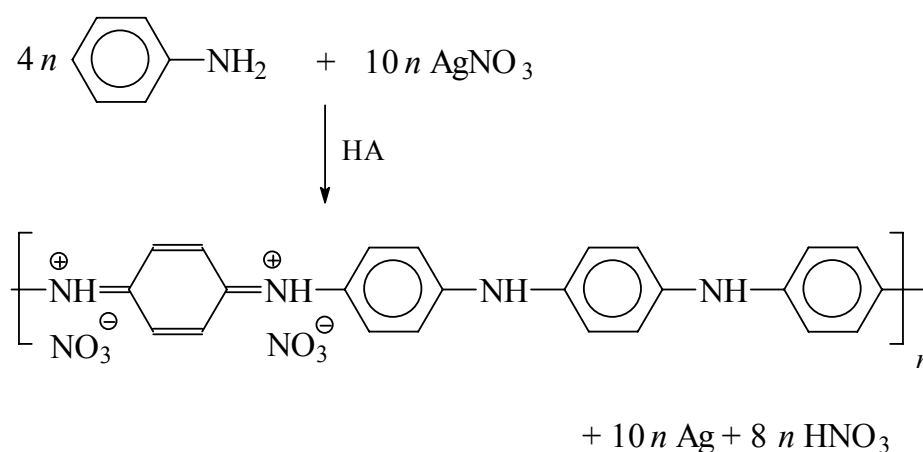


Fig. 1. Aniline is oxidized with silver nitrate to polyaniline–silver composite. HA is arbitrary acid, here, formic acid.

The true PANI–silver composites are produced at different concentration of formic acid, 0.1–5 mol L⁻¹. This is confirmed by UV–visible, FTIR, and Raman spectroscopy of products [3,4]. The highest conductivity of the composites was of the order of 10¹ S cm⁻¹. The high conductivity of composites after the deprotonation of PANI to its non-conducting

base form suggests that the overall conductivity is controlled rather by silver than by PANI. Silver nanowires of 20–80 nm diameter, as well as silver particles in the similar size range were coated with PANI, the hairy polymer overlayer having a thickness of 50–150 nm (Fig. 2).

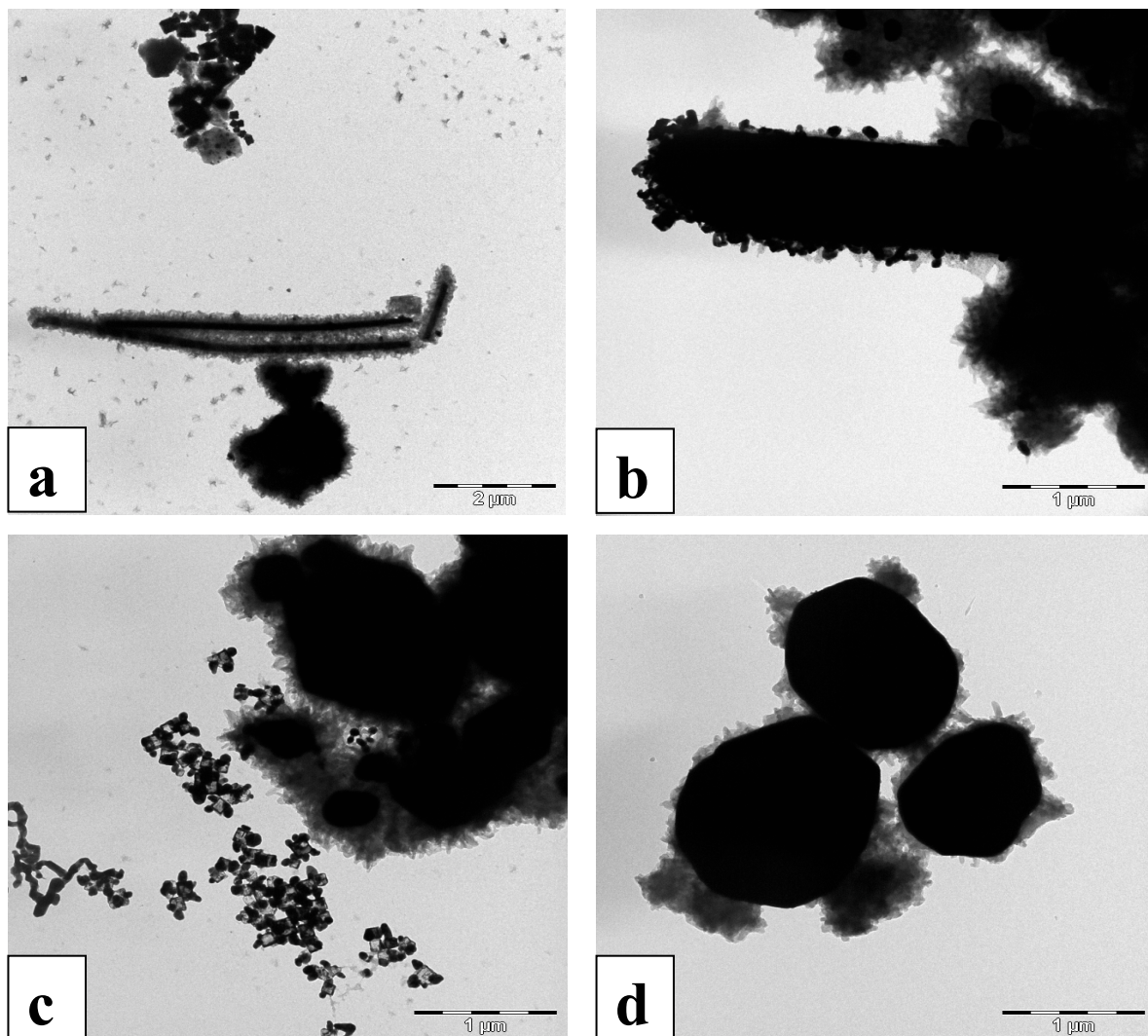


Fig. 2. The products of the oxidation of aniline with silver nitrate in (a) 0.1, (b) 0.5, (c) 1.0, and (d) 5.0 M formic acid.

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ORGANIC-BASED SOLAR CELLS WITH CdSe NANOPARTICLES AS ELECTRON ACCEPTOR MATERIAL

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Abstract

A promising concept to improve the efficiency of polymer/fullerene bulk heterojunction solar cells is to replace the fullerene component by inorganic semiconductor nanoparticles. The size-dependent, tunable optical properties of the nanoparticles should allow a better exploitation of the solar spectrum, and the possibility to use elongated nanoparticles should be favorable for efficient electron transport. Despite these advantages, efficiencies reported for hybrid solar cells are usually even below those of purely organic solar cells. In this contribution, hybrid solar cells containing a bulk heterojunction of poly(3-hexylthiophene) (P3HT) and colloiddally prepared CdSe nanoparticles were investigated. Systematic studies of correlations between the device performance and blend morphology are presented. Furthermore, the charge separation process was studied in detail by photophysical methods. Results point to the existence of a large amount of trap states which could provide an explanation for the still limited efficiency of this type of solar cells.

INTRODUCTION

Organic polymer/fullerene bulk heterojunction solar cells are perspective for low cost photo-voltaics, but their efficiency is still limited to about 5-6% [1,2]. One approach for improvement is to replace the fullerene component by inorganic semiconductor nanoparticles such as CdSe nanocrystals, giving rise to so-called hybrid solar cells. These have potential advantages over organic polymer/fullerene solar cells: First, based on the quantum size effect, tunable absorption properties enable a better exploitation of the solar spectrum [3]. Additionally, the possibility to use elongated semiconductor nanoparticles is regarded to be favorable for efficient electron transport because of a reduced number of

hopping steps [4]. However, despite these advantages, the efficiencies that have been reported for polymer/CdSe solar cells are still limited to about 3% [3,5]. The limited efficiency might partly be related to the morphology of the hybrid material blends which is even more difficult to control than in the case of purely organic composites. Additionally, more fundamental properties inherent to the nanoparticles might play a role.

In this work, we prepared hybrid solar cells with blends of poly(3-hexylthiophene) (P3HT) and CdSe nanoparticles. The mixing ratio was systematically varied, and the performance of the cells was characterized by current-voltage and quantum efficiency measurements. Atomic force microscopy (AFM) was used to study the structural properties of the films, and transport properties of charge carriers were investigated by measurements of the charge carrier mobility in organic field effect transistors (OFETs). Relationships between the structure, the charge carrier mobility and the device performance were analyzed. Moreover, light-induced electron spin resonance (L-ESR) and photo-induced absorption (PIA) spectroscopy were used to study the generation of long-lived charge carriers as well as their recombination kinetics.

EXPERIMENTAL

CdSe nanocrystals were prepared by colloidal synthesis with oleic acid as stabilizing ligand as described elsewhere [6]. After synthesis, the nanocrystals were treated with pyridine in order to remove the oleic acid ligand shell. The mean diameters of the nanoparticles prepared within this work were in the range of ~3-4 nm. Composites with different CdSe-to-P3HT mass ratios of 4:1 up to 12:1 were prepared under nitrogen atmosphere by mixing regioregular P3HT dissolved in chlorobenzene with CdSe nanoparticles dissolved in pyridine. Laboratory solar cells were prepared as described in Ref. [6] with the active layer consisting of the CdSe/P3HT blend sandwiched between an ITO/PEDOT:PSS anode and an aluminum cathode.

ESR and PIA measurements were performed as described elsewhere [7], a 532 nm cw laser was used for optical excitation. OFETs were prepared using highly doped p-Si wafers as the gate electrode. The gate insulator was a 200 nm layer of thermally grown SiO₂. Bottom Au contact devices were used in this study. The nanoparticle/ polymer blend was deposited by spin-coating and annealed for 20 min to 140°C afterwards. Solar cells were characterized by standard current-voltage (IV) measurements using a class B solar simulator for measurements under AM 1.5 conditions. Measurements of the external quantum efficiency (EQE) were performed with a xenon arc lamp as described in Ref. [6].

RESULTS AND DISCUSSION

Fig. 1 shows typical TEM images of CdSe nanoparticles after synthesis and after the ligand exchange with pyridine. After ligand exchange, the particles have a higher tendency to aggregate, indicating the successful removal of the comparably thick oleic acid shell.

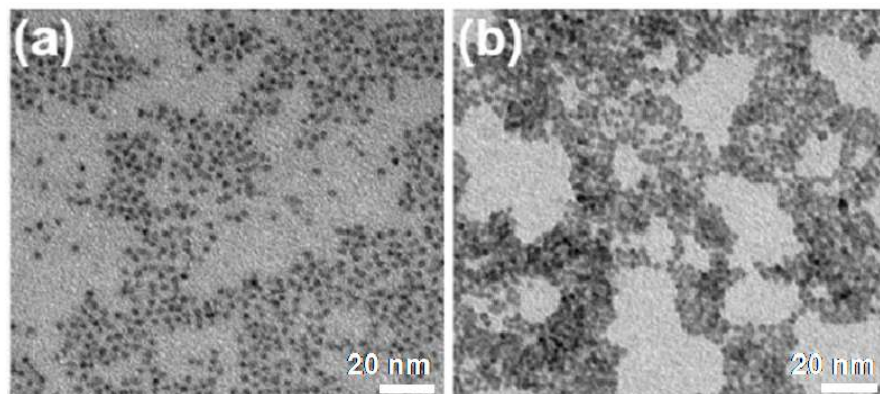


Figure 1 – TEM images of CdSe nanoparticles before (a) and after (b) ligand exchange with pyridine.

Figure 2 shows IV curves and EQE data for hybrid solar cells prepared with a systematically varied mass ratio of CdSe nanoparticles to polymer. At low nanoparticle content (ratio 4:1), the open circuit voltage, short circuit current density and fill factor are rather low and the efficiency under standard conditions (AM 1.5 irradiation, 100mW/cm²) is limited to ~0.2% [6]. At higher nanoparticle content (ratios around 10:1), the efficiency increases to ~0.6-0.7% [6], which is typical for hybrid solar cells based on quasi-spherical CdSe nanoparticles and P3HT [8,9].

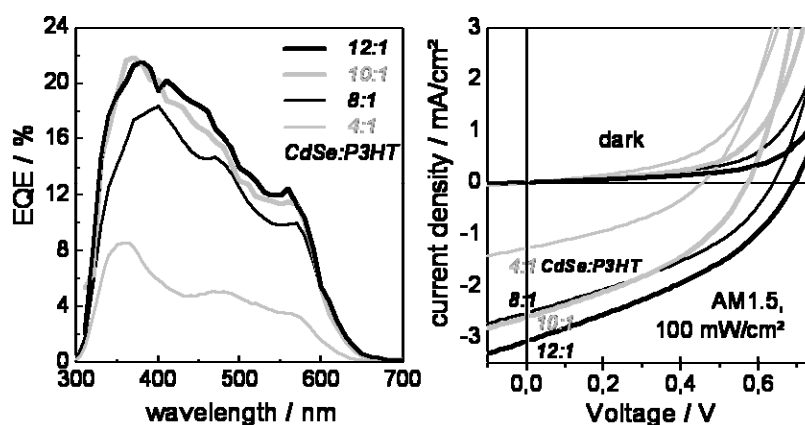


Figure 2 – EQE data (left side) and IV curves (right side) of CdSe/P3HT solar cells with varied CdSe-to-P3HT mass ratio.

The dependence of the performance on the CdSe-to-P3HT ratio was found to correlate with the morphology of the blends that was studied by tapping mode AFM (see Fig. 3) [6]. The phase images show contrast that is not correlated with the topographical features, meaning that this contrast can be attributed to material contrast. At low nanoparticle content (4:1), there is almost no phase contrast observable, suggesting that phase separation is not pronounced at this blending ratio and that percolation pathways for efficient charge transport are not sufficiently established. At higher nanoparticle content (around 10:1) material contrast indicating phase separation and the establishment of percolation pathways can be observed [6].

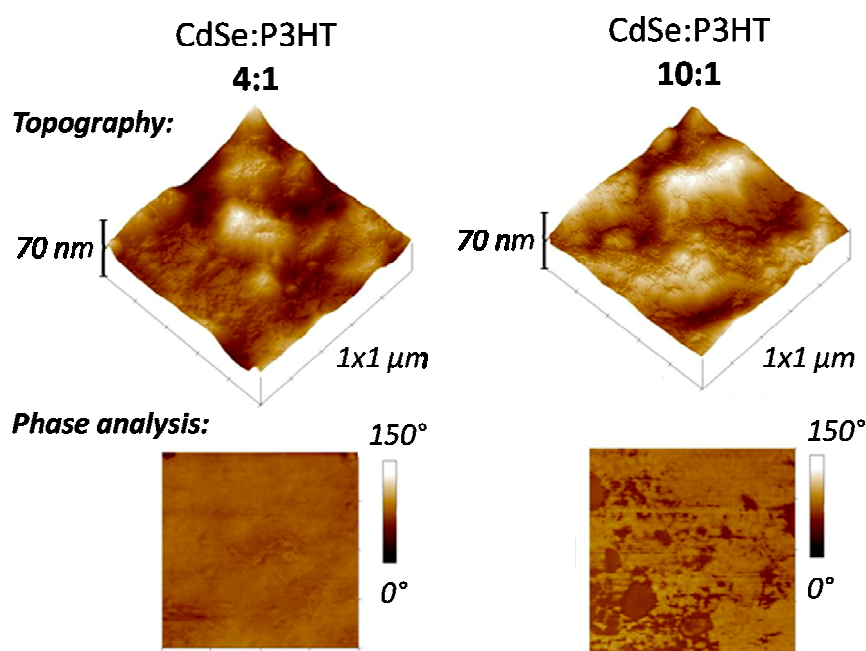


Figure 3 – AFM topography and phase images of CdSe/P3HT blends with different CdSe-to-P3HT mass ratio. The corner on the top of the topography images corresponds to the left upper corner in the phase images.

Preliminary experiments on the influence of the blending ratio on charge carrier transport were carried out by measuring hole mobility in OFET structures. At a mass ratio of 10:1 where reasonable power conversion efficiency is obtained, it was found that the presence of the nanoparticles does not reduce the hole mobility in the polymer phase [10].

ESR and PIA measurements were carried out in order to study charge separation and recombination in organic P3HT/PCBM and hybrid P3HT/CdSe blends [7]. Fig. 4 shows the temporal development of an ESR signal that can be attributed to positive polarons on the polymer. Under light-excitation, realized by switching on a 532 nm laser source, the signal increases in both cases, because additional polarons are generated as a consequence

of successful charge transfer at the donor/acceptor interface. However, when switching off the excitation source, a different recombination kinetics is observed for the organic and the hybrid blend. In the P3HT/PCBM blend, the charges recombine relatively fast and the polaron signal decays to its initial level. In contrast, in the hybrid blend, a fast and a slow decay are superimposed. Part of the signal decays very slowly, giving rise to the interpretation that part of the charge carriers is captured in trap states. PIA measurements supported this picture [7]. The presence of more and deeper trap states might play a key role for the comparably limited efficiency of CdSe/P3HT hybrid solar cells.

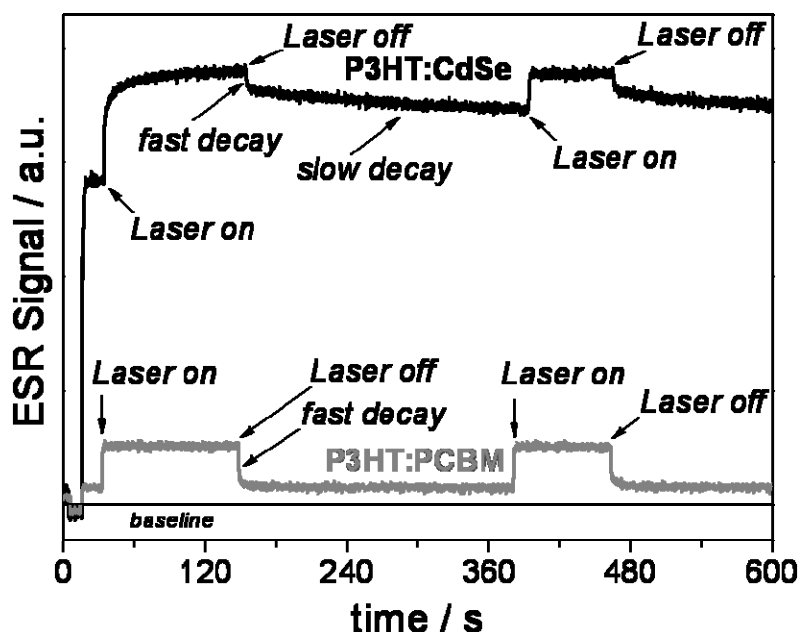


Figure 4 – ESR signal of positive polarons on the polymer in P3HT/PCBM and P3HT/CdSe blends. The intensity of the signal is monitored over time while switching the laser excitation on and off. The temperature was 50 K.

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goals :	Investigation of relationships between the surface of ligand-capped nanocrystals physico-chemical properties such as optical properties
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teaching : organisation of the practical exercises in Physical Chemistry, single lessons of lectures in Physical Chemistry, own lecture on nanostructured materials

ACTIVITIES AT THE UNIVERSITY OF BREMEN (2006-2007)

research area : **Catalysis by supported metal nanoparticles**
in detail: mono- and bimetallic Co/Pd nanoparticles on MgO as catalysts for CO oxidation and methanol decomposition; investigation of catalytic properties of ligand-capped metal nanoparticles on oxide supports

methods : FTIR spectroscopy (DRIFTS), usage of laboratory reactors and NDIR photometers

teaching : Lectures on electrochemistry, lectures on solid state and surface chemistry, exercises on electrochemistry

ACTIVITIES AT THE UNIVERSITY OF OLDENBURG (SINCE 2007)

research area : **Hybrid solar cells based on colloiddally prepared semiconductor nanoparticles and conductive polymer**

main goals : Understanding of elementary processes and limiting factors in hybrid solar cells composed of semiconductor nanoparticles (e.g. CdSe, CuInS₂) and polymer (e.g. P3HT) with the intention to elaborate concepts for improvement of this branch of photovoltaics

methods : Electron spin resonance (ESR), photo-induced absorption, current-voltage measurements, quantum efficiency, absorption and fluorescence spectroscopy, electron microscopy, X-ray diffraction

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P3HT-PERYLENEIMIDE SOLAR CELLS: PERFORMANCES OF BULK HETEROJUNCTIONS VS. BILAYER ARCHITECTURES

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Poly(3-hexylthiophene):N,N-dialkylperylene-tetracarboxydiimide (P3HT:PTCDI) bulk heterojunction (BHJ) solar cells have been already described in the literature, but the reported efficiencies are not high, probably because of the unoptimal morphology, caused by PTCDI aggregation [1]. With the aim to get a deeper insight on the subject, we have compared *BHJ* with *bilayer* devices obtained either through evaporation of a neutral PTCDI (Fig. 1a, also indicated as PDI) or spin coating of an anionic,

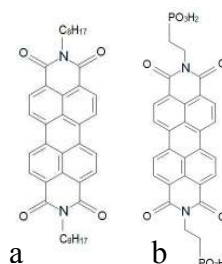


Figure 1

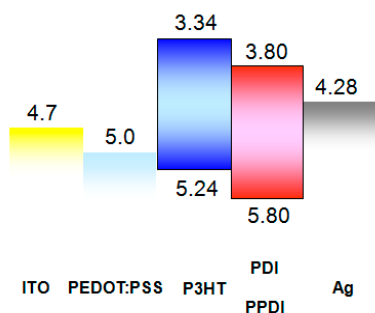


Figure 2

did non show a significant improvement over the literature reported data. However, with this approach, not subject to morphology influence, we were able to increase, to some extent, both the Fill Factor and the Open Circuit Voltage (V_{oc}).

As a comparison, BHJ P3HT:PCBM and bilayer P3HT/C60 cells have been also prepared and characterized. Provided that the BHJ architecture is the best performing one, PTCDI bilayer exhibit a higher V_{oc} than C60. In Figure 3 the main parameters are represented for comparison.

water soluble PTCDI (Fig. 1b, also indicated as PPDI) on top of P3HT.

The HOMO-LUMO energy of PDI and PPDI are depicted in Figure 2; they are suited for the photovoltaic process.

The efficiencies of the bilayer cells

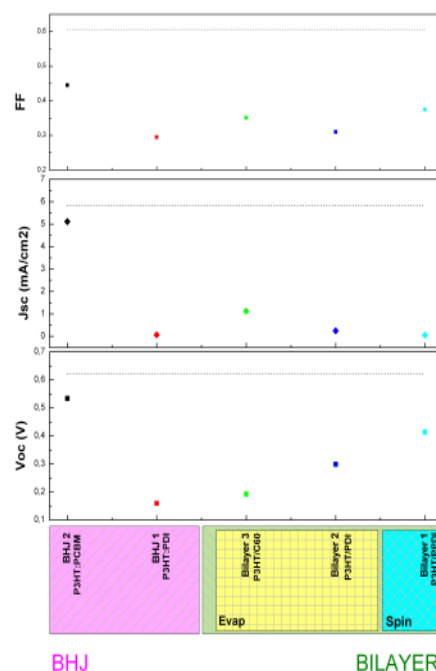


Figure 3

1. S. Rajaram, P.B. Armstrong, B.J. Kim, J.M.J. Fréchet ; *Chem.Mater.* 2009 , **21**, 1775

CURRICULUM VITAE AND SCIENTIFIC REFERENCES

Chiara Carbonera

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CURRENT STATUS

Since September 2008: Project Contractor at ENI S.P.A. - Research Centre for Non Conventional Energies - Istituto ENI Donegani, in the Solar Department, group of Dr. Riccardo Po'. **Subject:** "Polimer solar cells: realization and characterization".

My main task consists in the study, realization, characterization and development of organic solar cells based on polymeric thin films. Optical and physical characterization of polymers. Preliminary study of scale-up process for large area production of polymeric solar cells. Gained experience on nanotechnology and techniques for thin films deposition and new materials characterization.

DEGREES AND EDUCATION

2000-2003: PhD in Chemistry, Università degli Studi di Firenze, under Prof. Alessandro Bencini. **Title of the Thesis:** "Strongly Correlated Systems: Electronic Structure and Magnetic Properties by means of DFT and *ab initio* Approaches".

1993-1999: Graduation in Industrial Chemistry, Università degli Studi di Milano. Emphasis on applied physical-chemistry. Final Mark : 110/110 *cum laude*.

VISITING PERIODS

October 2009: Visiting scientist at M.I.T. Cambridge Massachusetts. Aim: preliminary tests for the realization of solar cells with architectures based on o-CVD PEDOT.

October-November 2006 and September-December 2007: Hosted in Grenoble (ILL) several times to perform measurements using ILL facilities for neutron diffraction techniques.

Two of the proposals were written by me and in the other four I was co-proposer. All of them concerned magnetic nanostructured molecular materials.

March 2004 and December 2003: Hosted in Mainz (Germany) to perform measurements using SQUID magnetometer at different pressures (Prof. Gütlich, University of Mainz).

July 2002: Hosted in Grenoble at High Magnetic Field Laboratory to perform High-Field EPR measurements with Dr. Anne Laure Barra.

SCIENTIFIC EXPERIENCE

February 2006 – August 2008: Juan de la Cierva contract at ICMA (Institute of Material Science of Aragon, belonging to CSIC and University of Saragossa) in the group of Dr. Fernando Luis Vitalla. **Subject:** "Magnetic and Morphological Investigation and characterization of Nanosized Biological and Metallic Systems".

My main task consists in the characterization of magnetic nanostructured materials by means of Chemical and Physical methods. I'm getting acquainted to the magnetic properties of nanosized materials, which are peculiar if compared to the "classical" magnetic materials.

June 2003 – Jan. 2006: Post-Doctoral position at ICMCB in the group of Molecular Sciences, under the supervision of Dr. Jean-François Létard. **Subject:** "Magnetic and Optical Investigation and characterization of Bistable Systems".

During this stay I was in charge of the Platform of Photomagnetism, and of the reflectivity equipment. On the other hand, I participated to the synthesis of some of the studied compounds, which belonged to the Spin Crossover System class. In the last few months of my stay, before getting the position in Spain, I've been involved into an industrial project, which aimed at optimizing the synthesis of the before mentioned compounds and their morphology, in order to develop technological applications.

April-May 2003: Post-doctoral work financed by Istituto Nazionale Scienza e Tecnologia dei Materiali. (INSTM) in the Research Unit of the Università di Firenze **Subject:** "Rationalisation of the Magnetic Coupling in Rare Earth Semiquinone Complexes".

April 2000 - March 2003: Post-graduate student in Chemistry, Università degli Studi di Firenze (Laboratory of Molecular Magnetism, LAMM, headed by Prof. Dante Gatteschi). Co-financed by INSTM and

Università di Firenze. Supervisor: Prof. Alessandro Bencini. Subject: "Magnetic Properties of Rare Earth and Transition Metals Containing Systems".

I worked mainly with computational chemistry methods, although I've spent some time in performing experimental measurements on the studied compounds.

Nov. 1999 - March 2000: Post-graduate course and training at Università di Milano-Bicocca, on "Methodology and Technology of Computational Chemistry" (METECO) held by Università di Milano-Bicocca in collaboration with Assolombarda and Federchimica, by which funding where assigned. Supervisor of the stage: Prof. Piercarlo Fantucci. Subject of the stage: "Studies on Biological Systems with Molecular Mechanic and Molecular Dynamic Methods".

May – Sept. 1999: Post-graduate training in Industry: at Enic hem Research Institute "G. Donegani" of Novara (Italy). Awarded with a grant financed by University of Uppsala (Sweden) within the European program "EU/DYNIR", relative to modelling of redox centres. Supervisor: Dr. Graziella Ranghino. Subject of research project: "Theoretic al Studies with Computational Chemistry Methods on Chemical Reac tions in Biologic al Systems".

March 1998 - March 1999: Graduation Thesis in Chemistry, Università degli Studi di Milano. Supervisor: Prof. Piercarlo Fantucci. Subject: "Relation between 3D Structure and Enzymatic Activity of Lactoperox ydase (LPO) studied with Computer Simulation Techniques".

Thanks to the thesis and the Post-graduate training, both centered on the computational study of the chemical and structural properties of proteic systems, I could acquire fundamental skills and training on proteic system, enzymes and their interaction with substrates.

SCHOOLS, CONGRESSES AND WORKSHOPS

- **June 2009:** (Poster) "International Symposium on Mesoscopic dye-sensitized and organic heterojunction solar cells", E-MRS 2009 Spring Meeting, Strasbourg (France).
- **Nov. 2008:** Workshop "A look inside solar cells", Ascona (Switzerland).
- **Oct. 2007:** (Poster) "6th International Conference on Fine Particles Magnetism" (ICFPM), Rome (Italy).
- **July 2007:**
 - ◇ Summerschool on "Nuevas fronteras en Magnetismo", Jaca (Spain)
 - ◇ Summerschool on "Nanotecnologías en Biomedicina", Jaca (Spain)
- **Oct. 2006:** (Poster) "European Conference on Molecular Magnetism" (MAGMANet-ECMM), Tomar (Portugal).
- **Sept. 2006:** Summerschool on "Neutron Techniques in Molecular Magnetism", Jaca (Spain)
- **July 2006:** Workshop on Nanomagnetism, Coma-Ruga (Spain).
- **June 2006:** (Oral Presentation) "MAGMANet Brainstorming Meeting - WP09", Paris (France)
- **June 2005:** (Oral Presentation) COST Meeting, San Feliu de Guixols (Spain).
- **May 2005:** (Poster) "Second International Conference on Photo-induced Phase Transitions" (PIPT'05), Rennes (France).
- **Feb. 2004:** (Oral Presentation) COST Meeting, Leuven (Belgium).
- **Oct. 2003:** (Poster) "GDR – CNRS: Molecular Commutation in Solid State (COMES)", Collonges-la-Rouge (France).
- **Jan. 2003:** "School of Biology 2", at Università di Firenze (Italy).
- **Oct. 2002:** (Poster with oral presentation) "VIII International Conference on Molecule Based Magnets" (ICMM2002), Valencia (Spain).
- **Feb. 2002:** "School in High Performance Computing on Linux Clusters" at ICTP, Trieste (Italy). (Awarded a grant for participation)
- **Nov. 2001:** Course: "Introduction to C++" at CINECA, Casalecchio di Reno (Bologna, Italy).
- **Sept. 2001:** (Poster) "9th International Conference on the Applications of the Density Functional Theory in Chemistry and Physics" (DFT2001), S. Lorenzo de El Escorial (Madrid, Spain).
- **Nov. 2000:** (Poster and flash presentation) "Theoretical Approaches to Molecular Magnetism" (TAMM), Vienna (Austria).
- **Sept. 2000:** (Poster) "Dalton Discussion 3. Inorganic Crystal Engineering", Bologna (Italy).
- **Sept. 2000:** "5th School of Inorganic Chemistry for PhD students: Chemistry of Advanced Materials", Castiglione della Pescaia (Grosseto, Italy).
- **July 2000:** "Summerschool on Computational Quantum Chemistry", Milano (Italy).
- **June 2000:** (Poster) "High Frequency EPR: New Frontiers in Biology, Chemistry and Physics. An European Workshop", Saint-Pierre de Chartreuse (Grenoble, France).
- **April 2000:** (INVITED) "Young Chemists Workshop - Magnetochemistry and Molecular Magnets", organised by European Science Foundation, Firenze (Italy).
- **Sept. 1999:** "DFT 1999", Roma (Italy).

TEACHING ACTIVITY AND OTHER CHARGES

Oct. 2007-Jan 2008: Teaching charge as laboratory classes Professor of "Física General" (for the first course of Superior Industrial Engineering) and "Fundamentos Físicos de la Ingeniería" (first course of Telecommunication Engineering) in the "Centro Politécnico Superior" of the University of Zaragoza (60 hours).

Jan. 2002-March 2003: During the PhD, at LAMM (Firenze), in charge of organizing the scientific activities of the research group such as group-meetings, people's participation to Congresses, and responsible for one of the group's web pages.

Oct. 1999-Jan 2000: Teaching Assistant for the first year course on General and Inorganic Chemistry at Biotechnology Department of Università di Milano-Bicocca.

SKILLS

COMPUTATIONAL CHEMISTRY AND INFORMATICS

- semi-empirical, force-field and ab initio calculations (InsightII, Cerius, Molden, Hyperchem, Gaussian98, Gamess, ADF2000, NWChem, Castep)
- experience with different kinds of hardware (PC, SGI) and operating systems (Windows, Linux, Unix)
- familiar with many standard programs (Excel, CorelDraw, Origin...)
- user's level skills of Labview; web page design

• PHYSICAL-CHEMISTRY

- Techniques for thin layer deposition (Spin coating, Evaporation, Sputtering...)
- Use of profiler, notions of ellipsometry
- TEM Measurements; sample preparation with Ion slicer and staining methods
- UV-Vis and Reflectance Spectroscopy
- Susceptibility measurements (Squid Magnetometer)
- Photomagnetic Measurements
- Use of data fitting and structure refinement programs (for susceptibility; for EPR: EprSim; for crystal structures: Shelx)
- Basic knowledge in EPR and HF-EPR spectroscopy, Mössbauer, SQUID+pressure
- Synthesis of some studied iron complexes
- Manipulation of cryogenic liquids, use of glove box, use of laser

• LANGUAGES

- fluent in English (this is written in English)
- fluent in French
- fluent in Spanish
- Italian: mother language

SCIENTIFIC PRODUCTION

• ORAL COMMUNICATIONS (4)

- ◇ MAGMANet Brainstorming Meeting - WP09, Paris, June 2006, "Study of Mn₁₂ Anisotropy in Saragossa and Barcelona".
- ◇ COST Meeting, San Feliu de Guixols, June 2005 "Reflectivity and photomagnetic Investigations within Cost members".
- ◇ Invited Seminar, Laboratoire de Minéralogie-Cristallographie, Université Pierre et Marie Curie, Paris, March 2005, "Etude de systèmes magnétiques moléculaires".
- ◇ COST Meeting, Leuven, February 2004 "A New Reflectivity Spectrometer: Application Towards the Study of Photomagnetic Properties".

• PUBLICATIONS (38)

Papers on ISI Journals

1. **Effect of crystalline disorder on quantum tunneling in the single-molecule magnet Mn₁₂ benzoate.** C. Carbonera, F. Luis, J. Campo, J. Sánchez-Marcos, A. Camón, J. Chaboy, D. Ruiz-Molina, I. Imaz, J. van Slageren, S. Dengler, and M. González, *Phys Rev. B*, 2010, 81(1), 014427.
2. **Alignment of magnetic anisotropy axes in crystals of Mn-12 acetate and Mn-12-tBuAc molecular nanomagnets: Angle-dependent ac susceptibility study.** E. Burzuri, C. Carbonera, F. Luis, D. Ruiz-Molina, C. Lampropoulos, G. Christou, G. *Phys Rev. B*, 2009, 80(22), 224428.
3. **Anion, Solvent and Time Dependence of High-Spin-Low-Spin Interactions in a 3D Coordination Polymer.** G.N.L. Jameson, F. Werner, M. Bartel, A. Absmeier, M. Reissner, J.A. Kitchen, S. Brooker, A. Caneschi, C. Carbonera, J.F. Letard, W. Linert, *Eur. J. Inorg. Chem.* 2009, 26, 3948-3959.
4. **Thermal and light-induced spin-transitions in iron(II) complexes of 2,6-bis(4-halopyrazolyl)pyridines: the influence of polymorphism on a spin-crossover compound.** R. Pritchard, H. Lazar, S.A. Barrett, C.A. Kilner, S. Asthana, C. Carbonera, J.F. Letard, M.A. Halcrow, *Dalton Trans.*, 2009, 33, 6656-6666.
5. **Photomagnetism of a Series of Dinuclear Iron(II) Complexes.** J.F. Letard, C. Carbonera, J.A. Real, S. Kawata, S. Kaizaki, *Chemistry-A European Journal*, 2009, 15(16), 4146-4155.
6. **Structural, magnetic and photomagnetic study of the [Fe(PM-NEA)(2)(NCS)(2)] spin crossover complex.** J.F. Letard, M. Kollmansberger, C. Carbonera, M. Marchivie, P. Guionneau, *Comptes Rendus Chimie*, 2008, 11(10), 1155-1165.
7. **A Novel Ni-4 Complex Exhibiting Microsecond Quantum Tunneling of the Magnetization.** G. Aromi, E. Bouwman, E. Burzuri, C. Carbonera, J. Krzystek, F. Luis, C. Schlegel, J. van Slageren, S. Tanase, S.J. Teat, *Chemistry-A European Journal*, 2008, 14(35), 11158-11166.
8. **Magnetic behaviour of Mn₁₂ single molecule magnet nanospheres.** C. Carbonera, I. Imaz, D. Ruiz-Molina, D. MasPOCH, F. Luis, *Inorg. Chim. Acta*, 2008, 361(14-15), 3951-3956. (Invited Article)
9. **Cooperative iron(II) spin crossover complexes with N4O2 coordination sphere.** B. Weber, E. Kaps, J. Weigand, C. Carbonera, J.F. Letard, K. Achterhold, F.G. Parak, *Inorg. Chem.*, 2008, 47(2), 487-496.
10. **Single-molecule magnet behaviour in metal-organic nanospheres generated by simple precipitation of Mn₁₂O₁₂ clusters.** I. Imaz, F. Luis, C. Carbonera, D. Ruiz-Molina, D. MasPOCH, *Chem. Commun.*, 2008, 10, 1202-1204.
11. **Stepwise Spin Transition in a Mononuclear Iron(II) Complex with Unusually Wide Plateau.** B. Weber, C. Carbonera, C. Desplances, J.F. Letard, *Eur. J. Inorg. Chem.*, 2008, 10, 1589-1598.
12. **Adaptable thermochromism in the CuMo_{1-x}W_xO₄ series (0 ≤ x < 0.1): A behavior related to a first-order phase transition with a transition temperature depending on x.** M Gaudon, C. Carbonera, A.E. Thiry, A. Demourgues, P. Deniard, C. Payen, J.F. Letard, S. Jobic, *Inorg. Chem.*, 2007, 46(24), 10200-10207.
13. **Unprecedented "One-Finger-Push"-Induced phase transition with a drastic color change in an inorganic material.** M. Gaudon, P. Deniard, A. Demourgues, A.E. Thiry, C Carbonera, A. Le Nestour, A. Largeteau, J.F. Letard, S. Jobic, *Adv. Mater.*, 2007, 19(21), 3517.
14. **Optical, Magnetic and Structural Properties of the Spin-Crossover Complex [Fe(btr)₂(NCS)₂]·H₂O in the Light-Induced and Thermally Quenched Metastable States.** V. Legrand, S. Pillet, C. Carbonera, M. Souhassou, J.-F. Létard, P Guionneau, C. Lecomte, *Eur. J. Inorg. Chem.*, 2007, 5693-5706.
15. **Relaxation dynamics of a Photoinduced Di-Cobalt-Tetraoxolene Valence Tautomer.** C. Carbonera, A. Dei, J.-F. Létard, C. Sangregorio, L. Sorace, *Inorg. Chimica Acta*, 2007, 360, 3825-3828.

16. **Mutual influence of spacer length and non-coordinating anions on thermal and light induced Spin-Crossover properties of iron(II) α , ω -bis(tetrazole-1-yl)alkane coordination polymers.** A. Absmeier, M. Bartel, C. Carbonera, G. N. L. Jameson, F. Werner, M. Reissner, A. Caneschi, J.-F. Létard, W. Linert, *Eur. Inorg. J.*, 2007, 19, 3047-3054.
17. **Interplay between kinetically slow thermal spin-crossover and metastable high-spin state relaxation in an iron(II) complex with similar $T_{1/2}$ and $T(\text{LIESST})$.** V. Money, C. Carbonera, J. Elhaik, MA. Halcrow, JAK Howard, JF Letard, *Chemistry-A European Journal*, 2007, 13 (19), 5503-5514.
18. **Study of the oxidative half-reaction catalyzed by a non-heme ferrous catalytic center by means of structural and computational methodologies.** G. Cicero, C. Carbonera, K. Valegard, J. Hajdu, I. Andersson, G. Ranghino, *Int. J. of Quantum Chem.*, 2007, 107 (6), 1514-1522.
19. **Photomagnetic Properties of an Iron(II) Low-Spin Complex with an Unusually Long-Lived Metastable LIESST State.** J.S. Costa, C. Balde, C. Carbonera, D. Denux, A. Wattiaux, C. Desplanches, J.-P. Ader, P. Gutlich, J.-F. Létard, *Inorg. Chem.*, 2007, 46 (10), 4114-4119.
20. **Unusual Spin Transition Behaviour in 2,6-Bis((pyrazol-3-yl)-pyridine) iron(II)-bis-oxalato-platinate(II).** M. Grunert, HA Goodwin, C. Carbonera, J.-F. Létard, J. Kusz, P. Gütlich, *J. Phys. Chem. B*, 2007, 111 (24), 6738-6747.
21. **Anion doping as a probe of cooperativity in the molecular spin-crossover compound $[\text{FeL}_2][\text{BF}_4]_2$ ($L = 2,6\text{-di}\{\text{pyrazol-1-yl}\}\text{pyridine}$).** C. Carbonera, C. A. Kilner, J.-F. Létard, M. A. Halcrow, *Dalton Trans.*, 2007, 13, 1284-1292.
22. **Magnetic and photomagnetic studies in $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$.** D. Bahadur, S. Asthana, C. Carbonera, C. Desplanches, J.-F. Létard, *Solid State Communications*, 2007, 142, 132-136.
23. **Optically induced valence tautomeric interconversion in cobalt dioxolene complexes.** A. Beni, C. Carbonera, A. Dei, J.-F. Létard, R. Righini, C. Sangregorio, L. Sorace, *J. Braz. Chem. Soc.*, 2006, 17 (8) 1522-1533.
24. **A typical example of a photomagnetic study carried out on a spin-crossover material.** J.-F. Letard, C. Carbonera, E. Courcot, J. S. Costa, *Bull. Mat. Science*, 2006, 29 (6), 567-571.
25. **Bifunctional materials based on the photochromic cation $[\text{RuNO}(\text{NH}_3)_5]^{3+}$ with paramagnetic metal complex anions.** L.A. Kushch, L.S. Kurochkina, E.B. Yagubskii, G. V. Shilov, S. M. Aldoshin, V. A. Emel'yanov, Y. N. Shvachko, V. S. Mironov, D. Schaniel, T. Woike, C. Carbonera, C. Mathonière, *Eur. J. Inorg. Chem.*, 2006, 20, 4074-4085.
26. **Photomagnetic properties of iron(II) spin crossover complexes of 2,6-dipyrazolylpyridine and 2,6-dipyrazolylpyrazine ligands.** C. Carbonera; J.S. Costa, V.A. Money, J. Elhaik, J. A. K. Howard, M. A. Halcrow, J.-F. Létard, *Dalton Transition*, 2006, 25, 3058-3066.
27. **Both spacer length and parity influence the thermal and light-induced properties of iron(II) α , ω -bis(tetrazole-1-yl)alkane coordination polymers.** A. Absmeier, M. Bartel, C. Carbonera, G. N. L. Jameson, P. Weinberger, A. Caneschi, K. Mereiter, J.-F. Létard, W. Linert, *Chemistry-A European Journal*, 2006, 12 (8), 2235-2243.
28. **Photo-crystallography: from the structure towards the electron density of metastable states.** V. Legrand, C Carbonera, S Pillet, M Souhassou, J F Létard, P Guionneau and C Lecomte, *J. Phys.: Conference Series*, 2005, 21, 73-80.
29. **Does cooperativity influence the lifetime of the photo-induced HS state?** J-F. Létard, J. Sanchez Costa, S. Marcen, C. Carbonera, C. Desplanches, A. Kobayashi, N. Daro, P. Guionneau, J.-P. Ader, *J. Phys.: Conference Series*, 2005, 21, 23.
30. **Combined Charge and Spin density study in the Y complex of the semiquinonate radical $\text{Y}(\text{HBPz}_3)_2(\text{DTBSQ})$.** N. Claiser, M. Souhassou, C. Lecomte, B. Gillon, C. Carbonera, A. Caneschi, D. Gatteschi, A. Bencini, Y. Pontillon, E. Lelièvre-Berna, *J. Phys. Chem. B*, 2005, 109 (7), 2723-2732.
31. **A typical Photomagnetic Properties in a Series of Binuclear Iron(II) Spin Crossover Complexes.** G. Chastanet, C. Carbonera, A. B. Gaspar, J. A. Real, J.-F. Létard, *J. Mater. Chem.*, 2004, 14, 3516-3523.
32. **Optically Switchable Behaviour of a Dioxolene Adduct of a Cobalt-macrocyclic Complex.** C. Carbonera, A. Dei, J.-F. Létard, C. Sangregorio, *Chem. Phys. Lett.*, 2004, 396(1-3), 198-201.
33. **Thermally and Light-Induced Valence Tautomeric Transition in a Dinuclear Cobalt Tetraoxolene Complex.** C. Carbonera, A. Dei, J.-F. Létard, C. Sangregorio, L. Sorace, *Angew. Chem. Int. Ed. Engl.*, 2004, 43, 3136-3138.
34. **DTF Description of the Electronic Structure and Spectro-Magnetic Properties of Strongly Correlated Electronic Systems. The Ni(II), Cu(II) and Zn(II) o-Dioxolene Complexes.** A. Bencini, C. Carbonera, F. Totti, *Chem. Eur. J.*, 2004, 10(6), 1472-1480.
35. **Tuning the physical properties of a metal complex by molecular techniques: the design and the synthesis of the simplest cobalt-o-dioxolene complex undergoing valence tautomerism.** A. Bencini, A. Caneschi, C. Carbonera, A. Dei, D. Gatteschi, R. Righini, C. Sangregorio, J. Van Slageren, *J. Mol. Struct.*, 2003, 656(1-3), 141-154.

36. **Magnetic Exchange Interaction between Paramagnetic Transition Metal Ions and Radical Ligands. Crystal and Molecular Structure of a 9,10-dioxophenanthrenesemiquinonato adduct of a nickel(II)-tetraazamacrocyclic complex and DFT Description of the Exchange Interactions.** A. Bencini, C. Carbonera, A. Dei, M. G. F. Vaz, *J. Chem. Soc., Dalton Trans.*, 2003, (9), 1701-1706.
37. **Magnetization and spin density in [FeCp]₂. A look-back at the magnetic interactions in the chains [FeCp₂]⁺[TCNE]⁻.** J. Schweizer, A. Bencini, C. Carbonera, A. J. Epstein, S. Golhen, E. Lelièvre-Berna, J. S. Miller, L. Ouahab, Y. Pontillon, E. Ressouche, A. Zheludev, *Polyhedron*, 2001, 20, 1771-1778.
38. **Inducing asymmetry in free-base, Mn(III), Ni(II) and Cu(II)(ethylsulfanyl)porphyrins: synthetic aspects and spectro-electrochemical implications.** S. Belviso, G. Ricciardi, F. Leij, L. Monsù Scolaro, A. Bencini, C. Carbonera, *J. Chem. Soc., Dalton Trans.*, 2001, 7, 1143-1150.

Papers on non-ISI Journals

1. **Il Lavoisium e il Davy: ascesa e declino di due metalli dai nomi illustri.** M. Fontani, M. Costa, C. Carbonera, (article written in Italian) *La Chimica e l'Industria*, January-February 2005.

• PATENTS

2009: Co-author of the patent "Electron mobility promoter". The granting procedure is ongoing.

• POSTER PRESENTATIONS (10)

1. **"Characterization of polythiophene composite multilayer thin films by spectroscopic ellipsometry"** – C. Carbonera, A. Bernardi, R. Po', S. Schutzmann, "International Symposium on Mesoscopic dye-sensitized and organic heterojunction solar cells", E-MRS 2009 Spring Meeting, Strasbourg (France), 8/10 June 2009.
2. **"Non-Linear Susceptibility of Ferritin: a Model Classical Superparamagnet"** – F. Luis, J.L. García-Palacios, C. Carbonera, M. Martínez-Júlvez, C. Gómez-Moreno, "6th International Conference on Fine Particles Magnetism" (ICFPM), Rome (Italy), to be held on 9/12 October 2007.
3. **"Crystal structure affects relaxation times in Mn₁₂ Acetate Single Molecule Magnets"** – C. Carbonera, F. Luis, J. Chaboy, J. Campo, D. Ruiz, "European Conference on Molecular Magnetism" (MAGMANet-ECMM), Tomar (Portugal), 10/15 October 2006.
4. **"Interesting influence of crystal structure on magnetic and magneto-optical properties of a series of α,ω -bis(tetrazole-1-yl)alkane ligands iron(II) complexes: a zig-zag shaped trend"** - A. Absmeier, M. Bartel, C. Carbonera, G.N.L. Jameson, J.-F. Létard, W. Linert, K. Mereiter, P. Weinberger, - "Second International Conference on Photo-induced Phase Transitions" (PIPT'05) – Rennes (France), 24/28 May 2005.
5. **"TLIESST Determination: Influence of Macroscopic and Microscopic Factors"** - C. Carbonera, G. Chastanet, J.-F. Létard. - "GDR – CNRS: Molecular Commutation in Solid State (COMES)", Collonges-la-Rouge (France), 8/11 October 2003.
6. **"Theoretical Study of the Valence Tautomeric Interconversion in a Cobalt-Tetraazamacrocyclic Complex" WITH ORAL PRESENTATION** - A. Bencini, C. Carbonera, A. Dei. - "VIII International Conference on Molecule Based Magnets" (ICMM2002), Valencia (Spain), 5/10 October 2002.
7. **"Density Functional Study of the Valence Tautomeric Interconversion in a o-dioxolene Adduct of a Cobalt-tetraazamacrocyclic Complex."** - A. Bencini, C. Carbonera, A. Dei. - "9th International Conference on the Applications of the Density Functional Theory in Chemistry and Physics" (DFT2001), S. Lorenzo de El Escorial (Madrid, Spain), 10/14 September 2001.
8. **"Gd(HBPz₃)₂DTBSQ Complex Magnetic Properties: a DFT Study" WITH ORAL PRESENTATION** - C. Carbonera, A. Dei, D. Gatteschi, L. Sorace, K. Vostrikova. - "Theoretical Approaches to Molecular Magnetism" (TAMM), Vienna (Austria), 21/26 November 2000.
9. **"A DFT Study of the Gd(HBPz₃)₂DTBSQ Complex: Magnetic Coupling and Spin Density Calculation"** - A. Bencini, C. Carbonera, D. Gatteschi, L. Sorace, K. Vostrikova. – "Dalton Discussion 3. Inorganic Crystal Engineering", Bologna (Italy), 9/11 September 2000.
10. **"High-Field EPR Studies on Gadolinium Semiquinone Complexes"** - C. Carbonera, A. Dei, D. Gatteschi, C.A. Massa, L. Pardi, S. Pous sereau, L. Sorace. - "High Frequency EPR: New Frontiers in Biology, Chemistry and Physics. An European Workshop", Saint-Pierre de Chartreuse (Grenoble, France), 21/24 June 2000.

LOW VOLTAGE SOLUTION PROCESSED ORGANIC LIGHT EMITTING P-I-N DIODES

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Organic light emitting devices (OLEDs) have been investigated intensively because of their potential for low cost and large area signage. Significant progresses towards higher efficiencies were achieved by utilizing new material systems for the active layer. A key issue for highly efficient OLEDs is a low driving voltage. The p-i-n architecture with its low injection barriers for charge carriers and subsequently low driving voltage is one solution for this problem. In terms of fabrication costs, solution processing will potentially be superior to vacuum process techniques when it comes to large area signage and display applications. Because of the solvent limitations it is challenging to build a p-i-n architecture completely from solution. In this work we present solution processed p-i-n OLEDs and investigate the dependence of the driving voltage of OLEDs on the n-doped buffer layer between the active layer and the cathode.

For the fabrication of a solution processed p-i-n OLED, the established poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was used as the p-doped hole transport layer. On top of the p-doped layer Super Yellow was chosen as emitter because of its easy processability.

The OLEDs without any buffer layer below the cathode have been investigated first. These devices exhibit an unbalanced charge carrier flow through the device, i.e. high current density at low brightnesses, and thus very low efficiencies. By adding a bathophenanthroline (BPhen) layer the non-radiative recombination at the organic/cathode interface was minimized leading to a significant reduction of the current density. However, the OLEDs with a pristine hole blocking layer need high onset voltages of almost 5 V. It is known that the onset voltage can be reduced by n-doping of the buffer layer under the cathode. As a stable dopant we chose cesiumfluoride. Subsequently, a cesiumfluoride doped bathophenanthroline (BPhen:CsF) layer fabricated from solution was utilized for efficient electron injection through an ohmic contact with the cathode. The onset voltage of the p-i-n-OLED was successfully reduced to 2,6 volt for the OLEDs with a n-doped interlayer. Consequently, the luminance and the efficiency of the device increased significantly due to improved and balanced charge carrier injection.

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Eur. Phys. J. Special Topics **166**, 49 (2009)

“**Plasma patterning of Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) anodes for efficient polymer solar cells**”, Thin Solid Films **517**, 1750–1752 (2009)

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MULTI-CRITERIA DECISION METHOD APPLIED TO FILM FORMING TECHNIQUES IN POLYMER SOLAR CELLS

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The main purpose of this work has been to evaluate a set of well-known and available commercially film-forming techniques from plastic packaging industry. Coating and printing techniques compatible with a roll to roll processing are the most promising manufacturing methods in the field of organic solar cells (OSC) in order to transfer the technology from laboratory scale to a large scale polymer solar cell industry [1].

Several attempts of this kind of processes have been carried out recently, mainly in European research centers [2, 3, 4], reaching power conversion efficiencies in the range of 2-3%; still well below the performance of small scale model cells.

A typical OSC structure device comprises a multilayer structure formed from different polymers, mainly polythiophenes and fullerene blends. Given that the deposition of these organic materials could be entirely from solution, each layer could be deposited by an individual film-forming technique. Nevertheless, an ideal process should involve multilayer solution processing, reducing coating and printing steps.

This assessment has provided us with an initial evaluation of the suitability of a given technique in the field of polymer solar cells. The analysis of the operation parameters of these technologies will lead to propose a low-cost patterning technique capable of a successful high-volume manufacturing of full organic solar cells.

The first stage consists of establishing the window of coatability or product requirements range, and preparing a basic data document specifying these requirements. During the second step, different coating or printing methods capabilities and operation data have been evaluated. There are approximately 1000 different coating configurations that are available and actually in use. We have considered the coating and printing methods shown in Table 1 as alternatives for the decision problem.

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Table 1. Set of deposition methods considered as alternatives

Coating methods	Printing methods
A1. Doctor blade	A6. Screen
A2. Knife over edge	A7. Inkjet
A3. Slot die	A8. Gravure
A4. Slide	A9. Flexography
A5. Curtain	A10. Offset

The operating range of any method depends on solution viscosity and wet thickness, line speed, desired quality level, thickness uniformity, cost, the fluid flow mechanisms in the method and the manufactured precision of the applicator. Quantitative and qualitative parameters, such as technical issues, environmental impact or reproducibility of the fabrication output, have been taken into account in the study, reaching to the following main criteria:

- 1) Design control, C1
- 2) Ink properties, C2
- 3) Reproducibility, C3
- 4) Energy input, C4

These four criteria are comprised of subcriteria and after having collected the information and data for each alternative film forming technique, they have been ordered in a so called decision matrix, as it is shown in Table 2.

Table 2. Matrix of decision making

	DESIGN CONTROL					INK PROPERTIES		REPRODUCIBILITY	ENERGY INPUT		
	Thickness Control			Dimensional Control	Number of layers	Viscosity (Pa-s)	Ink preparation		Ink waste	Max. Throughput (m ² /h)	Embedded energy
	Wet thickness (µm)	Volatility	Speed (m/min)								
A1. DOCTOR BLADE	10-100	medium	0.001-0.1	0	1	0.01-40	simple	very low	low	low	high
A2. KNIFE OVER EDGE	10-750	low	1-100	0	1	0.05-100	moderate	very low	very low	5000	medium
A3. SLOT DIE	10-500	medium	1-1000	1	3	0.01-300	moderate	high	very low	50000	low
A4. SLIDE	25-250	medium	1-1000	pseudo/quasi 2/3	17	0.01-300	critical	high	very low	100000	low
A5. CURTAIN	5-500	high	10-1000	pseudo/quasi 2/3	17	0.015-2	critical	high	very low	100000	low
A6. SCREEN	3-500	low	0.01-100	2	1	0.1-100	demanding	low	very low	100	high
A7. INKJET	0.3-500	high	0-1	digital master	1	0.001-0.01	moderate	medium	very low	50	high
A8. FLEXOGRAPHY	0.8-200	very high	1-1000	2	1	0.01-1	demanding	high	very low	50000	very low
A9. GRAVURE	0.8-80	very high	1-1000	2	1	0.01-2.5	difficult	high	very low	100000	very low
A10.OFFSET	3-210	very low	3-300	2	1	2-100	demanding-difficult	medium	very low	50000	medium

Data have been extracted from related literature [7, 8, 9], and coating and printing companies of new OSC markets and of the traditional packaging industry [10, 11, 12]. When uncertainty about a particular parameter was found, qualitative information from expert surveys was used.

Multi-criteria decision methods (MCDM) can serve as useful decision support for carrying out this assessment. The multi-criteria technique proposed herein [13], is a combination of an analytic hierarchy process (AHP), implemented in order to prioritize the criteria and organize the alternatives in descending order, and the fuzzy set theory, introduced by Zadeh [14] to deal with vague, imprecise and uncertain problems, commonly used as a modelling tool for complex systems.

Both criteria and subcriteria have been valued, according to the decision-maker preferences, with linguistic labels. The analytic hierarchy process (AHP) which was developed by Saaty (1980), is a simple but useful MCDM, when dealing with unstructured and multi criteria problems [15]. It consists of decomposing a complex problem into its components, organizing the components into levels and therefore generating a hierarchical structure. The purpose of constructing this hierarchy is to determine the impact of the lower level on an upper level, which is achieved by paired comparisons provided by the decision-maker. In AHP problems, where the values are fuzzy, not crisp; instead of using lambda as an estimator to the weight, we will use the geometric normalized average, in Eq. 1:

$$\omega_i = \frac{\left(\prod_{j=1}^n (a_{ij}, b_{ij}, c_{ij})\right)^{1/n}}{\sum_{i=1}^m \left(\prod_{j=1}^n (a_{ij}, b_{ij}, c_{ij})\right)^{1/n}} \quad \text{Eq. 1}$$

In this case, the Fuzzy AHP was only used in order to obtain the weight of each criteria in the decision problem. As a result of the AHP method application in the problem of a deposition method selection, the normalized weights of the criteria are obtained.

The Technique for Order Performance by Similarity to Ideal Solution (TOPSIS) is one of the well known classical MCDM methods, developed in 1981 by Hwang and Yoon [16]. In this study, the TOPSIS method was used to select the preference order of the alternatives. The chosen alternative should have the shortest distance from the positive ideal solution (PIS) and the farthest from the negative ideal solution (NIS). Therefore the final ranking is obtained by means of the closeness index. In Table 4, the fuzzy numbers of the ranking score are presented.

Table 3. Importance weight of criteria

	Normalized		
C1	0.3636	0.3947	0.4138
C11	0.2815	0.3148	0.3348
C111	0.1987	0.2344	0.2592
C112	0.0248	0.0335	0.0432
C113	0.0331	0.0469	0.0648
C12	0.0313	0.0350	0.0418
C13	0.0352	0.0450	0.0558
C2	0.0606	0.0789	0.1034
C21	0.0303	0.0395	0.0517
C22	0.0303	0.0395	0.0517
C3	0.3636	0.3947	0.4138
C4	0.0909	0.1316	0.2069
C41	0.0022	0.0060	0.0110
C42	0.0352	0.0837	0.2648
C43	0.0176	0.0419	0.0662

Table 4. The ranking score, computing the distance to ideal solution d^+ and the negative ideal solution d^- , by fuzzy numbers.

	A_1	0.0512	0.0772	0.1239
	A_2	0.0508	0.0744	0.1228
	A_3	0.0466	0.0692	0.1169
	A_4	0.0790	0.1211	0.1548
d^+	A_5	0.0210	0.0347	0.0660
	A_6	0.0290	0.0436	0.0899
	A_7	0.0268	0.0407	0.0753
	A_8	0.0264	0.0347	0.0672
	A_9	0.0250	0.0340	0.0672
	A_{10}	0.0281	0.0403	0.0683
	A_1	0.0404	0.0643	0.0740
	A_2	0.0401	0.0639	0.0631
	A_3	0.0423	0.0667	0.0815
	A_4	0.0314	0.0478	0.0770
d^-	A_5	0.0670	0.1023	0.1244
	A_6	0.0794	0.1214	0.1464
	A_7	0.0812	0.1235	0.1557
	A_8	0.0802	0.1244	0.1594
	A_9	0.0812	0.1258	0.1594
	A_{10}	0.0796	0.1226	0.1572
	A_1	0.2044	0.4545	0.8072
	A_2	0.2159	0.4621	0.6937
	A_3	0.2131	0.4908	0.9174
	A_4	0.1355	0.2829	0.6971
R	A_5	0.3518	0.7465	1.4150
	A_6	0.3360	0.7355	1.3509
	A_7	0.3515	0.7522	1.4414
	A_8	0.3542	0.7820	1.4940
	A_9	0.3583	0.7873	1.5002
	A_{10}	0.3533	0.7527	1.4584

Considering Fig. 1, where the score corresponding to each technology is represented in fuzzy numbers, a defuzzyfication process is needed in order to obtain the order of preference of the alternatives [17].

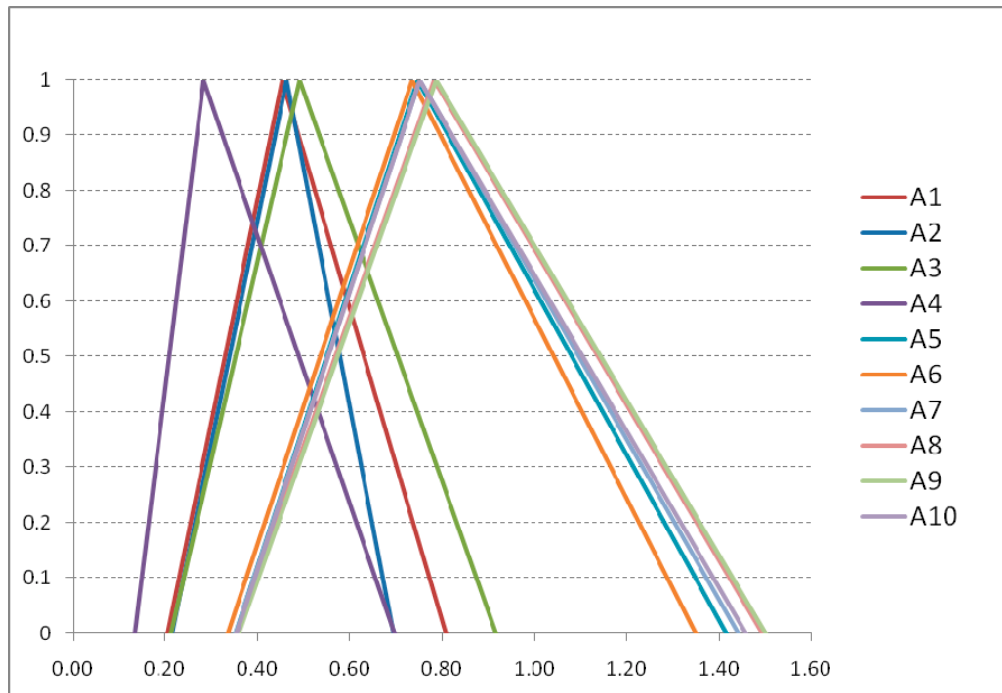


Fig. 1. Ranking score graphically.

From these results, we can conclude that three groups seem to appear in which the technologies have similar score:

- First scored group, formed by *Gravure, Flexography, Offset, Inkjet, Curtain and Screen Printing*. All of them have a short distance to positive ideal solution, because their operation values are inside the window of coatability, and they could fulfil the coating requirements of an organic solar cell. Furthermore, this first group reveals a certain predominance of *printing* techniques over *coating* ones.
- Second scored group, formed by *Slot die, Doctor Blade, Knife over edge*. The cited technologies have a farther distance to ideal solution, but could be acceptable methods.
- The third group is *Slide coating* scored as the worst technique for the purpose of organic layers deposition, mainly due to the low score in criteria such as: Thickness control, Reproducibility and Maximum throughput; which are parameters with high weights in the criteria selection process.

As a result no one method is capable of applying a quality coating over the wide range of potential coating conditions, and each method has an optimum range in which it should be operated. Outside of this optimum range quality and reproducibility will deteriorate.

The results have revealed a relative predominance of printing techniques over coating ones, which was, in some way, expected. Further refining of the parameter definition and relative importance of the weights of the used criteria, as well as environmental and cost considerations will provide a more accurate and definitive selection of technology.

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Research fellowship	<i>G&C Colors</i>	UPCT	01/10/2004	31/05/2005

LANGUAGES (N = NORMAL, G = GOOD, P = PERFECTLY)

<i>Idioma</i>	<i>Habla</i>	<i>Lee</i>	<i>Escribe</i>
<i>English</i>	<i>G</i>	<i>P</i>	<i>G</i>
<i>French</i>	<i>P</i>	<i>P</i>	<i>G</i>
<i>German</i>	<i>N</i>	<i>G</i>	<i>N</i>

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LENGTH: FROM 2008 TO 2011

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FINANCIAL ENTITY: Ministerio de Educacion y Ciencia. Consolider-Ingenio (CSD2007- 00007)

LENGTH: FROM : 2007 **TO:** 2012

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**PARTICIPATION IN RESEARCH CONTRACTS OF SPECIAL RELEVANCE WITH COMPANIES
AND/OR PRIVATE OR PUBLIC FUNDING BODIES**

CONTRACT TITLE: Caracterización de células fotovoltaicas para su uso mediante concentración con lentes tipo Fresnel en seguidores solares (Characterisation of photovoltaic cells for its use under concentrated sunlight using Fresnel lens)

FINANCIAL ENTITIES: Agencia de Gestión de Energía de la Región de Murcia (ARGEM)- Energy Agency from the Region of Murcia-

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TITLE: Hydrogen and electricity from photovoltaics: microgrid integration using a multi-agent-based control system

TYPE OF PRESENTATION: Visual Presentation

CONGRESS: 11th GROVE FUEL CELL SYMPOSIUM

MEETING PLACE: London, UK

YEAR: 2009

AUTHORS: R. García-Valverde, N. Espinosa-Martínez, J. Padilla, J. Abad, J. Colchero and A. Urbina

TITLE: Life Cycle Assessment of Organic Solar Cells

TYPE OF PRESENTATION: Oral Presentation

CONGRESS: HYBRID AND ORGANIC PHOTOVOLTAICS CONFERENCE 2009

MEETING PLACE: Benidorm, Spain

YEAR: 2009

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TITLE: Conducting polymers for photovoltaic and electrochromic applications. Research lines

TYPE OF PRESENTATION: Poster

CONGRESS: European school

PUBLICATION: Abstracts Book

MEETING PLACE: Les Houches, France

YEAR: 2009

AUTHORS: R. García-Valverde, N. Espinosa-Martínez, J. Padilla, A. J. Fernández-Romero and A. Urbina

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TYPE OF PRESENTATION: Poster

CONGRESS: European school

PUBLICATION: Abstracts Book

MEETING PLACE: Les Houches, France

YEAR: 2009

AUTHORS: N. Espinosa-Martínez, C. Romojaro

TITLE: La Energía Solar en la Región de Murcia

TYPE OF PRESENTATION: Poster

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PROFESIONAL EXPERIENCES

CONTRACT TITLE: Consultant in administrative special register for photovoltaic installation feed-in-tarif.

FINANCIAL ENTITY: Comunidad Autónoma de la Región de Murcia. Consejería de Agricultura y Agua. Climate Change Department.

LENGTH: FROM: 26/09/2008 TO: 30/11/2008

CONTRACT TITLE: Consultant in Greenhouse Gas Emission Permits, in processes of modifying and updating the permits and in the emissions verification processes in accordance with Law 1/2005 of Emissions Trading.

FINANCIAL ENTITY: Comunidad Autónoma de la Región de Murcia. Consejería de Desarrollo Sostenible y Ordenación del Territorio. Climate Change Department.

LENGTH: FROM: 01/12/2007 TO: 25/09/2008

CONTRACT TITLE: Consultant in Integrated Environmental Authorization for industrial sector in accordance to Directive "Integrated Pollution Prevention and Control".

FINANCIAL ENTITY: Comunidad Autónoma de la Región de Murcia. Consejería de Desarrollo Sostenible y Ordenación del Territorio. Climate Change Department.

LENGTH: FROM: 01/07/2007 TO: 30/11/2007

CONTRACT TITLE: Project Manager of Photovoltaic area in Solar Energy Department

FINANCIAL ENTITY: Tecsumaga, S.L.

LENGTH: FROM: 01/06/2005 TO: 15/12/2006

STABILITY IN BOTTOM- AND TOP-GATE ORGANIC FIELD-EFFECT TRANSISTORS

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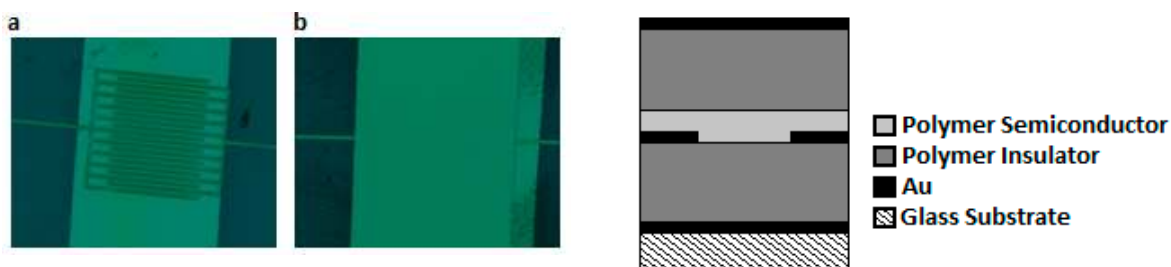
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1. Introduction

We have produced and investigated Bottom-Contact (BC), Bottom- and Top-Gate (BG, TG) Polymer Field-Effect Transistors (PFETs), in an effort to understand the challenges presented by BG and TG fabrication and any correlation to long-term mobility degradation, ultimately allowing greater flexibility in organic integrated circuit design. As PFETs are planar channel structures (Fig. 1), the gate can be deposited either above or below the channel yielding respectively TG and BG. The differences between the two gate-modes were investigated by producing Dual-Gate (DG) structures with a novel process, allowing for the direct comparison of gate-effects in a single transistor channel.

2. Device Structure



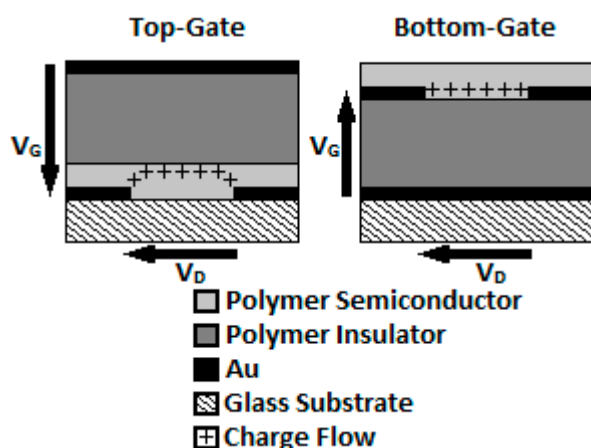
The gates of the DG PFETs were fabricated by thermally evaporating Au through a shadow mask. The electrodes were defined by evaporating Au and performing photolithography on the layer. All remaining device elements were deposited from solution. Devices were fabricated, stored, and characterized under ambient conditions. Both insulator layers were fabricated by spin-coating solutions of Cytop™, an excellent organic insulator in terms of resilience to atmospheric contamination and electrical stability¹. The semiconductor used is an amorphous air-stable conjugated polymer, offering significantly reduced disposition for morphological non-uniformity compared to crystalline organic semiconductors.

W. L. Kalb, T. Mathis, S. Haas, A. F. Stassen, and B. Batlogg. Organic small molecule field-effect transistors with Cytop™ gate dielectric: Eliminating gate bias stress effects. *Applied Physics Letters* 90, 092104. (2007)

3. Implications of different processing

In TG, as the insulator is deposited after the semiconductor, the semiconductor surface properties will determine the interface. Spin-coating is well suited for the formation of such interfaces as film uniformity is high. Also, it is crucial for the insulator solvent to be orthogonal to the semiconductor to avoid contamination². In this work orthogonality is ensured by using CytopTM, a fluoropolymer insulator.

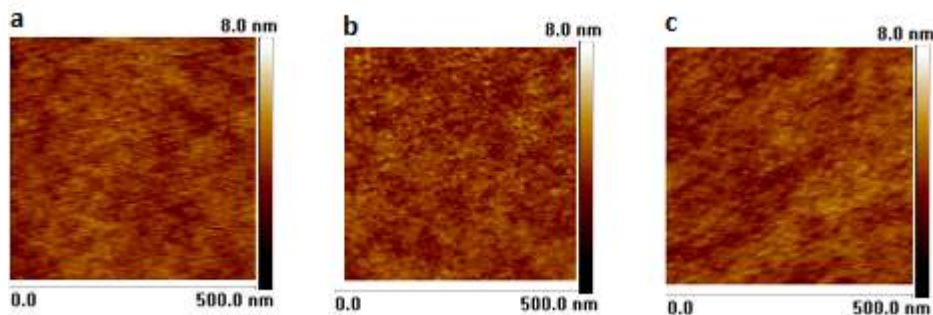
In BG, the semiconductor is deposited over the insulator. Reversing the deposition presents two challenges in fabrication. Firstly, spin-coating a hydrophilic semiconductor solution on CytopTM is impossible, unless the surface is exposed to appropriate surface chemistry modifying species. Even so, reproducing consistent film thicknesses can be hard, depending on the quality of the surface modification treatment. In this work, the hydrophobicity of the bottom-insulator is reduced by exposure to O₂ plasma.



The second challenge for BGs is related to the source and drain electrode deposition. As the BC configuration is used in this work, electrodes were deposited on the bottom-insulator layer. The electrodes were fabricated by evaporating a thin Au film, depositing and defining a photoresist structure onto the Au surface, etching, photoresist removal and cleaning. The bottom-insulator layer can thus be contaminated by the evaporated Au particles, the Au etchant, and photoresist during removal. In this work the damage sustained by the bottom-insulator is assessed by examining four indicators: the FET hysteresis, FET onset voltage, AFM images of the bottom-insulator surface, and FET mobility variation between the two gate modes, as described in the results section.

K. Taegeun, B. Changhoon, and H. L. Hong. Top-gate pentacene thin film transistor with spin-coated dielectric. *Organic Electronics* 8, 615-620. (2007)

4. Results



Atomic Force Microscope (AFM) images were taken by a Veeco Dimension 3100 in tapping mode at 1.5 Hz with 256 line resolution. Figure 4a shows the as-made CytosolTM surface exhibiting a roughness of 0.41nm. The surface in figure 4b has undergone Au evaporation and etching, and exhibits a roughness of 0.49nm. Finally, figure 4c shows an O₂ plasma ashed surface. The insulator roughness does not change significantly following electrode deposition and cleaning.

Electrical measurements were taken by a Keithley SC-4200 semiconductor parameter analyzer under dark ambient conditions. Three DG PFETs were characterized over a 102 day period. Transfer characteristics were taken by sweeping the gate voltage from 10V to -30V in steps of 0.5V, and stepping the drain voltage between -2V (linear regime) and -30V (saturation regime). No hysteresis can be observed from forward and reverse scans (Fig. 5). The onset voltage V_{ON} was extracted from semilogarithmic transfer plots at $I_{D,ON}=1pA$. V_{ON} values are stable within a window of 2V (Fig. 6). The difference in onset voltage ($V_{ON,TG}=-1V$, $V_{ON,BG}=+5V$) is attributed to the positive charging of the bottom-insulator interface caused by the O₂ plasma ashing required to clean the electrodes. Both gate modes of the transistors exhibit an on/off ratio of 10^6 for $V_D=-2V$ and 10^7 for $V_D=-30V$ over a range of $V_G-V_{ON}=20V$ (Fig. 7). Figure 7a displays the transfer characteristic of a PFET 6 days after fabrication and 7b displays the same device 84 days after fabrication. On/off ratios are maintained. The subthreshold swing for TG is stable at 0.5V/dec. For BG the initial value of 0.6V/dec increases to 0.8V/dec.

Output characteristics were taken by sweeping the drain voltage from 0V to -30V in steps of 0.5V and stepping the gate voltage from 0V to -30V in steps of -10V. Injection is linear (Fig. 8), as expected from the high workfunction thiol-treated Au electrodes used. The currents vary for TG and BG for 2 reasons: a) the two gate modes are experiencing different gate potentials due to different onset voltages, b) if the semiconductor thickness is 150nm and the electrode thickness 40nm, injected charges traverse a 100nm low conductivity region before entering the highly conductive channel, acting effectively as series resistance. This “access” resistance drops current output and results in mobility underestimation.

Field-effect mobilities were calculated with the classic equations for linear and saturation regimes. Mobility values represent peak values of a somewhat curved profile. Figure 9 displays the evolution of mobilities for 3 DG PFETs. For TG, an initial variation in mobilities settles down to more stable values after 2 weeks. The mobility then exhibits a steady decay of 5%-7%/month. For BG, the mobility degrades in a more rapid rate until day 60, at which point it also seems to stabilize to a similar decay rate, though with higher variation.

Conclusion

DG PFETs with similar interfaces have been successfully fabricated. Examination of the onset voltage reveals positive charging of the bottom-insulator interface. This is attributed to the O₂ plasma ashing treatment used to decrease the hydrophobicity of the bottom-insulator layer. The subthreshold swing is stable for TG at 0.5V/dec throughout device lifetime. For BG, the initial value of 0.6V/dec degrades to 0.8V/dec. The increased initial value of BG is attributed to slight (10%) mismatch between top- and bottom-insulator thicknesses. As the subthreshold swing is a measure of the deep traps in the semiconductor³, it is concluded that the bottom-insulator has sustained a moderate amount of damage, manifesting as higher interface deep trap density (30%) and onset voltage difference of 6V between BG and TG. The initial mobilities for TG and BG were calculated at 0.03cm²/Vs and 0.05 cm²/Vs respectively. This difference is very likely caused by the TG mobility underestimation due to high access resistance. Degradation-wise, TG decay appears steady and mobilities exhibit low variation. The decay for BG could not be measured precisely as variation is higher, though it appears to stabilize to TG-similar rate after 2 months. It is concluded that TG and BG exhibit similar performance. The surface chemistry modification step of the bottom-insulator layer is identified as the critical step in fabrication as it influences semiconductor thickness and thus access resistance for TG, charge accumulation at the bottom-insulator/semiconductor interface thus shifting the onset voltage, and deep trap density thus reducing the mobility and increasing the subthreshold swing.

W. L. Kalb, B. Batlogg. Calculating the trap density in organic field-effect transistors from experiment: A comparison of different methods. *Physical Review B* 81, 035326 (2010)

The Topic P11

from Dr. Enrico da Como

“Recombination via charge transfer excitons in
polymer/fullerene blends: the role of morphology and
molecular conformation”

was changed to a short lecture.

PRODUCCION TECHNOLOGIES FOR LARGE AREA FLEXIBLE ELECTRONICS AND OPV

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The poster gives an introduction to the variety of devices out of the area of large area printed electronics and polymer solar cells and the technology challenges implemented in these developments.

These influencing parameters are explained for the different coating and printing processes and systems used for flexible electronic systems and organic photovoltaic. A complete overview on the existing printing and coating methods used today is given.

Further an outlook on the development of different technologies and the possibility for scaling-up of processes during the next years is provided. Equipment in clean room conditions is described and specific Roll to Roll solutions in inert atmosphere are explained to the audience. Furthermore a case study of a European FP7 project called FACESS in which a printed thin film battery is powering an autonomous sensor is explained. The printed battery itself is powered by a printed polymer solar cell. Therefore a demonstrator will be shown.

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POLYANILINE, MWCNTs/PANI COMPOSITES – THEIR PROPERTIES AND POSSIBLE APPLICATION

E.N. KONYUSHENKO,* M. TRCHOVÁ, J. STEJSKAL

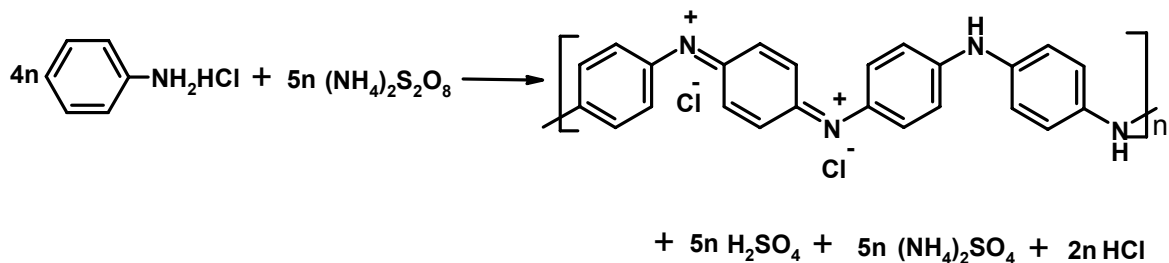
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Polyaniline (PANI) is one of the most interesting conducting polymers. It has unique electrical and optical properties and good environmental stability. Aniline or aniline hydrochloride can be oxidized by ammonium peroxydisulfate in the aqueous solutions of various acids to PANI. We have observed that, if we change the acidity of the reaction mixture, we can modify the morphology and properties of the final product.

The great variety of properties displayed by the organic conducting polymers has led to a large array of applications. These include conducting coatings for loudspeaker membrane, gas sensors ('electronic noses') to identify the presence of small quantities of different gases, battery electrodes, membranes to separate unwanted ions from solutions, corrosion-resistant coatings to prevent rusting, and cheap disposable electronic chips, and many others .

Multi-wall carbon nanotubes (MWCNTs) coated with conducting polymers have been proposed for widely differing applications including an amperometric biosensor for DNA or choline, a sensor for nitrogen oxide or an acidity sensor, as a contact in plastic electronics, and in electrorheology. The PANI-coated MWCNTs might prove to be an even more promising material.

The oxidation of aniline (or aniline hydrochloride) by commonly used oxidant, ammonium peroxydisulfate, is shown below:¹



Polyaniline film is formed during polymerization on any surface, preferably on hydrophobic ones. This property can be used for coating of MWCNTs by polyaniline (Figure 1).

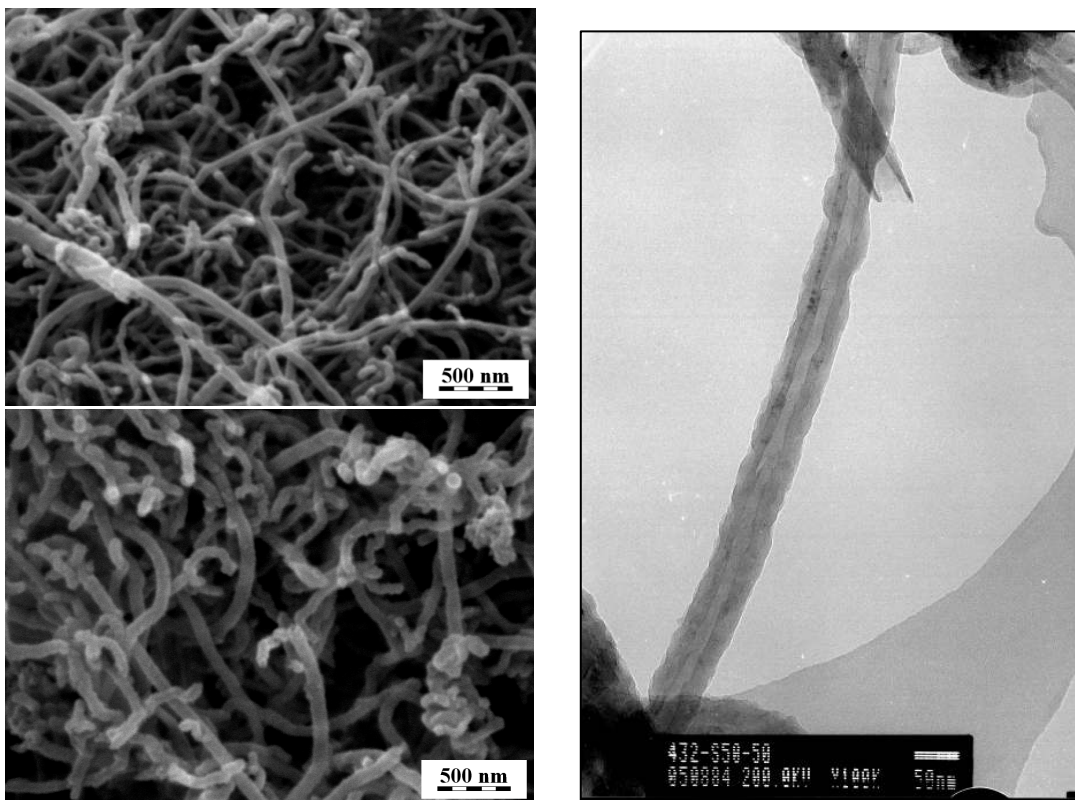


Figure 1. SEM images of pure MWCNTs (left top) and 50 % composite PANI/MWCNTs (left bottom) and TEM image of coated carbon nanotube by PANI (right).

Scanning electron microscopy (SEM) illustrates a uniform coating of MWCNTs with PANI. The coated MWCNTs become thicker as the amount of deposited PANI

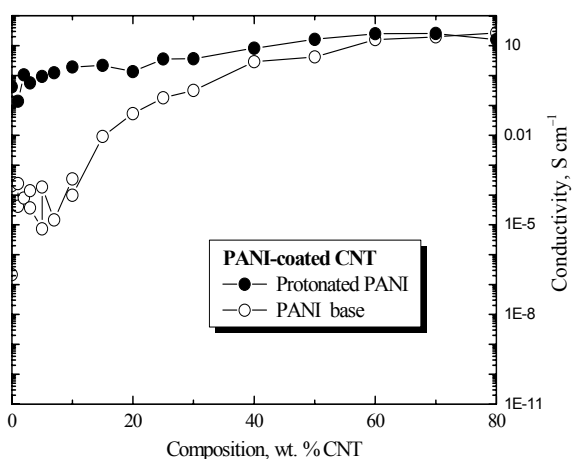


Figure 2. Conductivity of PANI coated MWCNTs.

increases. The uniform deposition of PANI on the MWCNTs is similarly demonstrated by transmission electron microscopy (TEM), which shows the bilayered structure of coated MWCNTs. As the internal cavity is well discernible, we conclude that the coating with PANI takes place only at the outer surface of the MWCNTs.² Such composite materials have good conductivity, which depends on the thickness of PANI film (Figure 2).

The conductivity is determined by the PANI as the main component at low fractions of MWCNTs. It increases moderately from 0.42 S cm^{-1} for neat PANI with increasing MWCNTs content. The decrease in the contact resistance of MWCNTs afforded by a PANI coating results in the maximum composite conductivity of 25.4 S cm^{-1} at 70 wt.% MWCNTs. The increase in the conductivity of MWCNTs coated with PANI base with increasing content of MWCNTs is moderate. At low concentrations of MWCNTs, the direct electrical contact between MWCNTs is prevented by the surface coating with a non-conducting PANI base and the percolation threshold is thus practically not distinguishable. Yet, the coating with PANI base seems to reduce the contact resistance between MWCNTs. The resulting conductivity of MWCNTs coated with PANI base thus reaches 19.6 S cm^{-1} at 70 wt.% CNTs. The conductivity is thus comparable with that of the MWCNTs coated with protonated PANI.²

Another interesting way to modify MWCNTs is to carbonize polyaniline film, which is deposited on the surface of MWCNTs during *in-situ* polymerization.^{2,3} Carbonization has been done in nitrogen atmosphere and was compared with the degradation in air (Figure 3). The composite material is composed of 50 % of polymer and 50 % of MWCNTs. When carbonization is done in inert atmosphere, and for the MWCNT/PANI base form,⁴ the composite is stable up to 500 °C and only at higher temperature starts to lose 15 % of its weight – the carbonization of PANI film takes place. When the heating was done in air, the composite is stable only up to 450 °C and during further heating decomposes completely.

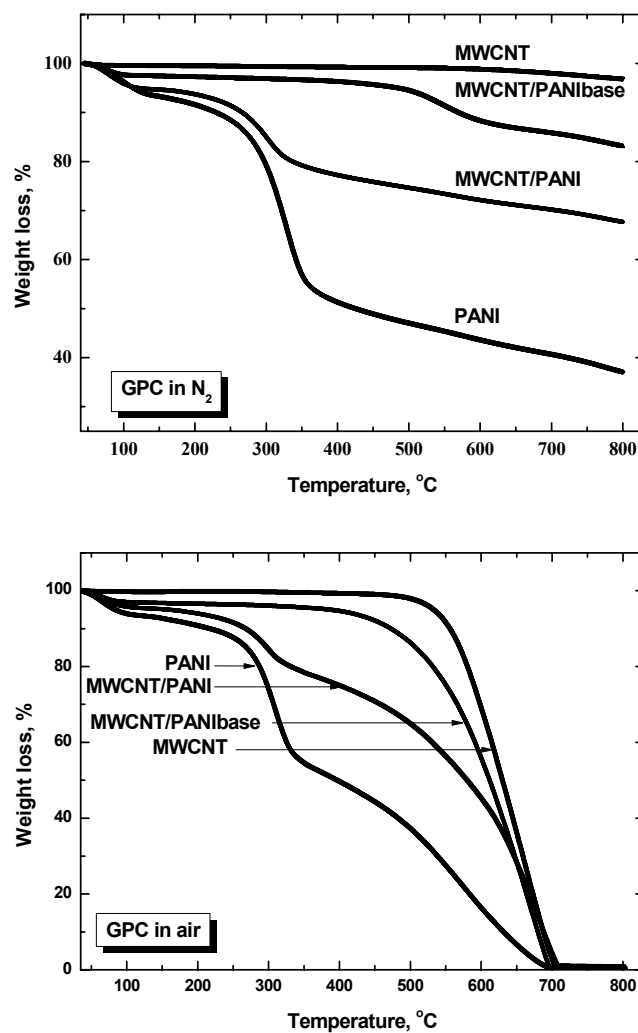


Figure 3. TGA of MWCNT/PANI base in N₂ (top) and in air (bottom).

TGA was done for the pure MWCNTs and PANI base form in order to show that individual PANI is the least stable of materials; on the other hand MWCNTs are the most stable. The combination of these two components gives us the composite with good stability and excellent conductivity properties.

Carbonized MWCNT/PANI composites represent a novel material which, in nanotubular form, may be considered in various applications. This is especially true when nitrogen-containing MWCNTs are desired.

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4. J. Stejskal, R.G. Gilbert, *Pure Appl. Chem.*, 74, 857–67, 2002.

Curriculum Vitae



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Research interests: Preparation of conducting polymers (polyaniline, polypyrrole); their characterization by various methods (FTIR spectroscopy, electron microscopy, conductivity, molecular weight, UV–visible spectra and others); preparation and application of composites materials based on conducting polymers, especially with carbon nanotubes, for fuel cells, heterogeneous catalysis, corrosion protection, *etc.*

List of selected papers – E.N. Konyushenko, January 2010:

Refereed original papers in international scientific journals: **15**
Oral or poster presentation with published abstracts: **28**

***h*-index =7, total citation number = 229** (autocitations excluded)

Impact factors (IF) are given for the year 2008 and numbers of citations are presented without self-citations of all authors.

1. Konyushenko EN, Stejskal J, Šeděnková I, Trchová M, Sapurina I, Cieslar M, Prokeš J,
Polyaniline nanotubes: conditions of formation
POLYMER INTERNATIONAL 55: 31-39 (2006).
IF2008=2.059 cited = 54
2. Trchová M, Šeděnková I, Konyushenko EN, Stejskal J, Holler P, Ćirić-Marjanović G,
Evolution of polyaniline nanotubes: The oxidation of aniline in water
THE JOURNAL OF PHYSICAL CHEMISTRY B 110: 9461–9468 (2006)
IF = 4.189 cited = 56
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Ferromagnetic behaviour of polyaniline-coated multi-wall carbon nanotubes containing nickel nanoparticles
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6. Stejskal J, Sapurina I, Trchová M, and Konyushenko EN,
Oxidation of Aniline: Polyaniline Granules, Nanotubes, and Oligoaniline Microspheres
MACROMOLECULES, 41: 3530-3536 (2008).
IF = 4.407 cited = 24
7. Stejskal J, Trchová M, Blinova NV, Konyushenko EN, Reynaud S, Prokeš J,
The reaction of polyaniline with iodine
POLYMER 49: 180–185 (2008).
IF = 3.331 cited = 4

and 8 other papers.

NOVEL LOW BAND GAP ELECTRON DONOR MATERIALS FOR ORGANIC SOLAR CELLS

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Here we report synthesis, spectroscopic and electrochemical characterization of different types of conjugated homopolymers and copolymers bearing cyclopentadithiophene units. Optical and electronic properties of the synthesized polymers can be easily modified by electron withdrawing units introduced either into the polymer backbone or attached as side chains. At the same time, physical properties of the polymers can be turned efficiently by appropriate selection of the solubilizing side chains. Preliminary data on photovoltaic performance of the synthesized polymers will be presented.

ELECTROCHEMICAL STUDIES ON NEW ELECTROCHROMIC POLYMER

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Introduction

Electrochromic materials change their optical properties in response to an electric field. There are three main types of electrochromic materials in terms of their optical properties. To the first type relate materials, that have at least one coloured and one bleached or transparent state, where the chromophore absorbs only in the UV-region. Wide used examples are wolfram oxide, viologens and PEDOT (poly(3,4-ethylenedioxythiophene)). Application fields of these materials are absorption/transmission-type devices such as smart windows and optical shutters. The electrochromes with two coloured states constitute a second class of electrochromics and are useful for display-type applications, also as optical filters and chameleon materials. A third type of chromophore exhibits more than two coloured states and attracts extensive attention in the electrochromic field. This is the area, where electrochromic polymers have several advantages over inorganic compounds, namely outstanding coloration efficiency, rapid response time, long lifetime as well as thin film flexibility, cost effectiveness and fine-tuning ability of the band gap (and the colour) through chemical structure modification [1].

Triphenylamine (TPA)-containing polymers have received considerable interest as electrochromic [2] and hole-transport materials for use in organic electroluminescence devices [3], because of their relatively high charge mobility and low ionization potentials [4-5]. The TPA radical cation is not stable and tends to dimerize rapidly forming tetraphenylbenzidine (TPB) by tail-to-tail coupling. The latter is more easily oxidized than the starting TPA and undergoes further oxidation at the applied potential [6]. The coupling reaction could be prevented by incorporating at the para-position of phenyl group electron-donating substituents [7-8]. So far, had been done some attempts to introduce TPA units into the main or side chain of the polymer backbone and in this way have been prepared new high-performance systems with novel optoelectronic functions [9-15].

Results

In this paper is reported on electrochromic properties on triphenyldiamine-based polymer. The synthesis of poly[(4-methylphenyl)imino-4,4'-diphenylene-(4-methylphenyl)imino-1,4-phenylene-phenylmethylene-1,4-phenylene-phenylmethylene-1,4-phenylene] (poly-TPD (4Me)-DPX) polymer and lasing characteristics are described in [16-17]. It is a non-conjugated copolymer having alternating triphenyldiamine and diphenylxylylene units in the backbone with good amorphous film forming properties and high glass transition temperature of $T_g \sim 240^\circ\text{C}$. The structural formula with oxidation scheme is presented in the Fig.1.

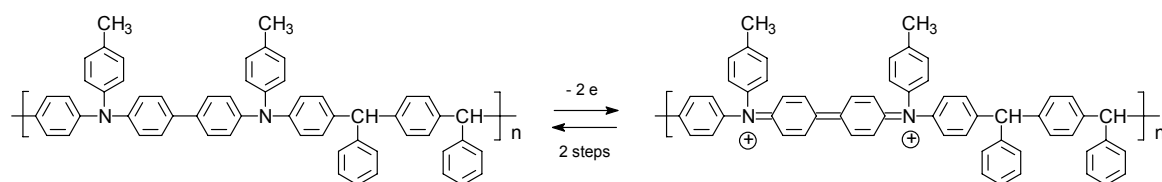


Fig.1 Electrochemical oxidation of poly-TPD(4Me)-DPX.

The oxidation is carried out in two steps with consistently oxidation of amino groups and creating radical cations and dication. The optical and electrochemical properties of poly-TPD(4Me)-DPX were investigated by UV-vis spectroscopy and cyclic voltammetry. As can be seen from Fig. 2 (a) the polymer solution exhibited two reversible oxidation potentials because of successive forming radical cation and dication. Anodic oxidation was cycled over 50 Cycles without noticeable change. At that time, in polymer film on FTO-glass the two peaks substantially merge together to become indistinguishable, where the anodic shoulder corresponds to the radical cation state (Fig.2 (b)).

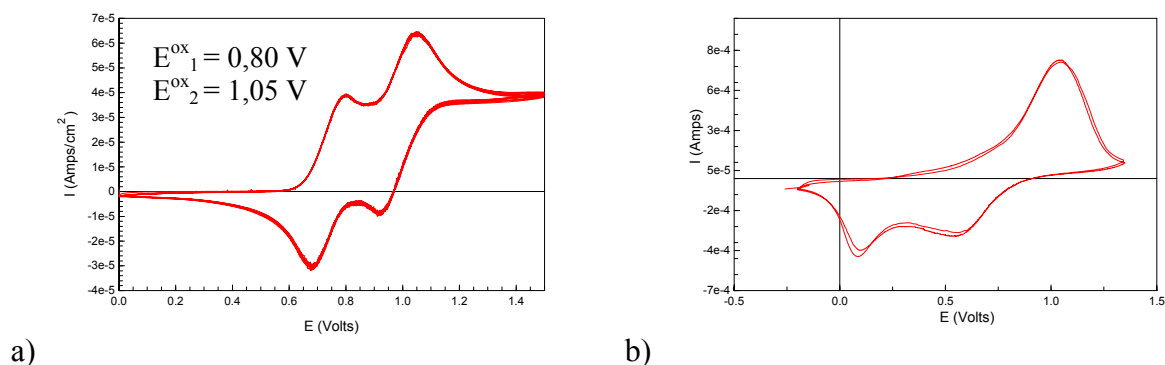


Fig.2. Cyclic voltammograms of poly-TPD(4Me)-DPX ; (a) in solution of methylene chloride, $c = 0.005 \text{ mol/l}$, Bu_4NPF_6 , $c = 0.1 \text{ mol/l}$, 50 Cycles, GE: Pt-disc electrode and (b) in film on FTO-Glass, Electrolyte: $0.5 \text{ mol/l LiTf}_2\text{N}$ (Lithium-bis(trifluoromethansulfonyl) imide) in H_2O , 5 Cycles, GE: Pt-sheet; RE: Ag/AgCl, scan-rate 15 mV/s .

The electrochemical characterization of polymer film is summarized in Table 1.

Table 1. Cyclic voltammetry data (Pt-Electrode, Ag/AgCl, Et₄NBF₄ in CH₃CN)

Material	E _p ^{ox} vs. Ag/AgCl	E _{onset} ^{ox} vs. Ag/AgCl	HOMO [eV]	E _p ^{red} vs. Ag/AgCl	E _{onset} ^{red} vs. Ag/AgCl	LUMO [eV]	E _g ^{CV} [eV]	E _g ^{opt} [eV]
Poly-TPD-(4Me)-DPX	+1,09 V	+0,98 V	-5,26	-2,02 V	-1,96 V	-2,32	2,94	3,05

HOMO, LUMO energy levels were calculated from CV and referenced to ferrocene (4,8 eV)

LUMO: HOMO (CV) + E_g^{opt}

$$E^{\text{HOMO/LUMO}} = [-(E_{\text{onset}}(\text{vs. Ag/AgCl}) - E_{\text{onset}}(\text{Fc/Fc}^+ \text{ vs. Ag/AgCl}))] - 4,8 \text{ eV (on Film)}$$

Electrochromism of the spin-coated poly-TPD(4Me)-DPX thin film on FTO-glass was monitored by a UV-vis spectrometer in 0.5mol/l LiTf₂N in H₂O at different applied potentials. Experiments were done in a quartz cuvette of 1 cm path length by assembling as electrochemical cells with polymer coated FTO-glass as working electrode, Ag/AgCl as reference electrode and Pt-wire as counter electrode. Poly-TPD(4Me)-DPX film showed multicolor electrochromic behaviour and colour was changed from neutral colourless to orange and then to blue. The measured transmittance spectra of the neutral and the two oxidized forms of the polymer film are shown in Fig. 3. When the applied potential increased positively from 0 to 0.25 V, the film turned into orange to give an intensive absorption band at 480 nm.

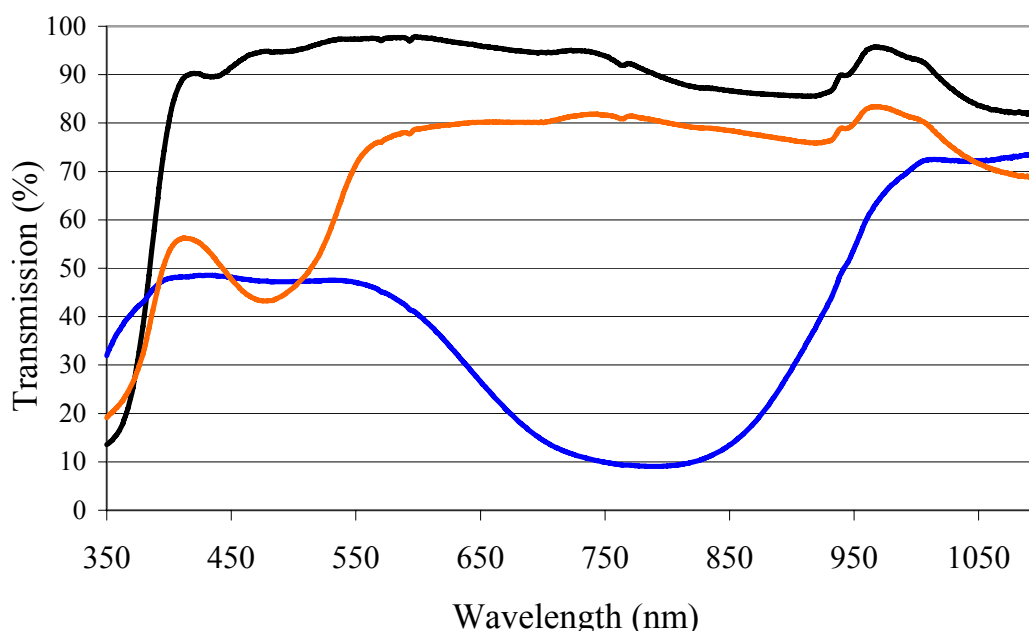


Fig.3. Transmission spectra of poly-TPD(4Me)-DPX film on FTO-glass and its two oxidized states) at E=0.25 V (orange, λ=480 nm) und at E=1.2 V (blue, λ=780 nm) , RE: Ag/AgCl, GE: Pt-wire, Electrolyte: 0.5 mol/l LiTf₂N (Lithium-bis(trifluoromethansulfonyl)imide) in H₂O.

Further raising the voltage up to 1.2 V resulted in the colour change of the film into blue accompanying the increase of absorption around 780 nm. The electrochromic characteristics of the poly-TPD(4Me)-DPX film are summarized in Table 2.

Table 2. Electrochromic behaviour of the poly-TPD(4Me)-DPX film

Characteristic	colourless/orange ($\lambda=480$ nm)	colourless /blue ($\lambda=780$ nm)
electrochrome contrast, $\Delta\%T$	51	82
optical density $OD = \log (T_{\text{Bleaching}}/T_{\text{Colouring}})$	0.34	1.0
Coloration efficiency (cm^2/C) $\eta = \log (T_{\text{Bleaching}}/T_{\text{Colouring}}) / Q$	486	357
Switching time, T (sec)	<10	<10

Thus, the electrochromism of poly-TPD(4Me)-DPX film was firstly studied in detail in present paper. The polymer demonstrates anodic multichromic behaviour with fine colour change from colourless to orange and blue and attractive coloration efficiency as well as good electrochemical stability.

Acknowledgement

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GRAYSCALE INKJET PRINTING OF PHASE-CHANGE MATERIALS WITH INCREASED RELIABILITY

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Inkjet printing has lately proven to be a viable alternative to a lot of subtractive patterning techniques. For some of these applications inkjet printing provides sufficient resolution, volume control and positioning accuracy, where the advantage of the versatility of fluids is of major interest to researchers and industrial users. In this paper we extend our previous study on inkjet printing of phase-change materials beyond the Xaar126/50 binary printhead¹ and move forward to the Xaar1001 technology,² which has been shown to reliably dispense droplets in grayscale up to 42 pL with a nominal increment of 6 pL and a natural resolution of 360 x 360 dpi. The investigated system utilizes Through-Flow Technology™ (TFT), which enables continuous circulation of the fluid through the channels and therefore increased reliability as a consequence of the removal of air bubbles and particles, which alter the acoustics of the channel. We show droplet formation and substrate interaction using *Dow's LithoJet™ Resist* series material alongside with a proprietary phase-change ink supply system.

While common inkjet ink formulations exhibit viscosities in the range of 10 mPa s, phase-change inks have drawn the attention due to the high contact angles achievable,³ resulting in high aspect ratio structures. For this evaluation of feasibility we selected LithoJet™ 210 Etch Resist to allow for evaluation and optimization of the required high temperature ink system alongside with the assessment of required driving waveforms and printouts. LithoJet™ 210 Etch Resist is a UV-curable phase-change ink designed for use as an acidic etch resist. It can be used for acid etching of copper, brass and steel substrates. Commonly used in applications such as printed circuit boards and chemical milling, this resist is removable in a caustic stripping solution.

As phase-change materials are characterized by relatively high viscosities at room temperature, the ink system needed for handling these kinds of fluids in the Through-Flow Technology™ unique to Xaar 1001 printhead requires careful system design in order to allow for constant low viscosities and the prevention of hot and cold spots. The former

would result in a decomposition of the ink upon excess temperature exposure, whereas the latter restricts circulation and therefore results in inconsistent operation and/or loss of the necessary meniscus vacuum (MV). The fluid is heated by a controlled arrangement of resistive elements, which are incorporated into the aluminum body of the header tanks, the printhead as well as around the transition path (cf. Figure 1). The fluid tanks, as can be seen in Figure 1, are positioned above the printhead to generate a hydrostatic overpressure. In order to generate a through flow and prevent the fluid from leaking through the nozzles, underpressure will be applied to the outlet cavity, establishing a pressure gradient between in- and out tank alongside with a constant meniscus vacuum. For convenience and larger operational windows, vacuum as well as overpressure may be attached to both tanks. Recirculation is ensured through a diaphragm pump.

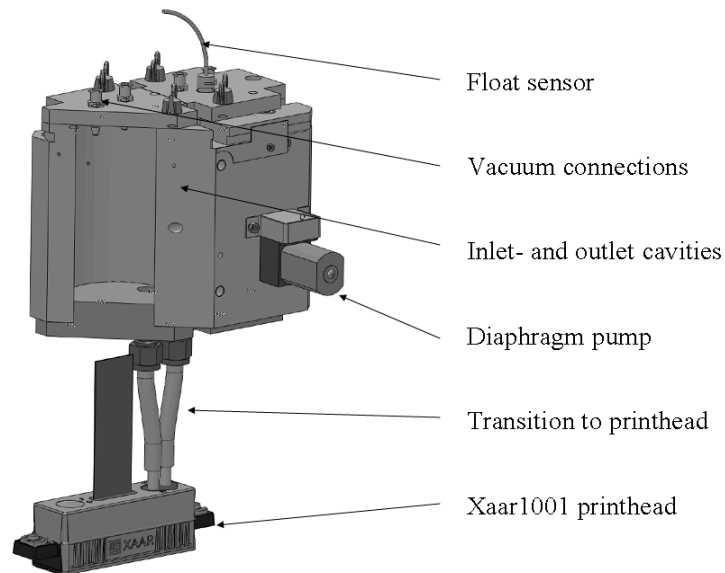


Figure 1: Schematic overview of the assembled ink system with a cut revealing the interior of the outlet tank

The performed experiments were carried out at temperatures of 90 °C and 100 °C and a meniscus pressure of –8 mbar. Printing was carried out on a xy-printer at printspeed of 0.1 m/s corresponding to 1500 Hz jetting frequency at a resolution of 360 dpi. Optical evaluation was performed using Quick Vision Elf pro (Mitutoyo).

Figure 2 shows print samples of LithoJet™ 210 Etch Resist operated at different temperatures onto unheated substrates. Apart from a well-defined drop placement resulting from the high droplet velocities of approx. 6 m/s, the influence arising from the differing temperatures can be clearly seen. Figure 2 (a) and (b) are clearly discerned by their

respective dot gain at a constant level of 1 drop per dot (dpd). While actuation was held constant lower viscosities may, due to the reduced dispersion of the acoustic wave in the channel, result in higher droplet velocities and higher discharge of volume including the formation of longer ligaments, which after disintegration are reflected as higher satellite counts on the prints. This alongside with the higher thermal mass of a larger droplet and the ensuing lower viscosity upon impact promotes a broader spreading of the droplet as a result of higher kinetic energy and reduced amount dissipated energy due to friction.⁴ Figure 2 (c) and (b) show clear transitions from fulltone areas to separate features with a pitch of 141 μm utilizing 7 dpd (approx. 42 pL).

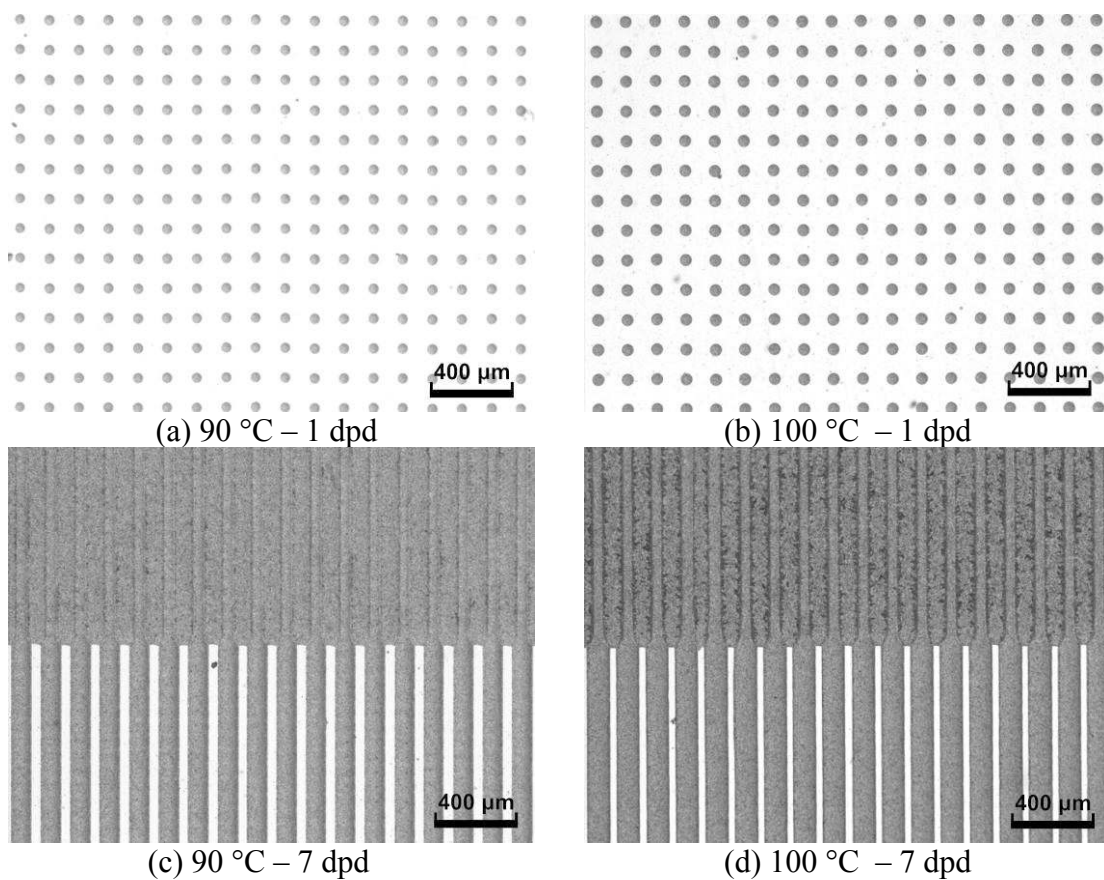


Figure 2: Print samples produced using LithoJet™ 210 and Xaar1001 at temperatures of 90 °C and 100 °C [driving frequency 1500 Hz, MV -8 mbar, 360 x 360 dpi]

Figure 3 furthermore underlines the visual results from Figure 2 (a) and (b) by measuring the deviation of printed dots from their designated location. The resulting error lies on average well within $\pm 5 \mu\text{m}$ for both investigated temperature regimes. The appearance of outliers is currently not fully understood, but may be most probably attributed to residues of fluid attached to the nozzle due to insufficient heating of the nozzle plate as well as

particle obstructions due to the lack of filtering in the current system causing strong angle deviation.

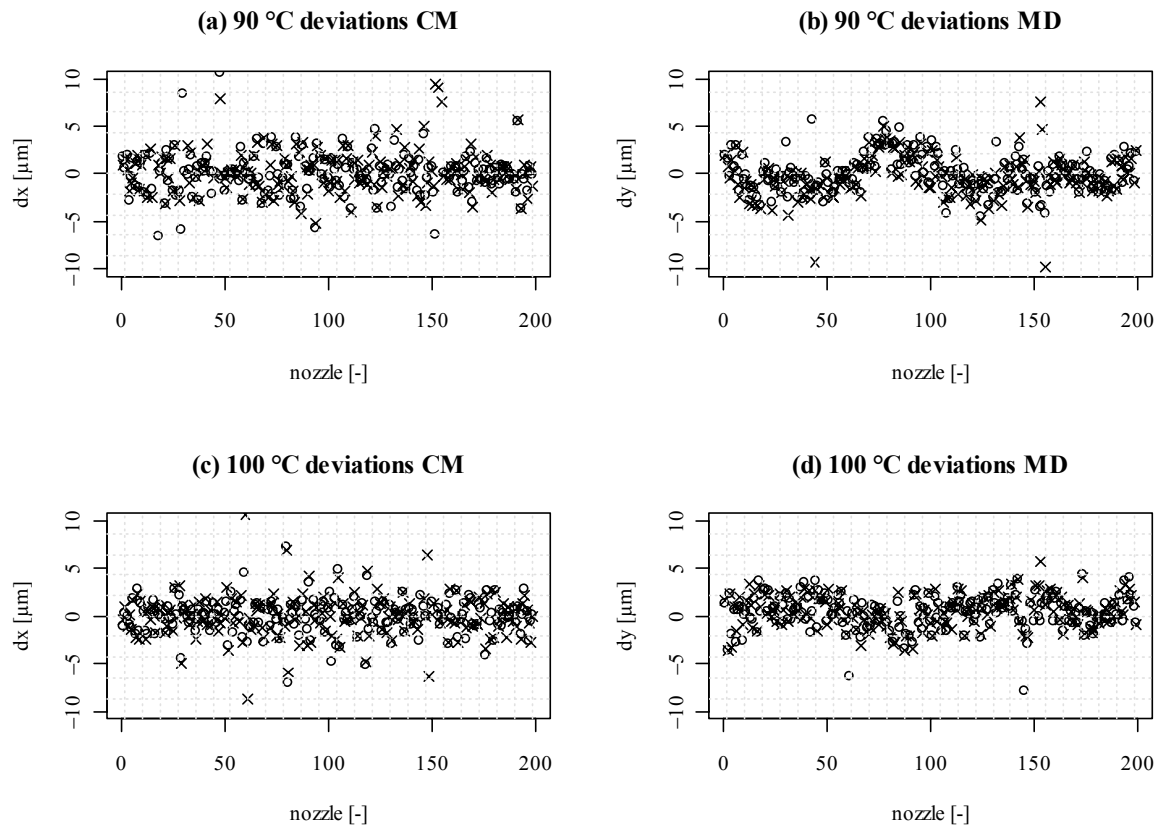


Figure 3: Dot placement accuracy cross machine (CM) and in machine direction (MD) for both actuator rows of Xaar1001 (o -- row 1, x -- row 2) with LithoJet 210™ Etch Resist at 90 °C and 100 °C.

Conclusion and Outlook

We have demonstrated first approaches of using the Xaar 1001 and its Through-Flow Technology™ in conjunction with phase-change materials at temperatures of 90 °C and 100 °C. First results indicate the basic applicability and good performance with respect to dot placement, coverage and channel recovery, while obvious outliers in the printouts still need further attention and system optimization.

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PRINTED FULL-SWING INVERTERS USING CHARGED DIELECTRICS

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Complementary circuits are desirable because of the high signal integrity and low power consumption but printable air-stable n-type semiconductors are rarely published yet [1].

One way to overcome these problems is the use of a so-called electret material as the dielectric in the organic field effect transistor (OFET). An electret is a type of dielectric that exhibits a quasi-permanent electric field due to dipolar polarization or trapped homopolar charge layers [2]. Electrostatic charging by means of corona discharges, as well as contact charging can be used to create electrets properties in organic field-effect transistors [3-5]. The high stability of the electret state, which is known to be higher than 10 years for some materials [6], makes electrostatic charging a promising technology for the realization of certain mass-printed circuits.

Here, we report on the successful fabrication of full-swing charged organic inverter circuits by means of continuous mass-printing technologies. Using an electrostatic charged perfluorinated gate dielectric (CytopTM), we demonstrate depletion-mode and enhancement-mode transistors with the same organic semiconductor (TIPS-Pentacene) in top-gate device structure. All functional layers are applied by a combination of flexography and gravure printing. The threshold voltage of the printed p-type transistors can be shifted by injecting stable positive charges by means of a corona discharge or contact charging, as illustrated in figure 1. Consequently, the transistors can be brought from enhancement-mode to depletion-mode due to an internal electrical generated by the injected charges.

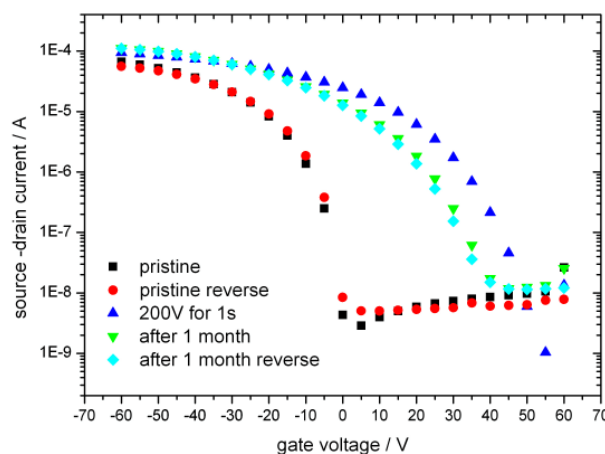


figure 1: Semilogarithmic I_{DS} - V_G curve of a transistor before (pristine), after contact charging (blue triangles) with a writing voltage of $V_w = 200$ V for 1 s and one month after charging (green triangles).

The excellent charge stability is proved by repeated measurement of the transistors. After 1 month the threshold voltage reduces to 5-10% of its original value after charging, depending on charging parameters (electrical field, charging time...). Consequently, we built up inverters, which consists of a p-type accumulation-mode drive and a p-type depletion-mode load transistor, each with the same geometrical dimensions (W/L ratio = 500). The uncharged printed transistors were brought from accumulation mode to depletion mode by applying a writing voltage of $V_{\text{Write}} = +200 \text{ V}$ for $t = 1 \text{ s}$. The static voltage characteristic of a unipolar inverter device is shown in figure 2.

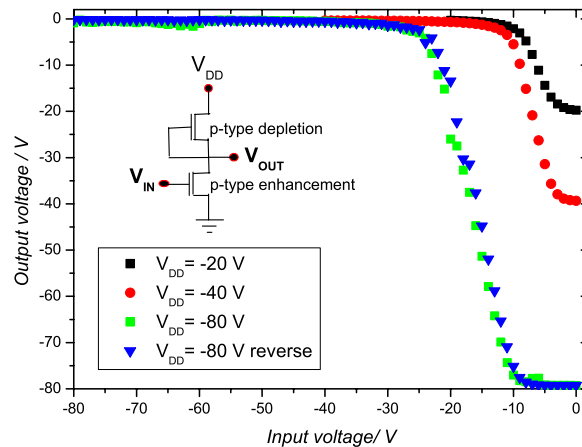


figure 2: Static voltage transfer characteristic of a printed inverter device measured for supply voltages V_{DD} of -20 V, -40 V and -80V. The inset shows the circuit diagram of the inverter comprising of a p-type depletion-mode load and a p-type enhancement drive transistor.

For negative values of drive voltages (V_{DD}) and input voltages (V_{IN}) the inverter works in the third quadrant of the output voltage (V_{OUT}) vs (V_{IN}) plot. Our devices show nearly full swing characteristic with a small hysteresis, similar to complementary inverters reported recently [7,8].

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FULLY PRINTED PVDF BASED PYROELECTRICAL SENSORS

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Innovative sensors enable diverse objects to see, hear, taste, smell and feel. Thereby, more and more applications emerge nowadays and in the future realizing advanced interactions of humans and objects. Successful and satisfying communication between objects and human beings often relies on the object's capability to recognize tactile information and distinguish humans from inanimate objects by sensing temperature and pressure and recognize their modulations in the ambience.

In this context we have developed a process for the fabrication of ferroelectric, organic sensor elements based on a PVDF-TrFE copolymer capacitor on PET foil serving as a flexible substrate. The various properties of PVDF make it suitable for a wide range of applications. Spin coating, screen printing and bar coating have been applied for producing the thin film capacitor arrays. With respect to the intended purpose – the detection of human-body radiation – the absorbance of the impinging IR-light is dramatically increased by the application of printed carbon/PeDot top electrodes, hence meeting the requirements for a cheap large area fabrication process.

1. Ferroelectric sensor material

PVDF is a well known semi-crystalline dipole electret, composed of ferro- or paraelectric crystallites embedded in amorphous regions with a quasi permanent dipole orientation polarization and Maxwell-Wagner compensation charges at the interface between amorphous and crystalline regions [1]. According to crystallization conditions, PVDF can crystallize into three structures: Form I (β -type crystal with planar zig-zag conformation), Form II (α -type crystal with TGTG⁻ conformation) and Form III (γ -type crystal with the TTTGTTTG⁻ conformation) [1]. When PVDF crystallizes from melt, it normally forms the

paraelectric α -phase, but adding different amounts of TrFE (trifluoroethylene) is known to stabilize the ferroelectric β -phase. Within this work samples are discussed which are based on a solution containing P(VDF:TrFE) in a ratio of 70:30mol%. This molar composition emerged to be the most promising precursor for obtaining highly crystalline, sufficiently flat, ferroelectric thin films by a low-temperature spin-on/printing process. 50ml of γ -butyrolactone is heated up to 453 K using a reflux condenser to avoid solvent evaporation. A known amount of P(VDF-TrFE) pellets (VDF:TrFE composition: 70:30) is added and dissolved under conditions of heating and agitating. The solution is kept at this temperature for two hours and afterwards cooled down to room temperature for gelation.

2. Methods for fabricating the ferroelectric layer

Different methods are applied for making the samples. One process is a spin coating technique: Aluminium layers with a thickness of 80nm are e-beam evaporated on the substrate (Melinex or Pet foil) serving as a bottom electrode for the capacitive sensor. Afterwards the sol is spin coated and calcined at 383 K. The samples are kept at this temperature for 5 hours and then slowly cooled down to room temperature for increasing the crystallinity of the P(VDF-TrFE) thin film. The average thickness of the pyroelectric layer varies between 4 μ m to 6 μ m. Finally 80nm thick top electrodes are deposited by e-beam evaporation of aluminum. As an IR-absorbing layer carbon is directly applied on the top electrodes.

Another processes used for the fabrication of P(VDF:TrFE) thin films is screen printing. For applying this technique a PET-foil with 1 μ m thick aluminium covering is used as a substrate on which the P(VDF:TrFE) gel is deposited via a stencil on the substrate. The attached stencil forms open areas of mesh that transfer ink as a sharp-edged image onto the Al/PET-foil substrate. A roller is moved across the screen stencil, forcing or pumping the gel in the threads of the woven mesh in the open areas. The thickness of the resulting layers varies between 5 μ m and 8 μ m. After the printing process the sample is kept at room temperature for about 10 minutes and subsequently exposed to a calcination step at 373 K for 75 minutes. As top electrode screen-printed carbon, inkjet-printed PEDOT or evaporated aluminium is used.

A further process which is applied for producing P(VDF:TrFE) based sensor layers is bar coating. This process is carried out using a "Byk Gardner Automatic film applicator". The substrate is the same Al/PET foil which was used for screen printing. Rods with a size of 15

and 25 μm (resulting film thickness in μm) with a speed of 50mm/sec are used to deposit the gel on the substrate. The rest of the process is done in the same way as described for screen printing.

3. Pyroelectric Characterization

Different sensor stripes have been fabricated based on varying solution composition (12, 15 and 18weight% of P(VDF:TrFE) 70:30). Sensor stripes, electrodes of different materials e.g. alumina, carbon paste or PEDOT and substrates (glass or PET foil) have been evaluated with respect to their electric properties. As reference material commercially available PVDF-sheets (Kureha®) have also been used for the fabrication of substrate-free stand alone sensor stripes. For the usage as transducer material, the crystalline domains must be aligned with respect to their electrical dipoles. Therefore a stepwise poling procedure above the coercive field strength of the ferroelectric material (55MV/m) is applied using a Keithley 6517A electrometer. The step-wise poling is performed by a series of pulses with increasing field strength lasting several minutes. The pulse width is 4 min and the interval between two pulses is 2 min. The maximum applied field strength is 100V/ μm , with a constant increase of 20V/ μm per step [2]. The setup for the pyroelectric measurements consists either of a Keithley 6221 function generator triggering a Newport 500B laser diode driver, an infrared laser diode with an emission of 70mW at a wavelength of 808nm, or a Synrad, Inc. Series 48 CO₂ laser with a variable emission ranging from 0 – 17W and a wavelength of 10,6 μm . These lasers are intensity modulated with a sine wave and the samples are placed in a position for illuminating the surface of the top electrode, which is coated with a black graphite absorber to achieve better absorption. The induced temperature variations in the sample generate pyroelectric current and voltage response. The responses generated within the P(VDF:TrFE) layer can be measured using a lock in amplifier (EG&G DSP 7280 with an input impedance of 100M Ω).

4. Results

Varying sensor stripes have been fabricated based on different solutions, electrodes and substrates and been evaluated with respect to their electric properties [Fig. 1]. Furthermore the influence of absorbing electrodes, different sensor sizes and fabrication processes has been evaluated and been verified using mathematic modeling of the electric measurements. In order to enable flexible integration with diverse electronic devices such as displays,

switches or read-out electronics, large-area industry-compatible processes such as screen printing or bar coating have been used for the fabrication of the sensors. With respect to the intended purpose for human body radiation the absorbance of the impinging IR-light is dramatically increased by the application of printed carbon/Pedot top electrodes [Fig. 1], hence meeting the requirements for a cheap large area fabrication.

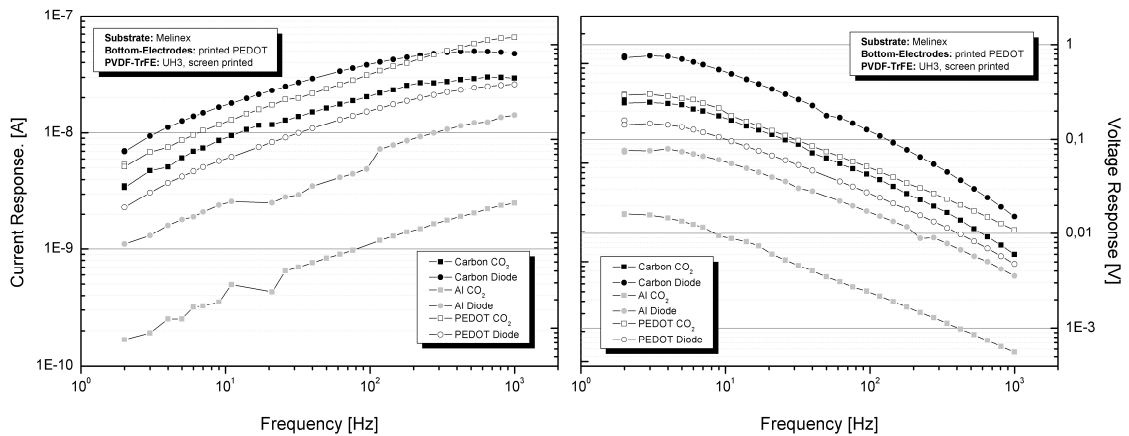


Figure 1: Current (*left*) and voltage (*right*) response of a P(VDF:TrFE) sensor. The pyroelectric outputs show a variation depending on the electrode material and the exciting wavelength due to changes in the absorption behavior.

The modulated incident laser light generates charge waves at the sensor electrodes and thus the sensor acts as a modulated current source. Via its intrinsic (very high) impedance the sensor can be operated in the voltage mode at least for frequencies higher than the cut-off frequency f_{co} . For potential applications such as optothermal switches, the sensors are connected to organic thin film transistors. One electrode of the capacitive sensor is connected to the gate of the transistor thus biasing the gate-voltage when excited by IR-light [3]. In this case the impedance matching between the sensor and the transistor is crucial because the lowest impedance in the circuit is limiting the voltage output of the sensor [Fig. 2]. In figure 3 it

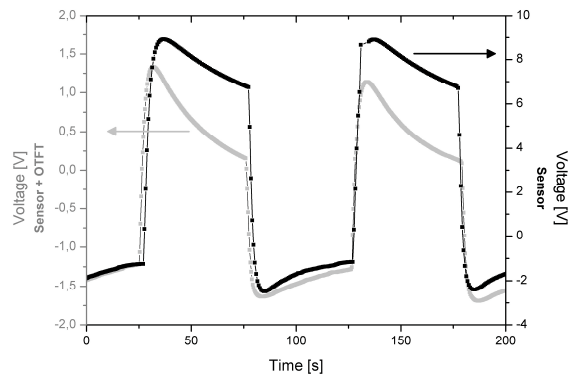


Figure 2: Reduction of the Voltage response of a pyroelectric sensor when it is connected to an OTFT caused by the gate current of the transistor (impedance matching). The response was generated with a square-wave modulated laser (45 mW, 0.01 Hz). The substrate was a PET film (Melinex) and the pyroelectric layer was a 4 μ m thick spin-coated P(VDF-TrFE) layer.

can be seen how the pyroelectric sensor voltage [Fig. 3 *left*] leads to a drain current modulation of the transistor [Fig. 3 *right*]. In the case that an absorber is applied on top of the sensor's electrode the drain current is modulated over 2-3 orders of magnitude (figure 2). Further information concerning the fabrication of OTFT's and their integration with the pyroelectric sensor elements is described elsewhere [3].

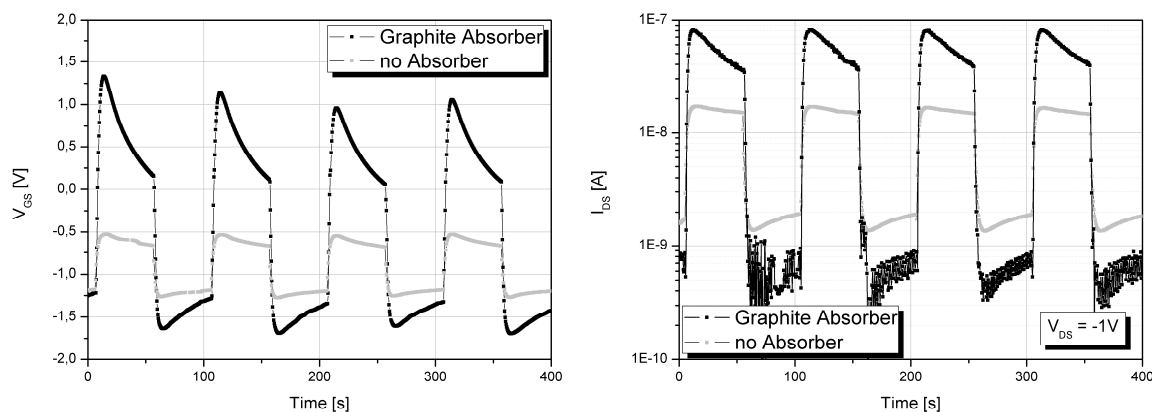


Figure 3: (*left*) Sensor (=gate) voltage of an integrated flexible pyroelectric sensor and (*right*) modulated drain current of the integrated OTFT before and after applying an absorbing graphite layer. The response was generated with a square-wave modulated laser (45 mW, 0.01 Hz). The substrate was a PET film (Melinex) and the pyroelectric layer was a 4 μ m thick spin-coated P(VDF-TrFE) layer.

5. Conclusion

We have shown that P(VDF:TrFE) based pyroelectric sensors have been fabricated by different coating processes. The sensor elements have been produced in lab scale format based on different solutions, electrode materials and substrates. The various electrodes have also been applied by printing techniques. Superimposed graphite absorber layers onto metal electrodes dramatically increased the pyroelectric output. Finally ferroelectric sensors have been combined with organic field effect transistors on flexible substrates being suitable for versatile sensor applications. Pyroelectric sensor outputs are biasing the gate of an OTFT by changing the drain current over 2-3 orders of magnitude.

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Publikationen

New geochronological data of the possible UHP metamorphic rocks of the Avren Complex; Rhodope Mountains, Bulgaria; Poster, MinPet 2009, Budapest; Ungarn
Fabrication, Characterization and Modeling of PVDF based organic IR-Sensors for Human Body Recognition; Poster and extended Abstract; IEEE Meeting 2009, New Zealand
Fully printed, flexible, integrated organic pyroelectric sensors for large-area human-machine-interfaces (HMI); Poster; MRS Fall Meeting 2009, Boston, USA

The abstract of the Poster P20 from Doris Sinwel
entitled
“Electrical characterization of organic vertical
transistors”
was not available to the editorial deadline.

EFFECT OF VARIOUS CHEMICAL ADDITIVES ON THE ACTIVE LAYER MORPHOLOGY AND PHOTOVOLTAIC PERFORMANCE OF THE FULLERENE/POLYMER BULK HETEROJUNCTION SOLAR CELLS

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It was shown recently that active layer morphology in organic solar cells can be controlled using some additives that serve as co-solvents dissolving selectively one component of the blend much better than another.

Here we investigated different types of chemical additives:

- small molecules such as 1,8-octanedithiole, 1,8-diiodooctane and etc.;
- fullerene derivatives possessing higher solubilities than conventional acceptor material PCBM;
- conjugated oligomers and polymers possessing lower solubilities than conventional material P3HT.

We showed that all types of chemical additives have strong influence on the device performance. Changes of the lateral and vertical blend morphologies as well as modification of the cathode/active layer interface are supposed to be the key mechanisms of action of different types of additives.

GROWTH OF ULTRA-THIN ORGANIC FILMS FOR MAGNETIC DECOUPLING IN HYBRID ORGANIC-INORGANIC HETEROSTRUCTURES

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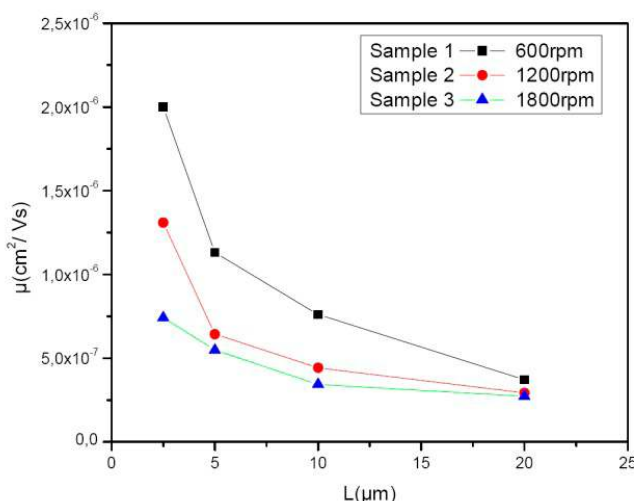
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INVESTIGATIONS OF THE DEPENDENCE OF THE SATURATION BEHAVIOUR AND CHARGE CARRIER MOBILITY ON THE FILM THICKNESS AND CHANNEL LENGTH IN MDMO-PPV ORGANIC FIELD EFFECT MEASUREMENTS

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In this study [2-methoxy,5-(3',7'-dimethyl-octyloxy)]-p-phenylene vinylene (MDMO-PPV) based organic field effect transistors (OFET) with different semiconductor film thickness and different channel lengths were investigated electrically. In the experiment, we use heavily doped Si wafers as the gate electrode, with a 100-nm thick layer of thermally oxidized SiO₂ as the gate dielectric layer. Interdigitated drain-source geometry was used to obtain higher currents for the short channel devices. The channel lengths were 2.5, 5, 10 and 20 μm with a fixed channel width of 10 μm. The source-drain current and the field effect mobility, determined in the saturation region of the OFET current-voltage characteristics, were found to increase with MDMO-PPV film thickness. The field effect mobility determined from the saturation region of the IV characteristics showed less dependence on the film thickness. Based on these results we investigated the correlation between the channel length and film thickness on device performance.



BIOGRAPHIC DATA OF ALI VEYSEL TUNC

Ali Veysel Tunc has been working at the University of Oldenburg as a PhD student since October 2008. The focus of his work is on the electrical characterisation of organic semiconducting materials for photovoltaic and field effect transistor applications. Before coming to Oldenburg, A. V. Tunc was working on holographic data storage and 3D display technology using photorefractive polymers.



DIELECTRIC PROPERTIES OF PET FILMS MODIFIED BY FUNCTIONAL CARBON NANOMATERIALS

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Thermoplastic composites with carbon carbon nanomaterials (CNM) have a great potential as structural materials because of their superior mechanical properties and ease of processing. It is reported about experiment on preparing and dielectric properties measurements of polymer composites containing unmodified and CNM-modified in different concentrations (0.1, 0.3 and 0.5 wt.%). Thermoplastic polyester – poly (ethylene terephthalate) (PET) was used as a composite matrix. All composite materials were obtained by *in situ* polycondensation in molten state (i.e. during the synthesis of polymer matrix). The process conditions were determined experimentally depending on the matrix type. The presence of CNM (regardless of modification or concentration) in a reactive mixture had no influence on the chemical reactions during synthesis what confirms a usability of the *in situ* method to polymer nanocomposites preparation. A microscopic analysis of composite structure revealed an uniform distribution of nanofillers in a polymer matrix. Bulk composite materials, after granulation and drying, were subjected to injection moulding in order to prepare samples for testing. The addition of nanofillers into polymers didn't affect their processability, even if the viscosity of composites was slightly higher compared to homopolymers.

CNM were obtained from methane-air mixture upon atmospheric pressure without catalyst on high voltage atmospheric pressure discharge set-up.

CNM specimens were studied by scanning (SEM) and transmission (TEM) electronic microscopy. According to SEM and TEM data CNM diameters are within 12-60 nm.

PET - based polymer composites containing different kinds of CNM (unmodified and functionalized with – F, - COOH, - NH₂, - C₂H₅, - Fe(C₅H₆)₂, - (CH₂)₁₅CH₃ groups) were characterized by following techniques: SEM, DSC, DETA and mechanical tests. TGA and WAXS/SAXS (for a few samples) analyses have been employed additionally for better interpretation of the results. The effect of CNM addition on composite physical properties depends on the character of polymer matrix significantly. Among PET-based composite materials only some revealed an increase of mechanical properties i.e. tensile strength (up to 14% for PET/unmodified CNM, PET/CNM-NH₂) and elongation at break (up to 25% for PET/unmodified CNM, PET/CNM-F, PET/CNM-COOH). An increase of composite brittleness resulted from CNM affect on crystallization of PET matrix and its final crystallinity. The DSC and WAXS/SAXS analyses confirmed that CNM-containing composites were characterized by lower/comparable crystallinity degree (in respect to unmodified PET), however the crystals structure was more heterogenous and defected. It is important to note that CNM used in this study included multi – walled carbon nanotubes, nanofibres and amorphous graphite with the average diameter of 100 nm. The presence of such relatively large inclusions in a polymer during condensation on one hand accelerated the crystallization, on the other hand could disturb the process of crystals formation. It could also contribute to lower molecular weight of polymer matrix, what rendered composites more brittle: during polymerization a reaction of polymer chains growth was difficult due to the presence of relatively large nanofibres increasing a viscosity of reactive mixture and limiting macromolecular mobility. A lack of significant changes in nanocomposite performance was also linked to low mechanical strength of nanofillers: the microscopic analysis of nanocomposites structure revealed nanofibres failures visible on a fracture surface. This CNM structure weakening could be a result of chemical modification. In the case of PET-based composites containing different kinds of CNM a slight increase of tensile stress (up to ca. 20% for all kind of composites) without an influence on elongation at break was observed. This effect of slight reinforcement could be attributed to nanofiller / polymer matrix interactions, as DSC analysis did not confirmed an increase of crystallinity degree of PET hard phase, however a distinct acceleration of crystallization process in the presence of CNM nanofillers was observed. In all cases the presence of CNM additives did not affect thermal properties of composites: thermal stability as well as characteristic temperatures (T_g, T_m) were comparable to homopolymers. It indicated that the effectiveness of CNM chemical modification was not sufficient to ensure strong polymer/ CNM bonding. The positive aspect of the addition of unmodified or modified by CNM were changes of dielectric behavior of polymers in

respect to current frequency. PET-based composites revealed changes in permittivity – a decrease of dielectric loss in low and high frequencies.

The results of dielectric properties measurements of PET films with CNT added in a various ratios are presented. Changes of capacitance and dielectric losses were measured in a frequency range 102-104 Hz at 300 K. Influence of type and amount of CNT in samples on dielectric properties was studied. Capacitance increase from 10 to 20% is observed even for minimal CNT amount (0,05 wt. %). Dielectric losses coefficient is decreased while CNT content increases. Approximation of dielectric spectrum with Havrila-Negami equation allowed to estimate changes of time constants of β -relaxation process.

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DEVELOPMENT OF AN INKJET PRINTING PROCESS FOR THE PRODUCTION OF OPV MODULES : THE SOLARJET PROJECT

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Within OPV domain, the PCE and lifetime expectancies of devices are suitable for nomad and indoor applications. To open up these markets, the OPV cells must be produced at low cost which can only be achieved by printing technology. Depending to the application, cells must be produced on flexible substrates allowing an important freedom of integration. The development of an inkjet printing process allows reaching a technology compatible with these types of substrates and with the criteria of productivity. The patterning capability of inkjet would bring a real breakthrough for the elaboration of OPV cells, by allowing the production on large and various substrates while easily varying the cell layout.

SOLARJET project consortium brings together French partners, **ARDEJE**, the coordinator, as well as **INES** (CEA Grenoble) and **HUTCHINSON**, to demonstrate that OPV technology can be scaled up to an industrial step with inkjet printing. Ending in 2011, **SOLARJET** aims at developing an advanced OPV process and its associated manufacturing equipments. Customized print modules, functional fluids and solar cell architectures are developing jointly to meet the requirements and to ensure scalability to production. The partners also address the key point of protection against moisture and oxygen for OPV solar cells. The research is focussing on high-value plastic films and encapsulations with high barrier properties to improve OPV solar cells lifetime.

Results presented here will mainly concern the setup of printing process of the OPV cells. The whole organic solar cell (4 layers) was deposited by inkjet printing technique on plastic substrates. Several parameters *i.e.* the choice of solvent, the annealing conditions, the inkjet parameters, which influence the morphology of each layer and thus the performances of the devices, were studied. First results can be obtained in a very short time by this technique. For example, power conversion efficiency up to 3 % was obtained on 0.28 cm² devices, measured under simulated white light AM 1.5, at 100 mW.cm⁻². First tests of stability were also conducted on these new devices.

NANOAGGREGATES OF PHTHALOCYANINE FOR ORGANIC PHOTOVOLTAIC APPLICATIONS

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Metal-phthalocyanines are used in organic solar cells as strong electron donating molecules. The structure of donor and acceptor components of organic solar cell is an important parameter and needs to be understood and optimized. Usually such organic solar cells are produced by vapor deposition, although low-cost wet chemical methods offer more possibilities to control the structure of phthalocyanine nanoaggregates on surface. In this case several parameters affect the nanoaggregate structures, such as the solvent, the deposition methods and the temperature of the solvent and substrate, etc. One of the reasons why vapor deposition is still preferred is the poor solubility of the metal-phthalocyanines.

We present a solubility study of the metal-phthalocyanines with conventional organic solvents, acids and ionic liquids. Several solvents with sufficient solubility are presented. With these solvents phthalocyanine nanoaggregates are prepared by spray-pyrolysis, spin coating and dip coating on silicon dioxide and indium tin oxide surfaces. Structures of copper, iron and zinc-phthalocyanine are investigated by AFM and optical spectroscopy. Solar cells based on a combined wet chemical and vapor deposition preparation procedure show an efficiency of up to 2%.

INTEGRATION OF TWO DIFFERENT SPIN-COATED OPTOELECTRONIC DEVICES ON A SINGLE SUBSTRATE

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Organic semiconductors became a popular subject of research and development interests over the past years. Efficient organic light-emitting diodes (OLEDs) and organic photodiodes (OPDs) were demonstrated and are in the market already [1–4]. Further research, such as material characterization and synthesis of new organic and organometallic materials are still under development. Research activities on OLEDs are mainly driven by display and general lighting applications, whereas most organic photodetector research has been performed in the area of solar cells [5]. Generally, organic devices can be fabricated in a cost effective way on a wide range of substrates. They emit and absorb light in the entire visible spectrum, as well as in parts of the near infrared [6]. Furthermore, a photolithographic structuring of these devices enables complex device layouts or an array patterning. Organic photo detecting semiconductor devices have been in the focus of joint research endeavour during the past decade, particularly in the field of photovoltaic [7]. Compared to the most common crystalline silicon solar cells, organic solar cells (OSCs) exhibit multiple advantages, such as higher absorption, the promise of low cost production by using roll-to-roll processing, as well as their mechanical flexibility [8]. The drawbacks of organic materials are their low carrier mobilities and the high band gap of organic semiconductors, resulting in smaller efficiencies for OSCs. A composite film of a blend of functionalized fullerenes as electron acceptor and conjugated polymers as electron donor bulk heterojunction is the most promising material class for organic devices [9], as high external quantum efficiencies were demonstrated in bulk heterojunction solar cells. In this type of structure the absorption of light results in excitons, which are split into free carriers at the interface between the donor and the acceptor material. The electron is transferred to the acceptor and the hole remains on the donor. After the exciton splitting, hole and electron transport occurs through respectively the donor and acceptor material towards the electrodes [10].

The integration of OLED and OPD on one substrate is a very promising perspective for applications as bio sensing, chemical sensing, or optical integrated systems [11–14]. The purpose of our group is to integrate two different optoelectronic devices, OLED and OPD,

in a lab-on-a-chip system. Lab-on-a-chip systems are devices that integrate one or several laboratory functions on a single chip of only millimetres to few square centimetres in size. It can deal with the handling of small fluid volumes down to less than pico litres. For realization of such a lab-on-a-chip system we investigate possibilities for manufacturing an optical measuring system on a single substrate. One possibility is the integration of two different spin-coated optoelectronic devices, OLED acting as a light source and OPD as receiver, on a substrate. As light source a polymer OLED containing the polymer Super Yellow (PDY-132) is used. On the receiver side of the optical system, we investigated OPDs based on the concept of a bulk heterojunction using a composite material blend of the polymer poly(3-hexylthiophene) (P3HT) and the fullerene-derivative phenyl-C61-butylric acid methyl ester (PCBM). It shows high carrier mobilities and external quantum efficiencies. The combination of the above described OLED and OPD material was chosen, because the absorption of P3HT:PCBM matches the Super-Yellow OLED emission in an advantageous manner.

The optical measurement system is fabricated on a glass substrate coated with an indium tin oxide (ITO) layer as the transparent conducting anode. The substrate is treated by an oxygen plasma in order to improve the wettability in the following spin coating deposition of the hole transport layer (HTL) poly(3,4-ethylenedioxythiophene:poly-styrenesulfonate) (PEDOT:PSS). In a second spin coating step the polymer Super Yellow (PDY-132) for emitting layer (EML) is deposited. For the cathode magnesium and silver have been evaporated through a shadow mask. After metal contacts were evaporated to complete the OLED, one half of the substrate is freed of the organic semiconductor layer using oxygen plasma treatment. In a subsequent step the OPD has been deposited by spin coating on the substrate. The chosen OPD materials for this device are poly(3-hexylthiophene) (P3HT) and phenyl-C61-butylric acid methyl ester (PCBM). PCBM act as acceptor material and on other hand P3HT act as donor material. Metal contacts for the cathode were evaporated on top of the polymer blend to complete the OPD, resulting in the desired integration of OLED and OPD on a single substrate for realization of an optical measurement system.

In conclusion we reported a fabrication procedure for the integration of a spin-coated OLED based on the emitting polymer Super Yellow and a spin-coated OPD based on P3HT:PCBM on a single ITO-coated glass substrate.

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Methods to Enhance the Efficiency of Organic Light Emitting Devices

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In recent years organic light emitting devices (OLEDs) have experienced a prolific time in university research as well as in industry. A big advantage is the combination of costeffectiveness with large area device fabrication. Even if OLEDs already appear in commercial displays, their performance is still behind schedule for lighting applications.

Most of the light generated in the emissive layer is trapped inside the device, either as waveguide modes in the ITO and organic layers or substrate modes in the glass substrate, which is shown in Fig. 1. Light confined in the substrate can be extracted by established methods such as applying microlenses [1] or by roughening the substrate-air interface [2]. The guided modes trapped in the ITO and organics however are a challenge to researchers worldwide, since any change in the device structure within the layers does not only affect the optical properties but also the electronic properties. Several approaches have been made to extract these guided modes: via nanoparticles [3], via scattering particles [4], via plasmonic cathode structures [5] or by structuring the ITO anode with Bragg-gratings [6,7].

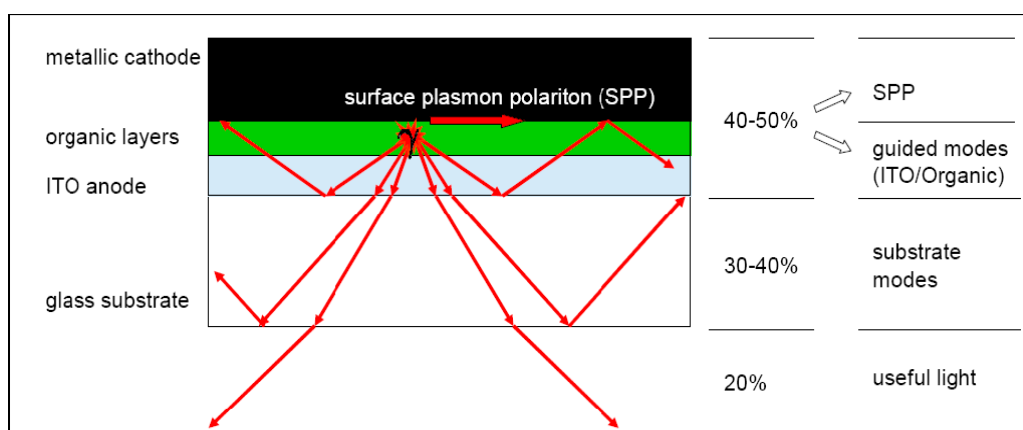


Fig. 1 Scheme of the loss channels inside an OLED.

We examine two different methods for increasing the performance of OLEDs – one is the roughening of the internal glass interface and the other is embedding one-dimensional gratings of different grating depths in a high-index layer on top of the glass substrate.

Roughening internal glass interface

In the first approach we fabricated ITO-free OLEDs on rough glass substrates with a subsequent Ta₂O₅-layer. The glass substrates were roughened by glass etching cream, sandblasting or grinding paste (see Fig. 2).

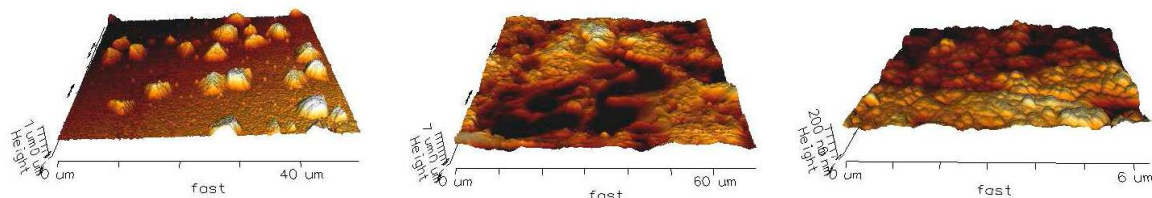


Fig. 2 AFM images of glass substrates which were roughened using glass etching cream, sandblasting or grinding paste (from left to right).

To prevent too high roughness peaks, the samples were then finished with a polishing paste. Afterwards, a transparent Ta₂O₅ layer was evaporated. It had a thickness of 50 nm and a refractive index of $n = 2.1$ (at a wavelength of 550 nm). In order to get a smooth surface a layer of SU-8 was applied on top of the Ta₂O₅ layer. ITO-free OLEDs were fabricated as described in the following. The anode was processed by spincoating a solution of PEDOT:PSS and DMSO onto the smooth SU-8 layer, resulting in a conductivity of about 300 S/cm. The emission layer was also applied by spincoating of Ph-PPV (Super Yellow).

Furthermore, a cathode of calcium and a cover layer of aluminum were evaporated. As a last step, the OLEDs were encapsulated with epoxy resin adhesive and a glass slide. The electroluminescence measurements are shown in Fig. 3.

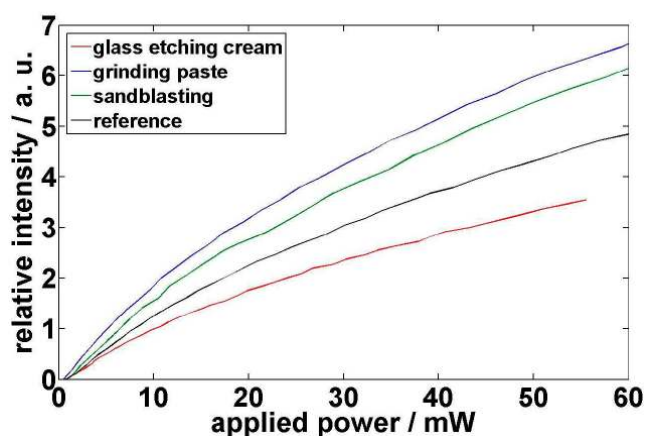


Fig. 3 Relative intensity vs. the applied power.

The devices treated by sandblasting and by grinding paste exhibit an enhancement of up to 1.25 compared to a reference device with a flat internal interface. Only the sample treated with glass etching cream performed worse than the reference. This is most likely due to a voltage drop that occurs along the anode if the roughness is too high. In principle,

roughening internal interfaces can be suited for extracting both, substrate and guided modes inside an OLED.

Introducing 1-dimensional gratings

In the second approach we processed ITO-free OLEDs on glass substrates with a periodically nanostructured, transparent Ta₂O₅-layer, with a thickness of 300 nm and a refractive index of $n = 2.1$ (at a wavelength of 550 nm). A one-dimensional grating with a period of 370 nm was brought into the surface by a combination of laser interference lithography and physical plasma etching. The OLED was then processed as described in the previous section.

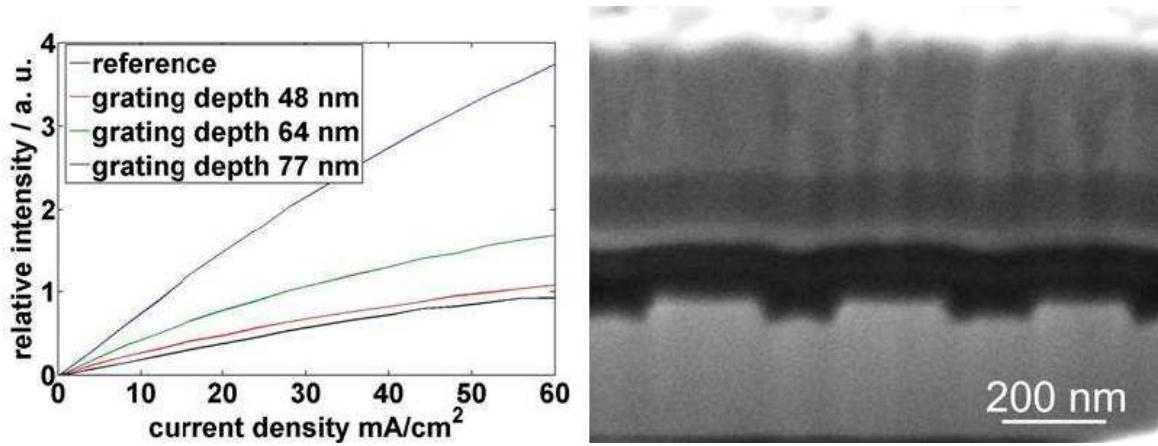


Fig. 4 Luminous flux vs. current density (left) and SEM image of the cross section of a nanostructured OLED (right).

The nanostructured devices had an up to 300% higher light output as compared to the unstructured reference device (see Fig. 4). Even if the emission profile (not shown here) reveals characteristic outcoupling peaks, they cannot account for this enhancement solely. Apart from that the emission profile of the devices with grating changes to a more Lambertian character, indicating that the substrate modes are strongly influenced. We investigated two approaches for light extraction by incorporating nanostructures into OLEDs. For ITO-free OLEDs with rough internal interfaces we found an enhancement of the efficiency by a factor of 1.25. ITO-free devices with a periodic nanostructure in a high-index layer showed an improvement by a factor of 4.

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NAFION MEMBRANE MODIFICATION FOR APPLICATION IN FUEL CELLS

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Perfluorinated polymer with chemically bonded sulfonic groups (Nafion) is used as a proton-conducting membrane in proton-exchange membrane fuel cells (FC). Nafion has an excellent balance of the main properties: proton conductivity, chemical and mechanical stability, long time durability. Membrane disadvantages include low temperature stability, humidity dependence of properties and high permeability for liquid fuels that reduce the efficiency of FC.¹

The volume modification of Nafion by inorganic compounds and by conducting polymers has been performed with the goal to minimize this disadvantage. When the conducting polymers are used for modification, aniline or pyrrole monomers polymerize inside of Nafion proton-conducting channels. This lowered the membrane dependence on water content and diminished methanol cross-over but the proton conductivity of Nafion is suppressed, too, because of the reduced transport of water inside Nafion channels.

The new approach consists in the surface modification of membrane while keeping Nafion pores free.² The method of surface Nafion modification by two symmetric polyaniline (PANI) layers with high level of electron and proton conductivity was developed.

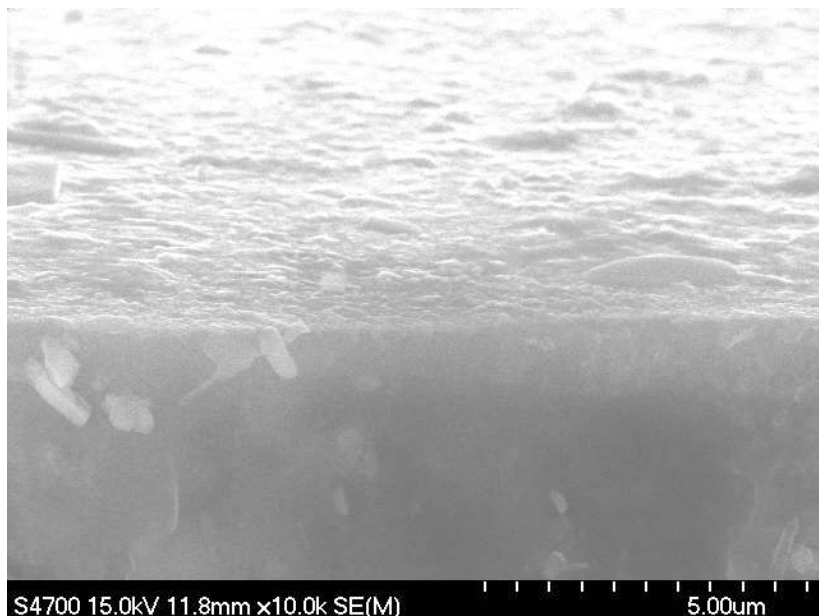


Fig. 1. PANI layer deposited on the surface of Nafion membrane.

Nafion membrane modified with two PANI surface layers demonstrated the same proton conductivity as a pristine Nafion. At the same time, methanol cross-over through membrane diminished from $3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ to $1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The investigation of thermal stability of surface modified Nafion showed that PANI lowered the membrane humidity dependence and changed the temperature of sulfonic-groups degradation from 315 to 355 °C.

Conducting PANI layers were used for the deposition of platinum catalyst on the membrane interface. Platinum particles of 20 nm diameter can be seen on the Fig 2c. Adhesion of PANI layer to Nafion and platinum to PANI is excellent. The modified membrane with catalytic layer can be used in the fuel cells with the direct oxidation of liquid fuels.

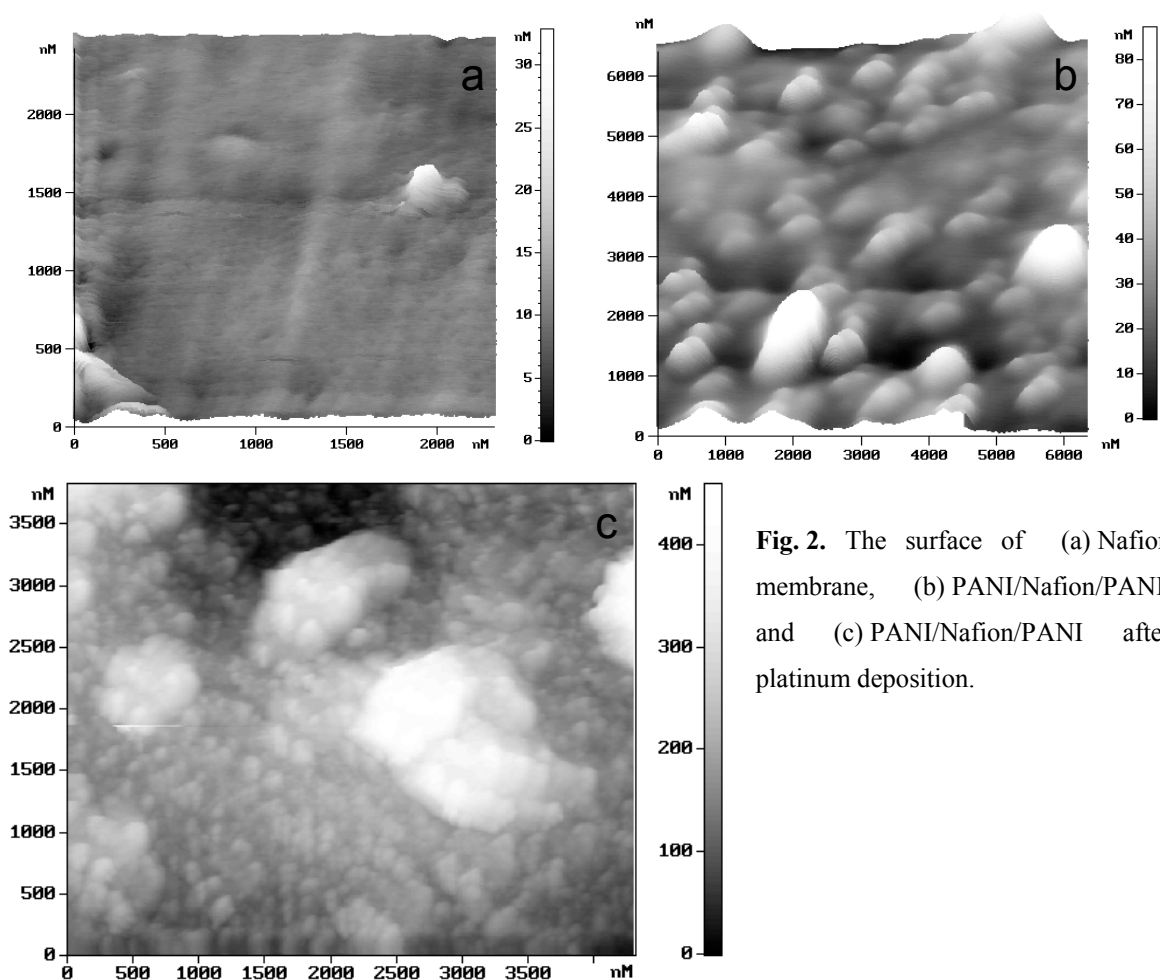


Fig. 2. The surface of (a) Nafion membrane, (b) PANI/Nafion/PANI, and (c) PANI/Nafion/PANI after platinum deposition.

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POLYANILINE: THE PRESENCE AND THE FUTURE

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1. Polyaniline nanostructures

Polyaniline, a conducting polymer, is prepared by the oxidation of aniline, peroxydisulfate being the first choice of an oxidant (Fig. 1):

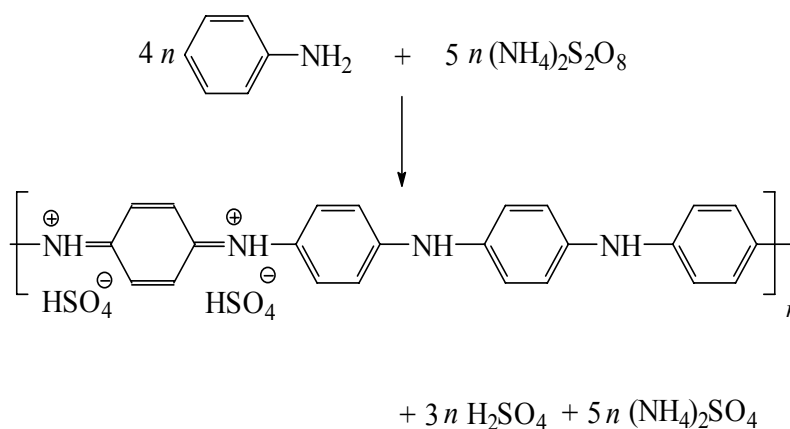


Fig. 1. The oxidation of aniline with ammonium peroxydisulfate in acidic medium yields the emeraldine form of PANI. Sulfuric acid and ammonium sulfate are by-products.

The reaction proceeds at room temperature, in aqueous medium, and it is completed in tens of minutes with a yield close to 100 %. Polyaniline is obtained as a precipitate, its

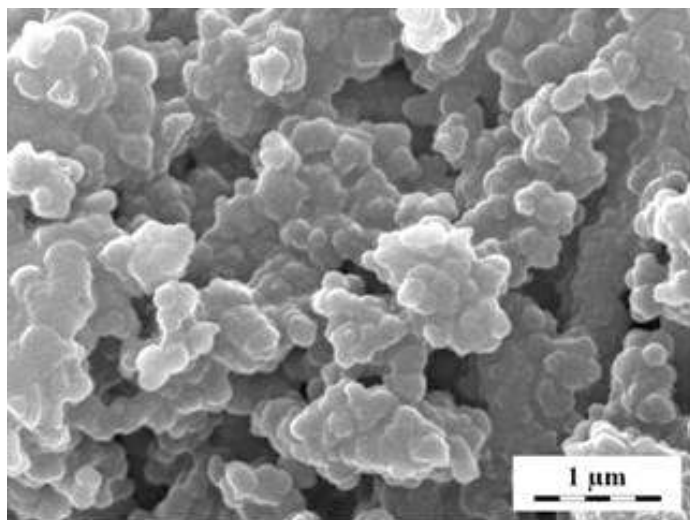


Fig. 2. Granular morphology of polyaniline powder.

conductivity is 4 S cm^{-1} [1]. Sulfuric acid is a by-product. This means that the acidity increases during the oxidation of aniline. Depending on the starting acidity and acidity profile, various morphologies are obtained [2–4]: polyaniline granules in strongly acidic media (Fig. 2), nanotubes at mildly acidic conditions (Fig. 3).

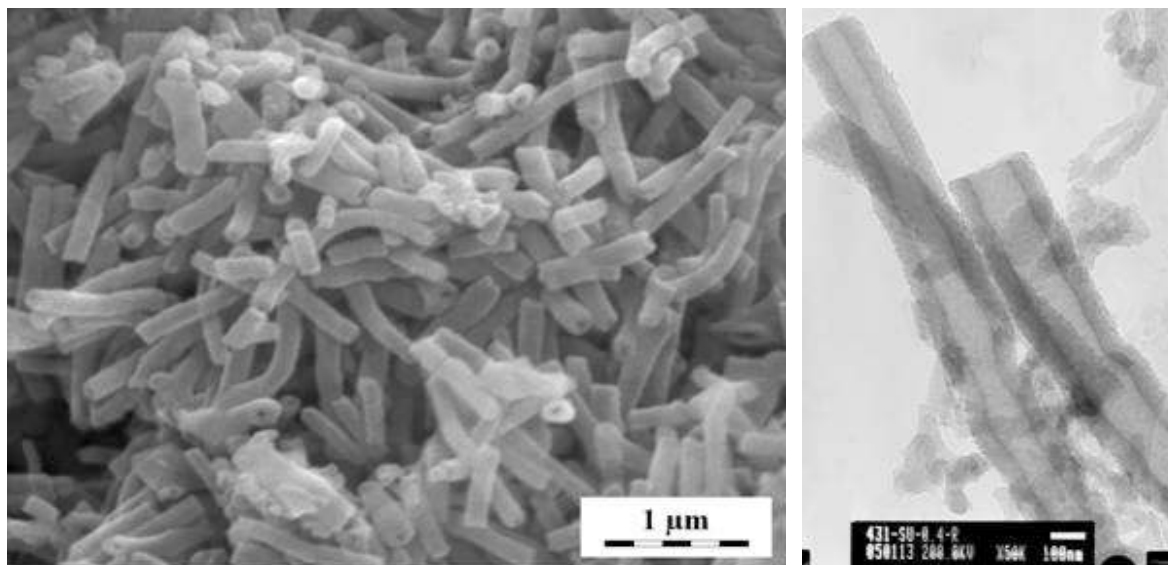


Fig. 3. Polyaniline nanotubes.

At the same time, the surfaces immersed in the reaction mixture become coated with a thin PANI film, ~100 nm thick [5]. This applies also to any particulate substrate, such as silica gel, ferrites, titanium oxide, *etc.* In the presence of a water-soluble polymer, such as poly(*N*-vinylpyrrolidone), polyaniline colloids having a particle size ~400 nm are obtained [5]. Polyaniline can be thus obtained in various forms.

2. Polyaniline: a responsive polymer for sensors

Polyaniline is prepared in protonated form (Figs. 1,4), a so-called emeraldine salt, which is conducting. In alkaline media this form is deprotonated to emeraldine base and the conductivity decreases by nine orders of magnitude. This process is reversible and makes a basis for the constructions of sensors. The most common is the sensor for ammonia, which operates on the conductivity decrease; the acid gases, such as hydrogen chloride, have a reverse effect.

The conversion of emeraldine salt to emeraldine base is also connected with the change in optical absorption, the colour changes from green to blue, which makes the basis for optical sensors. At the same time, the volume, the density, the permittivity, the wettability, and magnetic permeability change as well, and such properties can be used in sensing, too.

In addition to the "horizontal" acid–base processes, the vertical "reduction–oxidation" transitions are available (Fig. 4). The conversion of emeraldine to oxidized

form, pernigraniline, is similarly connected with the change in physical and chemical properties and can be used in sensing of oxidants, such as peroxides, halogens, *etc.* The reductants cause the conversion to leucoemeraldine. The chemicals, such as hydrogen, hydrogen sulfide, hydrazine, *etc.*, will cause the changes in physical properties of polyaniline. Thin polyaniline films are best suited for the sensing.

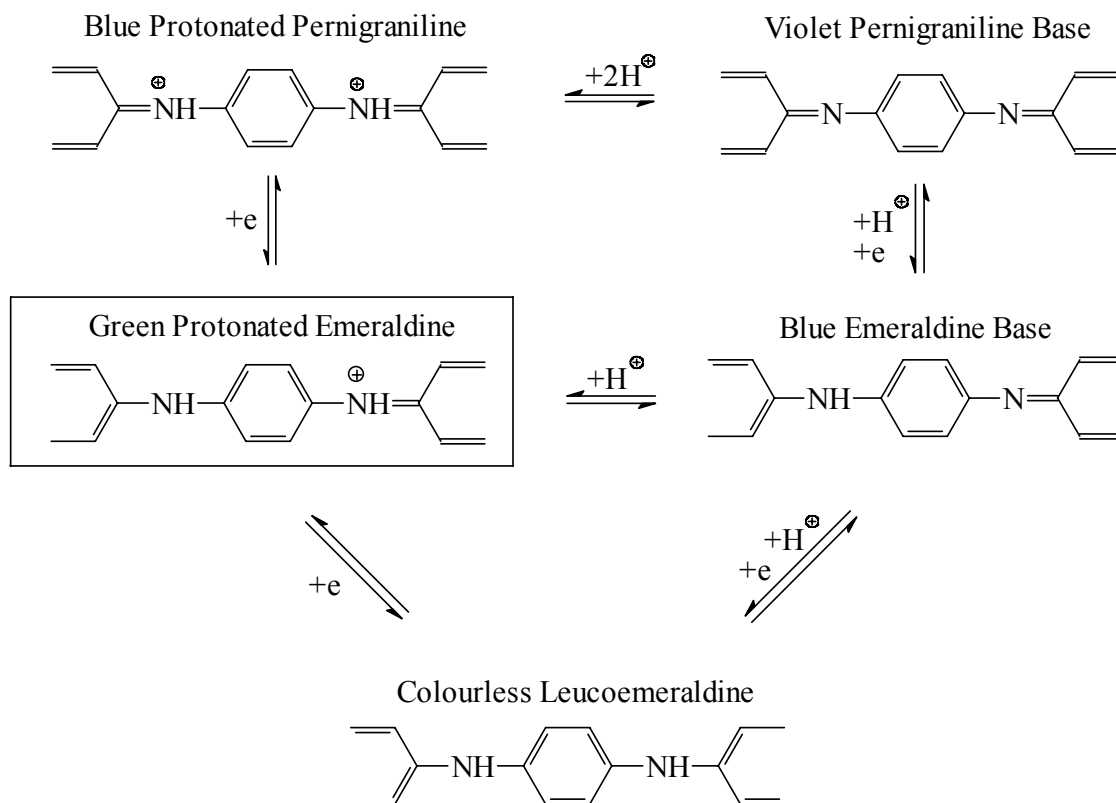


Fig. 4. Protonated emeraldine obtained after the polymerization of aniline can be oxidized to pernigraniline or reduced to leucoemeraldine [6]. Emeraldine and pernigraniline may be deprotonated to the corresponding bases.

3. Carbonization of polyaniline: new nitrogen-containing carbons

Polyaniline becomes carbonized to nitrogen-containing carbons above ~ 600 °C in inert atmosphere [7], probably due to the cross-linking of polyaniline chains (Fig. 5). Such carbons have low conductivity, improved hydrophilicity; the incorporation of nitrogen atoms may be useful when applied as catalysts supports. The morphology of polyaniline is preserved during the carbonization (Fig. 5). This means that polyaniline nanotubes can be converted to carbon nanotubes; their structure, however, is different compared with classical carbon nanotubes.

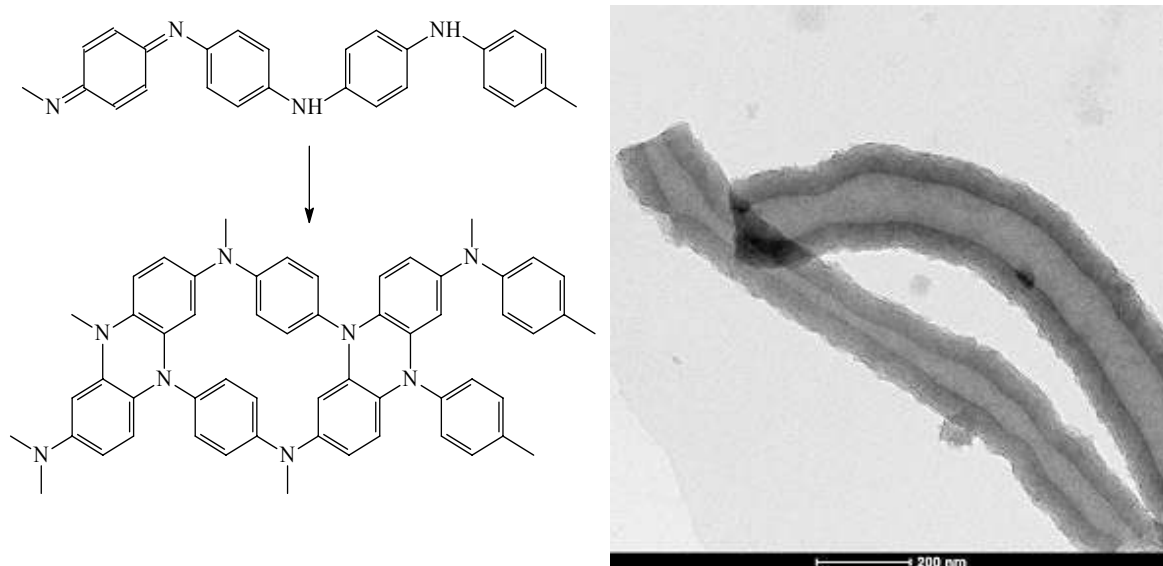


Fig. 5. Crosslinking of polyaniline chain during the carbonization. The morphology of polyaniline, such as nanotubes, is preserved after carbonization at 830 °C in nitrogen atmosphere [7].

4. Polyaniline and silver: highly conducting composites

Silver nitrate can similarly be used as an oxidant of aniline (Fig. 6). In such a case, the reaction between two non-conducting chemicals yields a composite of two conductors, a semiconducting polyaniline and a silver metal [8].

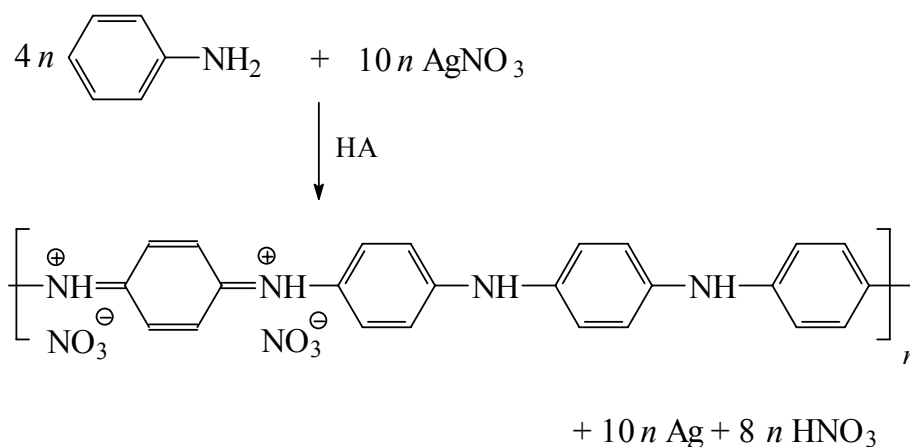


Fig. 6. Aniline is oxidized with silver nitrate to polyaniline nitrate and metallic silver. Nitric acid is a by-product.

The composites can have various morphologies, polyaniline nanotubes accompanied by silver nanoparticles or silver nanowires coated with polyaniline (Fig. 7) depending on acids used to constitute the reaction medium. The conductivity of such

composites may reach the order of 10^3 S cm^{-1} . The reaction (Fig. 6), however, is slow and takes several months to proceed. The means of its acceleration is currently investigated.

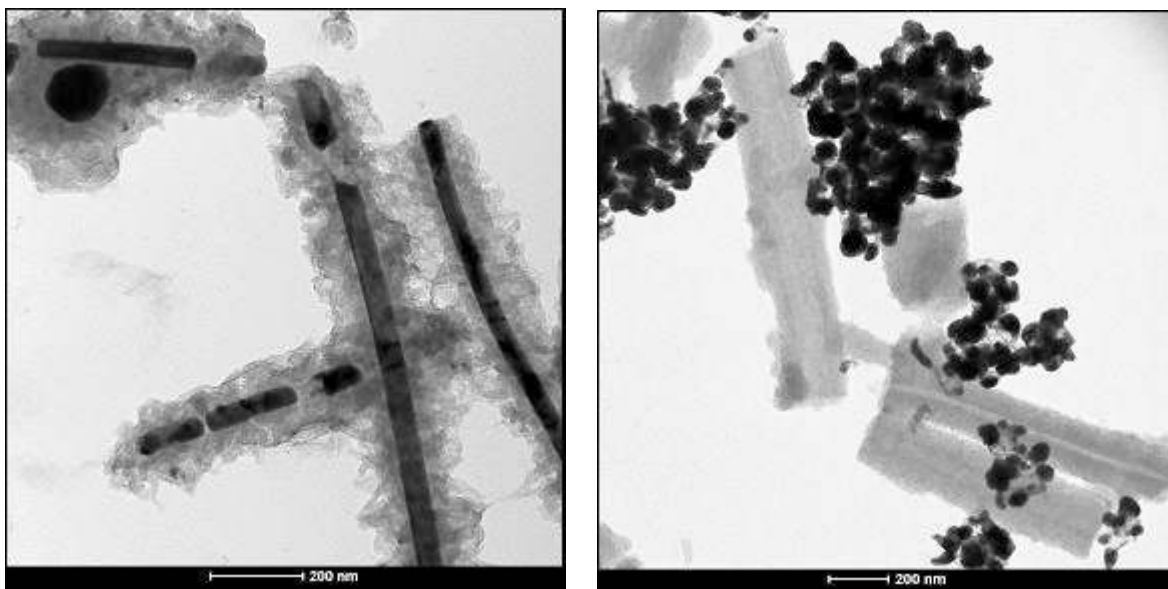


Fig. 7. Silver nanowires or nanoparticles along with polyaniline.

Conclusions

Polyaniline can be used alone as a conducting or responsive polymer, in various forms and morphologies. Its carbonized analogue represents a novel nitrogen-containing carbon. The composites with noble metals may be used as materials having a high conductivity.

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