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Fabrication, charge carrier transport, and application of printable nanocomposites based on indium tin oxide nanoparticles and conducting polymer 3,4-ethylenedioxythiophene/polystyrene sulfonic acid

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Printable transparent hybrid composites consisting of indium tin oxide ($\text{In}_2\text{O}_3\text{:Sn}$; ITO) nanoparticles and conducting polymer 3,4-polyethylenedioxythiophene (PEDOT) as matrix material were developed. The basic idea is to fill up the pores of the highly porous nanoparticulate ITO network to improve the interparticle contact and hence the conductivity of printed ITO thin films. Ready-to-use and stable aqueous dispersions were fabricated starting from ITO nanoparticles and aqueous formulation of conducting PEDOT and polystyrene sulfonic acid (PSS). This report presents and discusses key factors to obtain stable ITO-PEDOT dispersions with different mixing ratios and their application for printable devices as transparent electrode material. It was found that the ζ -potential value is crucial for preparation of stable dispersions. Electrical and optical properties of the hybrid ITO-PEDOT coatings were analyzed. Temperature dependent resistivity measurements reveal that conduction occurs by fluctuation induced tunneling. Transparent and conducting nanocomposite layers with a conductivity as high as $132\ \Omega^{-1}\text{cm}^{-1}$ were fabricated by a low-temperature ($T = 130\ ^\circ\text{C}$) and entirely vacuum-free process. An all-printed electroluminescent lamp on a flexible substrate was realized as a demonstrator showing the applicability of such coatings for voltage-driven optoelectronic devices. © 2011 American Institute of Physics. [doi:10.1063/1.3658634]

I. INTRODUCTION

Transparent conducting oxide (TCO) films are important components in numerous applications whenever the unique combination of electrical conductivity and high optical transmittance within the visible spectral range is required.^{1–4} TCOs have been known and extensively studied for more than 50 years as a result of their wide range of technical applications. These include electrodes in optoelectronic thin film devices, such as organic light emitting diodes (OLEDs),^{5,6} organic solar cells (OSCs),^{7,8} thin film transistor displays,^{9,10} electroluminescent lamps,¹¹ but also as coatings for energy-efficient windows.¹²

Most frequently used doped single-cation TCO materials are indium tin oxide (ITO), zinc oxide (e.g., ZnO:Al , Ga) and fluorine or antimony doped tin oxide.^{13–15} However, also multi-cation oxide TCOs have been developed and show a growing interest in the last few years.^{16,17} Thin films from these materials are commonly fabricated by physical vapor deposition (PVD) techniques, such as sputtering or thermal evaporation, and provide high-quality coatings but are rather expensive due to vacuum processing.^{18,19}

Novel low-cost approaches use wet chemical deposition of thin films from nanoparticle dispersions or a sol-gel process, especially if a low sheet resistance is not crucial. In the

latter case, a subsequent air-annealing step at high temperatures ($T > 350\ ^\circ\text{C}$) is unavoidable to initiate formation of a nanocrystalline film. In contrast to the sol-gel route, colloidal dispersions already consist of crystalline nanoparticles and hence low process temperatures are possible in principle providing the opportunity of using cheap polymer substrates. However, for such nanoparticulate coatings, the conductivity typically increases with increasing annealing temperatures due to enhancement of effective mobility as consequence of sintering neck formation and grain growth.²⁰

One very promising approach is to form hybrid nanocomposites consisting of nanoparticles and organic additives. A suitable organic component can positively affect the film formation and improve the electrical, optical, or mechanical layer properties even at process temperatures as low as $130\ ^\circ\text{C}$. Some successful results using ITO nanoparticles in combination with polyvinyl derivatives, such as polyvinylpyrrolidone, polyvinyl alcohol, and polyvinyl butyral, or by the use of the organofunctional silane 3-methacryloxypropyltrimethoxysilane were shown recently.^{21–23} The conductivity of best nanocomposites was as high as $9.8\ \Omega^{-1}\text{cm}^{-1}$ at a co-existent optical transmittance of at least 80%.

However, very little research has been conducted to develop hybrid coatings composed of ITO nanoparticles and conductive 3,4-polyethylenedioxythiophene/polystyrene sulfonic acid (PEDOT/PSS) as matrix material. Mechau *et al.* investigated this material combination for low ITO contents but only low conductivity in the range of $10^{-4}\ \Omega^{-1}\text{cm}^{-1}$ to

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TABLE I. Compositions, conductivity $\sigma(\text{RT})$, film thickness t , and surface roughness R_{rms} of fabricated ITO-PEDOT nanocomposite layers deposited on glass substrates.

Sample	Mixing Ratio (vol. %)	pH Value	Solid Content Ratio (wt. %)	$\sigma(\text{RT})$ [$\Omega^{-1}\text{cm}^{-1}$]		Thickness $t(\text{nm})$
				Undoped	Doped	
Pure ITO		12	100 ITO	0.014	0.019	295
ITO-PEDOT	9:1	12	99.4 ITO, 0.6 PEDOT	0.016	0.033	230
ITO-PEDOT	4:1	11.8	98.7 ITO, 1.3 PEDOT	0.018	0.032	225
ITO-PEDOT	1:1	10.1	94.9 ITO, 5.1 PEDOT	0.062	0.583	160
ITO-PEDOT	1:4	4.3	82.4 ITO, 17.6 PEDOT	1.596	85.57	125
ITO-PEDOT	1:9	3.9	67.5 ITO, 32.5 PEDOT	0.430	132.4	95
PEDOT/PSS		2	100 PEDOT	0.760	380.4	100

$10^{-3} \Omega^{-1}\text{cm}^{-1}$ was achieved, mainly due to the lack of stable colloidal dispersions.²⁴ To our knowledge, there have been no further reports on mixed ITO-PEDOT compounds. However, PEDOT/PSS on top of ITO is widely used in OLEDs or OSCs to improve carrier injection and for smoothing of the ITO surface.^{25,26} ITO forms an ohmic contact to PEDOT despite the fact that ITO is n-type and PEDOT a p-type material. The crucial factor here is that the electronic work function of ITO closely matches the HOMO energy level of PEDOT, resulting in an ohmic contact behavior. For this reason, the ITO-PEDOT system was chosen for our investigations in order to produce a hybrid nanocomposite consisting of an electrically conducting inorganic filler and a conductive organic matrix, which both contribute to charge carrier transport. The present paper discusses our recent progress in preparation, stabilization, and characterization of such hybrid ITO-PEDOT nanocomposites fully processed at temperatures as low as 130 °C.

II. EXPERIMENTAL DETAILS

A Preparation of dispersions

Indium tin oxide dispersions of different pH values were obtained by redispersing of ITO nanoparticles with a primary particle size of 10 to 20 nm (VP ITO TC8 provided by Evonik Degussa GmbH) in deionized water. The pH value was adjusted by addition of NaOH or HCl, respectively. Spherical yttrium stabilized zirconia grinding media with an average diameter of 100 μm , and a disperser unit DAS H 200-K with a cooling device (LAU GmbH) was used for dispersing of the aqueous ITO suspensions. The dispersing time was set to 60 min at a maximum energy input. These parameters were determined and optimized in previous investigations, which have been described in detail elsewhere.²⁷ The resulting ITO dispersions have a solid content of 20 wt. % and an average aggregate size of approximately 80 nm, which was determined by dynamic light scattering.

Hybrid ITO-PEDOT dispersions with different volumetric ratios of ITO and commercially available PEDOT/PSS (Clevios PH 1000, Heraeus Holding GmbH) were fabricated by adding the PEDOT/PSS formulation into the ITO dispersion and subsequent homogenization for 10 min under ultrasonic agitation.

B. Deposition of thin films

Transparent conducting nanocomposite coatings were fabricated by spin-coating on $20 \times 20 \times 1 \text{ mm}^3$ glass substrates (Menzel glasses) using a Polos 200 spin-coater. Prior to the deposition, the substrates were cleaned and ozonized in an UV-ozone photoreactor PR-100 to improve wetting. After deposition or doping step, the samples were dried for 15 min on a hot plate at 130 °C. Doping was carried out by immersing the ITO-PEDOT nanocomposite samples in dimethyl sulfoxide (DMSO) for 60 min at room temperature.

All samples consist of only one layer, whose thickness strongly depends on dispersion viscosity, surface tension, wetting behavior, and deposition parameters. Uniform films were obtained keeping the spin-coating parameters constant at 1500 rpm and 30 s. However, the dispersion viscosity, surface tension, and wetting behavior vary for different ITO-PEDOT dispersion compositions resulting in different layer thicknesses between 295 nm and 95 nm. The average film thickness of all coatings is listed in Table I.

C. Characterization

ζ -potential measurements of the dispersions were done on a Zetasizer Nano ZS (Malvern Instruments Ltd) at room temperature. Due to the high solid content, the dispersions were diluted to an optimal loading factor of 0.6 wt. % for the measurement. The pH values of the final ITO-PEDOT dispersions were obtained with the pH meter inoLab (WTW GmbH) after mixing.

Temperature dependent resistivity $\rho(T)$ measurements were performed under vacuum in a closed cycle cryostat in a range of 40 to 260 K. The samples were cut into $8 \times 8 \text{ mm}^2$ squares, and four gold wires fixed by silver paste were attached in the corners. The sheet resistance R_s at room temperature was measured by a linear four-point-probe technique using a Keithley SMU 236 and correction factors according to Smits.²⁸ The layer thickness t was determined optically with a confocal white light microscope NanoFocus μsurf . To account for the layer inhomogeneities, several resistance R_s and thickness t measurements at different positions on at least 15 samples (processed from 3 different dispersions with the same mixing ratio) were averaged. The conductivity σ was then calculated from $\sigma = \rho^{-1} = (R_s \times t)^{-1}$.

Optical spectra were obtained using a Perkin Elmer Lambda 950 UV-VIS-NIR spectrometer. Morphological surface characterization was performed with a Zeiss FESEM Ultra 55 (accelerating voltage 10 kV).

III. RESULTS AND DISCUSSION

Wet chemical thin film deposition using pure ITO nanoparticle dispersions leads to highly porous layers with a porosity of about 45% and a pore size in the range of the diameter of primary particles.^{20,29–31} High porosity is one of the reasons why nanoparticulate coatings are not yet competitive with their sputtered counterparts, at least with regard to the electrical performance, as conductivity strongly depends on the interparticle contact. As we have shown in previous studies,^{21–23} filling up the pores with additives causes a significant improvement of electrical, optical, and/or mechanical film properties due to improved network formation. However, only electrically non-conductive materials, such as thermoplastic polymers or organofunctional silanes, were applied so far. The use of the intrinsically conducting polymer PEDOT allows the transport of charge carriers to take place both within the ITO nanoparticle network and also across the organic matrix.

A. Dispersing and stabilizing

The first and crucial step is the preparation of a stable ITO-PEDOT dispersion which shows no sedimentation over a period of up to one month. Just mixing of both commercially available dispersions leads to flocculation of the particles and redispersing is not possible. This behavior can be attributed to the strong electrostatic attraction between the ITO and PEDOT/PSS particles. By properly adjusting the ζ -potential of the particles, repulsive forces prevail preventing the particles from coagulation.

Colloidal PEDOT is stabilized by PSS to allow liquid processability. Its ζ -potential can be tuned in the negative range between about -40 mV to -100 mV by varying the pH from 2 to 7, indicating that excess PSS on the particle surface stabilizes the dispersion in water. It is therefore not possible to reverse the ζ -potential without losing the dispersability. The used PEDOT/PSS formulation Clevios PH 1000 showed a ζ -potential of approximately -40 mV at pH 2.

In contrast to PEDOT, the ζ -potential of ITO nanoparticles can easily be modified by varying the pH value of the dispersion (see Fig. 1). The ζ -potential is positive for low and negative for high pH values, as it is common for inorganic oxides. This fact is due to protonation and deprotonation of surface oxide bonds or hydroxyl groups and is well known for ITO.³² The isoelectric point is at a pH of ~ 8 and corresponds quite well to the published data.^{33,34}

Commercial ITO dispersions commonly consist of nanoparticles which are electrosterically stabilized with long-chain acids, such as 3,6,9-trioxadecanoic acid.^{27,35} They are stabilized within the acidic pH range and show a positive ζ -potential, which leads to coagulation of ITO and PEDOT particles. The objective pursued was the preparation of an

FIG. 1. ζ -potential of a 0.6 wt. % ITO dispersion as a function of pH value.

ITO dispersion with a ζ -potential similar to that of PEDOT. The value of approximately -40 mV was obtained at a pH value of ~ 11.5 . In order to verify our presented stabilization concept based on matching ζ -potentials 20 wt. %, ITO dispersions with pH values of 4, 7, 10, and 12 were fabricated and mixed with the PEDOT/PSS formulation in a ratio of 1:1 by volume. Stable hybrid ITO-PEDOT dispersions could only be achieved using the pH 12 ITO dispersion. Other dispersions showed immediate flocculation upon direct contact and redispersion failed. Furthermore, stable ITO-PEDOT dispersions for almost any mixing ratios could be obtained by the use of the pH 12 ITO dispersion confirming our stabilization concept. For very high PEDOT contents, gelation of the mixed dispersions occurs after a storage period of several hours, but these dispersions can be easily redispersed by applying ultrasound. It is noteworthy that the resulting pH value of the mixed dispersions, made from ITO (pH 12) and PEDOT/PSS (pH 2) dispersions, does not influence the colloidal stability (see Table I). For different mixing ratios, a broad range of pH values from acidic to alkaline were achieved without any flocculation or sedimentation of particles for up to one month, offering the possibility to widely adjust the pH with respect to any specific application. This is a strong indication that the critical parameters are the initial ζ -potential values of the dispersions. Due to repulsion of PEDOT and modified ITO particles no agglomeration occurs.

B. Optical properties

Regarding the main application of ITO and PEDOT as transparent conducting materials for electrodes, the optical transmittance T of the hybrid ITO-PEDOT nanocomposites subsequently doped with DMSO was investigated. The corresponding total transmittance of the layers including the glass substrate is displayed in Fig. 2(a). Furthermore, the absorption coefficients are shown in Fig. 2(b).

All coatings exhibit good optical transmittance of at least 80% at 550 nm, which is sufficient for typical applications in touchscreens, electroluminescent lamps, or electrochromic displays. The spectral transmission behavior of the ITO-PEDOT layers is based on superposition of pure

FIG. 2. (Color online) (a) Transmittance spectra and (b) absorption coefficients of DMSO doped ITO-PEDOT nanocomposites in the visible region.

ITO and PEDOT data. As one can deduce from the shape of the absorption coefficients shown in Fig. 2(b) the ITO-rich samples are obviously dominated by the absorption characteristics of ITO material. With increasing PEDOT content, the overall absorption increases, especially in the range above ~ 600 nm, which indicates the strong contribution of PEDOT. Only the 1:1 ITO-PEDOT layer shows deviating absorption behavior which can mainly be attributed to scattering effects caused by the layer morphology. This fact is described in more detail in Sec. III C.

Particular attention should be given to the overall absorption characteristics of ITO-PEDOT nanocomposites. The addition of ITO nanoparticles into PEDOT significantly lowers the absorption coefficient in the visible range, providing nearly constant optical performance over the whole visible spectral region.

C. Morphological properties

Typical SEM images of ITO-PEDOT nanocomposites with different mixing ratios are shown in Figs. 3(a)–3(e). Phase separation for low contents of PEDOT is observed. In contrast to the ITO-PEDOT 9:1 sample which exhibits a very similar surface morphology as pure ITO and is therefore not shown here explicitly, some surface “dents” can be found on the 4:1 coating indicating local segregation of PEDOT. This phenomenon is even more pronounced for the mixing ratio of 1:1, as can be seen in Fig. 3(c). It also explains the reason for the poor optical transmittance of the 1:1 mixture due to scattering of the μm -sized agglomerates. We assume that their formation can be attributed to the volume exclusion effect, which disturbs the random distribution of the ITO nanoparticles in the presence of PEDOT. This effect is also

FIG. 3. SEM micrographs of (a) pure ITO, ITO-PEDOT samples deposited from stable dispersions with different mixing ratios of (b) 4:1, (c) 1:1, (d) 1:4, (e) 1:9, and (f) an unmodified unstable ITO-PEDOT dispersion.

FIG. 4. (Color online) Normalized resistivity ρ vs. temperature T for (a) undoped and (b) DMSO doped ITO-PEDOT samples. Experimental data are shown together from the fluctuation induced tunneling model using the fitting parameters T_0 and T_1 in Table II.

well known for ceramic-polymer blends.³⁶ In this particular case, it seems to have an unusual dependence on polymer concentration. For higher PEDOT contents, a relatively homogeneous surface structure can be observed (see Figs. 3(d) and 3(e)). The ITO nanoparticles are embedded in the PEDOT matrix, which causes blurred SEM image appearance. For comparison, a layer deposited from an unstable ITO-PEDOT dispersion is shown in Fig. 3(f). Strong agglomeration of ITO nanoparticles can be observed, which negatively influences the optical and electrical properties.

Another aspect that also has to be considered is a potential vertical phase separation, which cannot be observed by SEM. Further investigations need to be done using atomic force microscopy to reveal the actual surface morphology and transmission electron microscopy to unveil the distribution of ITO nanoparticles within the PEDOT matrix.

D. Electrical properties

Measured data of normalized temperature dependent resistivity $\rho(T)/\rho(260\text{ K})$ of pristine and DMSO-doped ITO-PEDOT nanocomposites are presented in Fig. 4. A negative temperature coefficient of resistance (NTCR) is clearly observed for all samples within the entire temperature range.

Several models of electrical conduction can describe NTCR behavior of nanoparticulate thin films. However, the conduction mechanism in ITO-PEDOT composites was to our best knowledge so far not studied. We therefore take the well-known models of hopping and fluctuation induced tunneling (FIT) into account whose applicability was proved successfully for pure PEDOT and ITO nanoparticle coatings by experimental results elsewhere.^{29,37,38}

The temperature dependence of resistivity $\rho(T)$ of hopping conduction is given by³⁹

$$\rho(T) = \rho_0 \times \exp \left[\left(\frac{C}{T} \right)^{1/(1+d)} \right], \quad (1)$$

where ρ_0 and C are constants and d represents the dimensionality of hopping. 3D variable range hopping (VRH) is a

well-known conduction mechanism of undoped PEDOT, which describes electron tunneling between localized states distributed randomly in the thin film.³⁹ Fig. 5 presents the measurement data of undoped samples plotted as $\ln(\rho(T)/\rho(260\text{ K}))$ vs. $T^{-1/4}$. As expected, a linear behavior is observed for the pure PEDOT layer indicating the applicability of the 3D-VRH conduction model. However, none of the hybrid ITO-PEDOT samples can be fitted linearly. Based on these results, it can be assumed that the charge carrier transport is obviously not solely dominated by either PEDOT or ITO material. On the contrary, a kind of “mixed” carrier transport through PEDOT and ITO can be presumed showing a clearly different behavior of temperature dependent resistivity.

A suitable model to describe this behavior could be the above-mentioned FIT model. It presumes clusters of well connected primary particles, which are separated by tunneling barriers. It can be represented by the following exponential equation⁴⁰

$$\rho(T) = \rho_0 \times \exp \left[\frac{T_1}{T + T_0} \right], \quad (2)$$

FIG. 5. (Color online) Natural logarithm of the normalized resistivity ρ vs. temperature $T^{-1/4}$ for undoped ITO-PEDOT samples. The straight line indicates the applicability of 3D variable range hopping.

where ρ_0 is a constant and T_0 and T_1 are parameters which are related to the properties of the insulating barriers and are given by

$$T_0 = \frac{16\varepsilon_0\hbar}{\pi(2m_e)^{1/2}e^2k_B} \times \frac{AV_0^{3/2}}{w^2} \quad (3)$$

and

$$T_1 = \frac{8\varepsilon_0}{e^2k_B} \times \frac{AV_0^2}{w}. \quad (4)$$

Here, ε_0 is the vacuum permittivity, $\hbar$ is the reduced Planck constant, m_e is the effective electron mass, e is the elementary charge, and k_B is the Boltzmann constant. A , V_0 , and w are the barrier area, energetic height and width, respectively. T_1 can be considered as a measure of the energy required for an electron to overcome the potential barrier and T_0 , which appears as an additive constant to T , can be regarded as the temperature below which thermal fluctuation effects become insignificant. Since at $T \ll T_0$, Eq. (2) is essentially temperature independent and reduces to the expression for elastic tunneling.

Nanoparticulate ITO layers can be described very well by this FIT model.^{29,37} But it also seems to be capable of representing the experimental data of hybrid ITO-PEDOT samples. In Fig. 4(a), the measured resistance values are compared to data obtained from Eq. (1). A very good agreement is observed for all samples and mixing ratios in the whole temperature range. The fitting parameters T_0 and T_1 are listed in Table II for all the curves depicted in Fig. 4. As already mentioned before, the thin film network consists of ITO clusters and PEDOT nanoparticles. Transport of charge carriers takes place by “hopping” across the single highly conductive particles, which are separated by tunneling barriers. These barriers are present either between ITO and PEDOT or at ITO-ITO interfaces and limit the charge carrier transport within the hybrid composite. The fitting parameters T_0 and T_1 describe the properties of the insulating barriers, which vary for different ITO-PEDOT mixing ratios.

Both undoped and DMSO-doped measurement data of ITO-PEDOT samples can be fitted by means of the FIT model. Doping with DMSO was carried out subsequently after film deposition and drying in order to improve the electrical conductivity of the hybrid layers. This effect of conductivity enhancement by addition of high-boiling solvents is well-known for PEDOT, although the mechanism is still under some debate. For example, Jönsson *et al.* pointed out that the excess PSS is washed away from the surface of the PEDOT/PSS particles leading to an improved interconnection.⁴¹ Similar behavior was observed by Nardes *et al.* for sorbitol treated PEDOT/PSS. They explained the conductivity enhancement by a decreased thickness of the insulating PSS barrier layer which separates the highly conductive PEDOT particles.³⁸ Ouyang *et al.* reported that conformational changes increase intra- and inter-chain charge carrier mobility.⁴² Finally, Kim *et al.* suggested that the conductivity is increased due to the

TABLE II. Computed fit parameters T_0 and T_1 according to fluctuation induced tunneling model.

Sample		Undoped		DMSO doped	
		T_0 [K]	T_1 [K]	T_0 [K]	T_1 [K]
Pure ITO		166	288	427	917
ITO-PEDOT	9:1	144	285	383	796
ITO-PEDOT	4:1	173	385	365	716
ITO-PEDOT	1:1	547	1891	331	1251
ITO-PEDOT	1:4	228	914	427	535
ITO-PEDOT	1:9	227	802	536	1071
PEDOT/PSS		—	—	—	—

screening effects of polar solvents.⁴³ However, an improvement of electrical conductivity for all samples is obtained (see Table I).

The temperature dependent resistivity of pure DMSO-doped PEDOT sample follows a power law, which is described as⁴⁴

$$\rho(T) \propto T^{-\beta}. \quad (5)$$

The value of β is ~ 0.33 for our measurement data, which implies that the system is in the critical regime of the metal-insulator transition.⁴⁴ The highly conductive PEDOT PH 1000 formulation shows clearly this power law behavior after doping with DMSO, unlike the quasi 1D-VRH charge carrier transport, which is commonly observed for doped PEDOT of lower conductivity.³⁸

A good agreement of experimental results obtained for the DMSO-doped ITO-PEDOT layers and theoretical values is only achieved by the application of the FIT model. The fitting curves are drawn as solid lines in Fig. 4(b) and the computed parameters are given in Table II.

Several other conduction models, such as ionized-impurity scattering, granular-metal, or ionic conductivity has been applied but none of this models was applicable to fit the experimental data of the hybrid ITO-PEDOT thin films, with except of the presented fluctuation induced tunneling model. Of course, it is still possible that a mixed conduction of ITO and PEDOT exists in parallel and therefore cannot be described by only one single conductivity model. But in conclusion, it can be stated that the mixed system is not entirely dominated by one of the components and can be explained best by means of the FIT model.

The conductivity values summarized in Table I were obtained at room temperature in air using the four-point-probe technique. As expected, the subsequent doping with DMSO significantly improves the conductivity of the samples. With increasing PEDOT content, also the conductivity of the hybrid ITO-PEDOT nanocomposites increases showing that both components contribute to the transport of charge carriers. The comparison between our present results and the best electrical conductivity values of approximately $120\text{--}130 \text{ } \Omega^{-1}\text{cm}^{-1}$ for nanoparticulate ITO thin films reported in the literature^{37,45,46} shows that the hybrid ITO-PEDOT layers are very competitive despite the fact of a low-temperature fabrication process. The achieved

FIG. 6. (Color online) Image of an all-printed electroluminescent lamp on a PET foil using a hybrid ITO-PEDOT layer as front electrode.

conductivity of about $132 \Omega^{-1}\text{cm}^{-1}$ surpasses all of the previously presented values for films consisting of ITO nanoparticles, although those layers have been annealed at a minimum temperature of 500°C and additionally post-treated under reducing conditions in forming gas or vacuum.^{37,45,46} By contrast, the ITO-PEDOT nanocomposites provide superior performance at significantly lower process temperature of 130°C . However, the conductivity is lower compared to pure PEDOT but the hybrid coatings show better optical transmittance. A possible reason for the lower conductivity could be the presence of sodium ions that have a negative effect on conductivity of both ITO and PEDOT.^{47,48} As described above, NaOH was used to adjust the pH value and hence the ζ -potential of the ITO dispersions to achieve homogeneously mixed ITO-PEDOT dispersions without flocculation. Our next approach is to replace NaOH by a suitable alkali metal free base to overcome this problem and to enhance the overall conductivity. Furthermore, the doping parameters, in particular the influence of the solvent and immersing time should be investigated in more detail. Nevertheless, a significant conductance enhancement is achieved compared to pure nanoparticulate ITO layers. A sheet resistance of $<1000 \Omega/\square$ can be easily achieved by this hybrid ITO-PEDOT dispersions with a mixing ratio of 1:4 and 1:9.

E. Device fabrication

To demonstrate the feasibility of the presented hybrid ITO-PEDOT layers for device fabrication, an electroluminescent (EL) lamp was built up by printing of all layers on a polyethylene terephthalate (PET) foil. In the first step, a layer of approximately 100 nm was deposited by doctor blading using the ITO-PEDOT dispersion with a mixing ratio of 1:9. After doping and drying the subsequent phosphor (ZnS:Mn,Cu,Cl; $20 \mu\text{m}$), dielectric (BaTiO₃; $10 \mu\text{m}$), and silver ($10 \mu\text{m}$) layers were screen printed by applying the ready-to-use pastes provided by Metalor Technologies. The fully functional and flexible EL lamp is shown in Fig. 6. This all-printed device was fabricated in an entirely vacuum-free deposition process at temperatures that did not exceed 130°C . A long-term stability over at least three months was

demonstrated by periodic functional testing of the device stored under ambient conditions.

IV. CONCLUSIONS

Transparent and conducting ITO-PEDOT nanocomposite layers were fabricated from mixed ITO and PEDOT/PSS dispersions. Stable dispersions with various mixing ratios were obtained by adjusting the pH value and hence ζ -potential of the ITO dispersion, making it compatible with the commercially available PEDOT/PSS PH 1000 formulation. The key parameter is to introduce repulsive forces which prevent the particles from coagulation by adapting the ζ -potentials.

In order to understand the electrical properties of the hybrid thin films, temperature dependent resistivity measurements were performed. It was found that the fluctuation induced tunneling model is in good agreement with the experimental results for both undoped and DMSO doped samples. It presumes the presence of a network structure comprising clusters of individually well connected primary particles, which are separated by tunneling barriers. This corresponds quite well with the layer morphology observed by SEM.

An electrical conductivity as high as $132 \Omega^{-1}\text{cm}^{-1}$ was achieved for the hybrid ITO-PEDOT nanocomposite made from the dispersion with a mixing ratio of 1:9. This corresponds to a sheet resistance of approximately $800 \Omega/\square$ and a coexistent transmittance of about 85% at 550 nm for a layer thickness of $\sim 100 \text{ nm}$. We limit us to a maximum process temperature of 130°C , which allows the use of cheap polymer substrates, such as PET, and fabricated an all-printed flexible electroluminescent device to demonstrate the feasibility of printable electronics. Nevertheless, the conductance of nanoparticulate layers has to be further improved to become competitive with layers made using the state-of-the-art PVD techniques. For voltage-driven devices, such as electroluminescent lamps, electrochromic displays, or touchscreens, however, the achieved sheet resistance of $<1000 \Omega/\square$ for the hybrid ITO-PEDOT thin films already meets the required specifications.

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