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Disruption of the Electrical Conductivity of Highly Conductive Poly(3,4-ethylenedioxythiophene):Poly(styrene sulfonate) by Hypochlorite

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ABSTRACT: The effect of hypochlorite treatment on the layer thickness and conductivity of a state-of-the-art high conducting poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is investigated as a function of exposure time and hypochlorite concentration. Because of overoxidation by the hypochlorite the PEDOT:PSS conductivity is decreased by 10 orders of magnitude. Comparison of thickness and conductivity as a function of time shows that a residual insulating layer remains on the substrate upon treatment. Going from a low (<0.01%) to a high (>0.1%) hypochlorite concentration the interaction between PEDOT:PSS and hypochlorite changes from reaction- to diffusion limited. The decrease in conductivity can be interpreted in terms of the interruption of percolating conductive pathways by the reaction between PEDOT and hypochlorite.

INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT), processed as aqueous dispersion, stabilized by poly(styrenesulfonate) (PSS) (Figure 1a), is the most widely applied transparent organic semiconductor in organic electronics (OE) applications, such as organic light emitting diodes (OLEDs) and photovoltaic cells (OPV).^{1,2} A typical aqueous PEDOT:PSS solution consists of a dispersion of nanoparticles (with a typical average diameter of ~50 nm), constituted by both blend components PEDOT and PSS in a predetermined ratio. Because of its hydrophobicity, the PEDOT fraction resides predominantly in the core region of a nanoparticle, whereas PSS, which is usually present in excess to PEDOT, is mostly present in the shell regions. Hence, the particles are effectively stabilized against agglomeration in solution via electrostatic repulsion between the like-charged PSS shells. Upon coating and film formation the water evaporates, initially leaving a dense-packed layer of PEDOT:PSS particles on the substrate. In the late stages of drying, the layer collapses to yield more or less flattened structures,³ during which conductive percolating pathways are established via partial coagulation of the PEDOT domains.

For display OLED pixels and millimeter-sized lab scale OPV cells, so-called low conductive (LC) PEDOT:PSS, typically <10 S/cm, is used. The advantage of this relatively low conductivity is that cross-talk between neighboring pixels or devices is effectively suppressed. Recent efforts have shown that the conductivity of thin films of PEDOT:PSS can be significantly

enhanced by various additives, such as high boiling cosolvents,⁴ ionic liquids,⁵ surfactants,⁶ salts,⁷ zwitterions,⁸ and inorganic acids.⁹ The mechanism behind the enhancement of the conductivity of PEDOT:PSS by aforementioned additives depends on the way these chemicals interact with the individual blend components and whether/how the PEDOT:PSS phase morphology is affected. In general, the following three causes for conductivity enhancement by additives are identified: (i) increased doping of the PEDOT chain segments, for example, in case of extensive protonation by strong acids,⁹ (ii) increased internal ordering and (nano)crystallization of the PEDOT fraction, for example, such as observed upon addition of ethylene glycol,¹⁰ and (iii) enhanced coagulation, for example, as observed for polyhydroxy-type additives such as sorbitol,¹¹ or polar high-boiling solvents.¹¹ Application of these additives has led to a boost of the conductivity to up to ~10³ S/cm,^{12,13} making PEDOT:PSS also suitable for large area OLED and OPV applications as well as for other areas, such as conductive clothing¹⁴ and electrochromic windows.¹⁵ High conductivity (HC) PEDOT:PSS grades are often even capable of fully replacing traditionally used inorganic semiconductors, such as indium tin oxide (ITO), as transparent anode.

The downside, however, of a high in-plane conductivity in a coated or printed PEDOT:PSS layer is the risk of the

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Figure 1. (a) Molecular structure of PEDOT:PSS; (b) overoxidation reaction scheme of PEDOT by NaClO (adopted from ref 21).

occurrence of considerable parasitic currents. If not controlled properly, these currents provide leakage pathways and cross-talk between device areas intended to operate autonomously. It has been shown, for instance, that parasitic currents cause significant overestimation of the light-to-power conversion efficiency of OPV cells.¹⁶

Hence, for applications where device design requires the conductivity to be contained to specific predefined areas, it is often desirable to (pre)pattern or structure either the PEDOT:PSS layer itself, that is, by on-demand printing of the formulation in specific areas, or its conductive properties, that is, via disruption of the conductivity in selected areas by deliberate chemical degradation. On-demand printing technologies, such as inkjet printing offer full digital form-freedom but are not preferred for large area applications due to low throughput and issues regarding layer homogeneity, process robustness, and stability. Instead, large area OE applications are much better compatible with continuous roll- or slot-coating methods allowing homogeneous deposition of integral layers of organic semiconductors. Hence, chemical patterning based on local disruption of the conductivity of pre-coated PEDOT:PSS layers is highly desirable as a fabrication step in large area OE device manufacture.

Chemical patterning of PEDOT:PSS layers can be achieved lithographically,^{17,18} that is, by subsequent resist masking, treatment with an oxidizing solution, and stripping, as well as by means of locally contacting the layer with prestructured stamps loaded with oxidizing solution.^{19,20} Lithographic patterning and direct stamping each have advantages and disadvantages. Lithography allows the fabrication of structures with high definition at the expense of the requirement of multiple additional process steps, whereas stamping produces structures with lower resolution but with relative ease. Depending on the final application one or the other is preferred.

Irrespective of the application technology, definition of suitable operation windows for reproducible device fabrication requires fundamental understanding of the mechanisms behind reactive conductivity disruption of PEDOT:PSS as a function of oxidizer concentration and treatment time. At present,

mechanistic studies concerning systematic variation of treatment conditions are virtually absent in literature. Instead, the focus is primarily on the actual devices to which chemical patterning of PEDOT:PSS layers is applied.^{19–21} Nevertheless, the mechanistic complexity of chemical degradation of PEDOT:PSS is acknowledged, as it is well-known that depending on treatment conditions the chemical changes in the PEDOT:PSS may not only lead to mere disruption of electrical conductivity, but also to loss of material, possibly due to chain scission and disruption of the attractive interaction between PEDOT and PSS. Hence, depending on treatment duration and oxidizer concentration, chemical patterning may either lead to mere deterioration of the conductivity or to complete removal of the PEDOT:PSS in treated areas.

Of several oxidizing agents known to effectively reduce the conductivity of PEDOT:PSS,¹⁸ the most widely used is aqueous sodium hypochlorite ($\text{NaClO}_{(\text{aq})}$).^{17–22} As has been suggested previously,²¹ aqueous hypochlorite overoxidizes PEDOT in three consecutive reaction steps, each requiring one ClO^- ion (see Figure 1b). In the first and second step a PEDOT thiophene unit is converted into, respectively, its thiophene-1-sulfoxide and thiophene-1,1-disulfoxide analogues. The third (tentative) step, in which nucleophilic attack by water and substitution of OH-groups takes place, yields a nonsaturated polyol with concomitant elimination of sulfur under formation of sodium sulfate. Although an electronically conjugated structure can still be drawn for the final reaction product, its conductivity is apparently low.

In this work the effect of hypochlorite treatment on the layer thickness and conductivity of a novel HC PEDOT:PSS developed for state-of-the-art OLED and OPV applications is investigated as a function of exposure time and hypochlorite concentration. A comparison is made between the time scales of loss in thickness and conductivity. It is demonstrated that, going from a low to a high hypochlorite concentration, the time-dependent decrease in conductivity follows a regime transition. The decrease in conductivity is interpreted in terms of the interruption of percolating conductive pathways by the reaction between PEDOT and hypochlorite. By curve-fitting experimental data to a general effective medium (GEM) model

values for the percolation threshold and critical conductivity exponent are obtained. The modeling data are then interpreted in terms of morphological aspects of the layer.

EXPERIMENTAL SECTION

Dispersions (0.8% solids) of HC PEDOT:PSS either or not containing 1% of an aqueous solution of a polymeric adhesion promoter (the latter indicated below as "HC PEDOT:PSS*") were supplied by AGFA Gevaert (Mortsel, Belgium) and were used as received. $\text{NaClO}_{(\text{aq})}$ solution (reagent grade, available chlorine 4.00–4.99%) was purchased from Sigma-Aldrich and diluted with deionized water to concentrations in the range 0.0025%–5% by weight.

Glass substrates (30 × 30 mm) were cleaned with soap and deionized water, followed by sonication in acetone and isopropanol. The substrates were subsequently dried for 10 min at 140 °C in air. The wettability of the substrates was improved by UV-ozone treatment for 20 min. Thin layers ($l = 100$ nm) of HC PEDOT:PSS* were spincoated on the glass substrates within 20 min of finishing the UV-ozone treatment. The HC PEDOT:PSS* layers were then annealed for 10 min at 180 °C. The layers were subsequently allowed to cool down to ambient temperature.

Treatment with $\text{NaClO}_{(\text{aq})}$ occurred by fully submerging the HC PEDOT:PSS* layers in the $\text{NaClO}_{(\text{aq})}$ solutions for durations ranging from 0 s to 24 h. The samples were rinsed with deionized water for 5 s in order to remove excess NaClO from the surface of the layers. The substrates were then spin-dried and vacuum-dried ($<10^{-3}$ mbar) for one hour.

In order to measure in-plane conductivity of the treated HC PEDOT:PSS* layers in a statistically meaningful way, five sets of two gold contacts were evaporated on top of the treated and dried HC PEDOT:PSS* layer, sufficiently remote from the edges of the substrate. The separation between the two contacts in one set was 200 μm . Evaporation was performed at a pressure $<10^{-6}$ mbar. The conductivity of the HC PEDOT:PSS* layers was determined by measuring I – V curves using a Keithley 4200 SCS. The thickness of the layers (i.e., averaged over at least five different locations) was measured with a Veeco Dektak 6 M stylus profilometer.

RESULTS AND DISCUSSION

Submerging glass-borne spin-coated layers of unmodified HC PEDOT:PSS into $\text{NaClO}_{(\text{aq})}$ solutions typically resulted in complete detachment from the substrate, thus prohibiting systematic study of the effect of the treatment itself. Hence, for the investigations reported here a modified grade HC PEDOT:PSS (HC PEDOT:PSS*, see Experimental Section) containing 1% of an aqueous solution of a polymeric adhesion promoter was used instead, which exhibited improved adhesion to glass without significantly influencing conductivity.

The thickness of the HC PEDOT:PSS* layers was found to decrease exponentially with exposure time to $\text{NaClO}_{(\text{aq})}$ to a final residual value of at least $\sim 75\%$ of the initial thickness, the decay rate being a function of NaClO concentration. Even after prolonged treatment (e.g., 24 h treatment in 0.01% $\text{NaClO}_{(\text{aq})}$) the thickness did not decrease beyond this limiting value. The experimental results, together with empirical fits to mono-exponential functions are shown in Figure 2. Interestingly, no (significant) decrease in layer thickness was observed upon treatment with pure water (dark blue symbols in Figure 2). This observation contradicts the conclusion by DeLongchamp

Figure 2. Thickness of HC PEDOT:PSS* layers plotted as function of immersion time in $\text{NaClO}_{(\text{aq})}$ solution for various hypochlorite concentrations: 5 wt % (light gray), 0.5 wt % (magenta), 0.05 wt % (green), 0.01 wt % (red), 0.005 wt % (black), 0 wt % (blue); the data points corresponding to 0.0025 wt % $\text{NaClO}_{(\text{aq})}$ are omitted to render more clarity to the graph; solid lines represent empirical fits to monoexponential functions.

et al.²³ that the thickness of a PEDOT:PSS layer decreases considerably by treatment with pure water due to physical dissolution of unbound PSS. It should, however, be noted that their study concerned a different PEDOT:PSS grade than the one used here. In any case, our experiments show that the removal of material from the HC PEDOT:PSS* layers is principally caused by chemical degradation due to reaction with hypochlorite, rather than to mere physical dissolution.

The effect of NaClO concentration on the conductivity of the HC PEDOT:PSS* layer is plotted in Figure 3a as a function of exposure time. Similar to the effect on layer thickness, no change in conductivity was observed upon treatment with pure water (blue points), which, again deviates from the result reported by DeLongchamp who observed an increase in the conductivity due to removal of unbound PSS.²³ As expected, a pronounced decrease of 10 orders of magnitude in conductivity was observed when NaClO is present in solution. At sufficiently long treatment times the conductivity eventually dropped below the sensitivity limit of the measurement equipment. Plotting the thickness and conductivity curves corresponding to treatment with 0.01% $\text{NaClO}_{(\text{aq})}$ in the same graph (Figure 3b) shows that the conductivity can be lowered substantially without drastically influencing the layer thickness. Comparison of thickness and conductivity as a function of time also leads to the conclusion that a residual layer consisting of an electrically insulating material remains on the substrate upon treatment of HC PEDOT:PSS* with $\text{NaClO}_{(\text{aq})}$.

The (approach to) overlap of the curves obtained for 0.5 and 5% $\text{NaClO}_{(\text{aq})}$ shows that the influence of concentration diminishes at high NaClO content. As the eventual decrease of the conductivity will be controlled by diffusion of NaClO in the (probably swollen) HC PEDOT:PSS* layer and subsequent reaction with the PEDOT backbone, we interpret this observation in terms of a transition from a reaction-limited regime at low hypochlorite concentration to a diffusion-limited regime at high concentration. Another important observation is the fact that for NaClO concentrations exceeding 0.05% the conductivity no longer converges to the value at short exposure times, that is, ~ 250 S/cm. This suggests that in this concentration regime breakdown of the conductivity occurs too fast compared to the experimental handling times and is therefore less well controlled than for lower hypochlorite

Figure 3. (a) Conductivity of HC PEDOT:PSS* layers plotted as function of immersion time in $\text{NaClO}_{(\text{aq})}$ solution for various hypochlorite concentrations: 5 wt % (light gray), 0.5 wt % (magenta), 0.05 wt % (green), 0.01 wt % (red), 0.005 wt % (black), 0.0025 wt % (dark gray), 0 wt % (blue); the red, black, and dark gray solid lines represent fits to the GEM-reaction model defined by eqs 2 and 4; the green solid line represents the curve corresponding to $[\text{NaClO}] = 0.05$ wt %, calculated using input parameters obtained from curve fitting; the thin black lines are guides for the eye; (b) Comparison between normalized HC PEDOT:PSS* layer thickness (blue) and conductivity (black) as a function of immersion time in 0.01 wt % $\text{NaClO}_{(\text{aq})}$ solution.

concentrations. Hence, especially the initial part of the corresponding curves becomes ill defined due to a large error in the plotted treatment time.

A quantitative argument can be given in support of the hypothesis that for low NaClO concentrations (i.e., typically <0.01%) the decrease in conductivity is reaction-limited. Diffusive mass transport is characterized by the dimensionless Fourier number for mass transport, given by²⁴

$$Fo = \frac{D_{\text{eff}} t}{l^2} \quad (1)$$

Here, D_{eff} is an effective diffusivity (in the present case that of the hypochlorite anions in the swollen HC PEDOT:PSS* matrix), t is time, and l is a characteristic length scale for the problem under consideration. In our case, l represents the initial dry thickness of the HC PEDOT:PSS* layer: $l = 100$ nm. In the reaction-limited regime the concentration profile of the hypochlorite anions in the HC PEDOT:PSS* layer will be (near) steady state, which corresponds to $Fo \sim 1$. Equation 1 then shows that if the curve corresponding to treatment with 5 wt % $\text{NaClO}_{(\text{aq})}$ purely reflects the diffusive time scale, one would require D_{eff} to be of the order 10^{-16} to 10^{-15} m^2/s to allow for the steady state profile to be installed within tens of seconds, that is, as indicated by the light blue symbols.²⁵ Intuitively, this value for D_{eff} seems rather low, as, for instance, the diffusivity of a small molecule such as water in a glassy polymer is known to be a few orders of magnitude higher (i.e., typically 10^{-13} to 10^{-11} m^2/s).²⁶ In other words, D_{eff} may be higher, especially considering the fact that ingressing water is likely to plasticise the HC PEDOT:PSS* medium.

Irrespective of the exact value of D_{eff} the important message of this exercise is that in case $[\text{NaClO}] \leq 0.01\%$, the time scale for reaching a steady state hypochlorite concentration profile in the HC PEDOT:PSS* layer is significantly smaller than the time scale of the conductivity decay, showing that at low hypochlorite concentration the process becomes reaction-limited. In view of what follows, it is important to realize that in the reaction-limited regime the situation is simplified compared to the transitional region, since diffusion can be ruled out as process parameter. Our study and conclusions on the mechanism of conductivity decrease in HC PEDOT:PSS* due to hypochlorite intrusion will therefore be based on the results obtained for $[\text{NaClO}]_{(\text{aq})} = 0.01, 0.005$, and 0.0025% .

It has been shown previously that the bulk (volume-averaged) conductivity of all-organic composites based on a

conducting filler in a sparsely conducting matrix, such as LC PEDOT:PSS²⁷ and poly(aniline):polystyrene-polybutadiene-polystyrene (PANI:SBS),^{28,29} is well described by general effective medium theory (GEMT). This theory has been derived based on a combination of classical percolation theory and effective medium theory (EMT).³⁰ In contrast to percolation theory, GEMT is valid for filler fractions in the vicinity, as well as away from the percolation threshold and assumes the conductivity ratio between the conductor and the matrix to be finite. In other words, it assumes the matrix to have a low but nonzero conductivity, which is true for many organic substances generally considered as insulators. GEMT has been presented as a generalized version of Bruggeman's symmetric and asymmetric models,³⁰ capable of describing volume-averaged physical properties of composites based on domains with anisotropic grain structures. The GEM equation for electrical conductivity reads

$$\frac{(1 - \varphi)(\sigma_l^{1/x} - \sigma_m^{1/x})}{\sigma_l^{1/x} + \left(\frac{1 - \varphi_c}{\varphi_c}\right)\sigma_m^{1/x}} + \frac{\varphi(\sigma_h^{1/x} - \sigma_m^{1/x})}{\sigma_h^{1/x} + \left(\frac{1 - \varphi_c}{\varphi_c}\right)\sigma_m^{1/x}} = 0 \quad (2)$$

Here, φ and φ_c are the volume fractions of conductive filler and the threshold (critical) volume fraction. σ_l , σ_h , and σ_m are the conductivities of the matrix ("low"), the pure conductor ("high"), and the composite (i.e., the "effective medium"), respectively.

Stöcker et al.,²⁷ applied the GEM equation to describe the decrease in effective medium conductivity of LC PEDOT:PSS as a function of PEDOT:PSS ratio. Along the same philosophy we propose that the loss in conductivity due to reaction between PEDOT and hypochlorite can also be considered a percolation problem, as during oxidation the volume fraction of conductive material (PEDOT) decreases in time, eventually reaching a threshold around which the conductivity critically drops. This view is supported by the shape of the curves presented in Figure 3a. A difference between the present process and the study performed by Stöcker on LC PEDOT:PSS, however, is the accumulation in time of the nonsaturated polyol-type reaction product (see Figure 1). One could argue that the reason for the (apparent) low conductivity of this reaction product, despite its conjugated electronic structure, might be due not only to loss of doping or even possible chain scission but also to the occurrence of tautomeric

rearrangement, as suggested by Scheme 1. Clearly, the conjugation in the ketone-type tautomer would be disrupted.

Scheme 1. Tautomeric Rearrangement of the Presumed Reaction Product of the over-Oxidation of PEDOT by Hypochlorite

As GEMT describes the conductivity as a function of filler concentration rather than time, we require an additional function which gives the temporal changes in the fraction of conductive material. Two counteracting processes can be identified that influence the volume fraction of conductive material (i.e., PEDOT): (i) a decrease in φ is expected due to the reaction between PEDOT and hypochlorite, but (ii) an increase in φ is expected if dissolution of nonconducting material from the layer is significant, given the assumption that the pristine PEDOT does not dissolve into the aqueous phase due to its hydrophobicity. Considering the fact that in the reaction-limited concentration regime removal of material from the layer only becomes significant after considerable decrease in conductivity has occurred (see Figure 3b), we deem the reaction between PEDOT and hypochlorite to be the dominant process. Hence, without considerably increasing complexity, we summarize the multistep overoxidation of PEDOT by formulating an effective rate law, which is to be solved in conjunction with the GEM equation

$$\frac{d\varphi}{dt} = -k_{\text{eff}}c^n\varphi \quad (3)$$

Here, k_{eff} is the effective reaction rate constant, c is the hypochlorite concentration (here in expressed in wt %) in the HC PEDOT:PSS* layer, and n is an exponent allowing higher order dependence on hypochlorite concentration (i.e., for $n > 1$). The latter is certainly not unlikely, considering the fact that hypochlorite plays a role in several, if not all, steps of the overoxidation mechanism (Figure 1). Integrating eq 3 yields

$$\varphi = \varphi_0 e^{-k_{\text{eff}}c^n t} \quad (4)$$

with φ_0 representing the initial fraction of PEDOT in the PSS matrix,³¹ corrected for the amount of adhesion promoter present in the dry layer. Substituting eq 4 for φ in eq 2 yields the conductivity versus treatment time, and hence a fit function for the experimental data plotted in Figure 3a.

In the reaction-limited regime c is considered spatially constant in the HC PEDOT:PSS* layer and assumed equal to the hypochlorite concentration in solution. The remaining parameters, φ_0 , σ_l , σ_h , x , n , and k_{eff} were used as free variables in a simultaneous fitting procedure of the data for $[\text{NaClO}]_{(\text{aq})} = 0.01, 0.005$, and 0.0025% . The number of fitting parameters leaves the curve fitting process not fully unambiguous, as the same fit quality was obtained for different value sets. This was

especially the case for the coupling between φ_0 , σ_h , and k_{eff} whereas the remaining variables, that is, σ_l , x , and n , showed considerably less ambiguity. Hence, constraints of $\sigma_h < 6 \times 10^5$ S/cm, that is, the conductivity of bulk silver, and $\varphi_c > 0.01$, that is, a typical value for the percolation threshold of isotropically distributed conductive filler particles with extreme aspect ratio,³² were implemented in order to ensure the outcome of the fitting procedure to remain physically reasonable. Best simultaneous fits of all three data series (solid colored lines in Figure 3a) were obtained for single sets of parameter values. Table 1 lists these values in terms of coupled ranges

Table 1. Values for the Parameters of the GEM-Reaction Model Giving the Best Simultaneous Fit of the Transient Conductivity Data of HC PEDOT:PSS* Layers Immersed in $\text{NaClO}_{(\text{aq})}$ with Hypochlorite Concentrations of 0.01, 0.005, and 0.0025 wt %

σ_l (S/cm)	σ_h (S/cm)	φ_c (S/cm)	x	n	k_{eff} s ⁽⁻¹⁾
8.4×10^{-6}	$8 \times 10^4 < \sigma_h < 6 \times 10^5$	$0.01 < \varphi_c < 0.1$	3.5 ± 0.3	2	$75 > k_{\text{eff}} > 35$

interpolating between the extremes imparted by the mentioned constraints. Besides the fitted curves of the conductivity data corresponding to $[\text{NaClO}]_{(\text{aq})} = 0.01, 0.005$, and 0.0025% , Figure 3a also shows the theoretical curve for $[\text{NaClO}] = 0.05\%$, calculated using the values listed in Table 1. Clearly, in this case the simulated result overestimates the degradation rate, further evidencing that the process becomes diffusion-limited at increased hypochlorite concentration.

As indicated by Figure 3a, the fit to the model presented above is considered applicable for the initial and critical part of the curves, as the measured conductivity does not saturate at the value for σ_l . Instead, at long treatment times, the conductivity keeps decreasing after initially attempting to indeed curve off toward a saturation value. The straight black lines in Figure 3a suggest a second mechanism of conductivity decrease to take over in this regime, following a power law with time for all hypochlorite concentrations. We speculate that the underlying cause for this second process is related to some loss of ionic conductivity due to release of PSS upon elimination of its ion-pairing interaction with PEDOT, once the latter becomes oxidized. The best fit value for σ_l is of the same order of magnitude as previously reported values for ionic conductivities of PSS samples containing a residual amount of water.³³ A fraction of water is plausibly also present in the HC PEDOT:PSS* layers, as they do not undergo a thermal drying treatment after submersion in aqueous hypochlorite and rinsing. A single value of $n = 2$ describes the shift in time of the reaction-limited conductivity curves very well, in combination with one single value for k_{eff} . Varying n and k_{eff} for each data set would seem unreasonable considering the fact that the decrease in conductivity is likely due to the same reaction mechanism, irrespective of hypochlorite concentration.

As a last step we will attempt to relate the fitting results for σ_h , φ_0 , and x to the nanomorphology of the HC PEDOT:PSS* layers. First of all, the seemingly high value for σ_h is dictated by the fact that at the given φ_0 a sufficiently high σ_h is required to make sure that the effective medium value σ_m represents the measured conductivity of the untreated layers. Besides this rather abstract description, a more physical interpretation is that σ_h represents the intrinsic conductivity of the quasi-metallic, highly doped, probably partially crystalline,¹⁰ PEDOT

core regions, characterized by a high degree of molecular ordering.³⁴ We note that our definition of σ_h is in that sense different from the approach followed by Stöcker et al., who set σ_h equal to the conductivity indicated by the first data point in their concentration series, that is, corresponding to the sample with the highest PEDOT:PSS ratio (1:1). The difference between their (2.3 S/cm) and our value may therefore be explained by (i) the fact that according to their definition the conductive remains effectively “diluted” with PSS, and (ii) a significantly lower charge carrier mobility due to a higher degree of disorder of the PEDOT oligomers in case of LC PEDOT:PSS.^{10,34}

Another contribution may be expected from the nature of the larger length scale morphology of the PEDOT domains in the PSS matrix. Despite its uncertainty we can safely state that the value for φ_c is significantly lower than the percolation threshold of $\varphi_c = 0.29$ of a 3D system of randomly packed spheres.³⁵ This suggests a filament-like arrangement of conductive domains, rather than an isotropic globular or “pancake” morphology, as observed for various older types of PEDOT:PSS.³⁶ In fact, our value range for φ_c is in good agreement with the conclusions of a recently published study combining field-dependent conductivity measurements and TEM analysis of the same type of PEDOT:PSS as studied in this work, though lacking the adhesion promoter.³⁷ Indeed, fibrillar structures were observed both in dispersion and in the dry layer, consistent with a quasi-1D variable range hopping behavior of the in-plane conductivity and a percolation threshold of $\varphi_c \ll 0.125$.

Although some care should be taken in relation to the absence of the adhesion promoter in the PEDOT:PSS formulation used in the study by Kemerink et al.,³⁷ we observe that the value we obtain for the critical exponent x , that is, expressing the steepness of the rise in composite conductivity with PEDOT fraction near criticality, agrees strikingly well with their result ($x = 3.5$). What's more, comparable exponents have been reported for other composites which conductivity relies on the percolation of high aspect ratio filler particles, such as carbon fiber/polymer,³⁸ graphite/polymer,³⁹ and metal/polymer.⁴⁰ In contrast, the value for x found by Stöcker et al.²⁷ for LC PEDOT:PSS ($x = 1.05$) is significantly lower and closer to the “universal” number of ~ 1.7 , theoretically predicted for ideal (lattice) percolation in three space dimensions.⁴¹ Considering the above, this is explained by the higher shape isotropy of the globular or “pancake”-like PEDOT domains typically encountered in these more “traditional” types of PEDOT:PSS.³⁶

CONCLUSIONS

This work reports on the effect of $\text{NaClO}_{(\text{aq})}$ treatment on the thickness and conductivity of thin, highly conductive HC PEDOT:PSS layers. The thickness of the layers decayed exponentially with treatment time, to saturate at a residual thickness of at least $\sim 75\%$ of the initial layer thickness. No decrease in layer thickness was observed upon treatment of HC PEDOT:PSS* with pure water, evidencing that the loss of material is principally caused by the reaction between hypochlorite and PEDOT. Using theoretical and experimental arguments, we showed that the decrease in conductivity as a function of treatment time is reaction-limited for hypochlorite concentrations below 0.01%, but seems to enter a diffusion-dominated regime once the hypochlorite concentration is increased. The decrease in conductivity with treatment time follows a critical behavior followed by a power law at long exposure times. The curves corresponding to the reaction-

limited regime were fitted to a general effective medium (GEM) model, integrated with an effective rate law for the overoxidation of PEDOT. Obtained values for the percolation threshold and critical exponent are in good agreement with recent studies and suggest a filamentary rather than an isotropic globular morphology of the conductive PEDOT domains, typically observed for “traditional” low conductive PEDOT:PSS types.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future. *Adv. Mater.* **2000**, *12*, 481–494.
- (2) Groenendaal, L.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. Electrochemistry of Poly(3,4-alkylenedioxythiophene) Derivatives. *Adv. Mater.* **2003**, *15*, 855–879.
- (3) Nardes, A. M.; Kemerink, M.; Janssen, R. A. J.; Bastiaansen, J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W.; van Breemen, A. J. J. M.; de Kok, M. M. Microscopic Understanding of the Anisotropic Conductivity of PEDOT:PSS Thin Films. *Adv. Mater.* **2007**, *19*, 1196–1200.
- (4) Kim, J. Y.; Jung, J. H.; Lee, D. E.; Joo, J. Enhancement of Electrical Conductivity of Poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) by a Change of Solvents. *Synth. Met.* **2002**, *126*, 311–316.
- (5) Döbelin, M.; Marcilla, R.; Salsamendi, M.; Pozo-Gonzalo, C.; Carrasco, P. M.; Pomposo, J. A.; Mecerreyes, D. Influence of Ionic Liquids on the Electrical Conductivity and Morphology of PEDOT:PSS Films. *Chem. Mater.* **2007**, *19*, 2147–2149.
- (6) Fan, B.; Mei, X.; Ouyang, J. Significant Conductivity Enhancement of Conductive Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) Films by Adding Anionic Surfactants into Polymer Solution. *Macromolecules* **2008**, *41*, 5971–5973.
- (7) Xia, Y.; Ouyang, J. Salt-Induced Charge Screening and Significant Conductivity Enhancement of Conducting Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate). *Macromolecules* **2009**, *42*, 4141–4147.
- (8) Xia, Y.; Zhang, H.; Ouyang, J. Highly Conductive PEDOT:PSS Films Prepared through a Treatment with Zwitterions and their Application in Polymer Photovoltaic Cells. *J. Mater. Chem.* **2010**, *20*, 9740–9747.
- (9) Xia, Y.; Ouyang, J. Significant Conductivity Enhancement of Conductive Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) Films through a Treatment with Organic Carboxylic Acids and Inorganic Acids. *ACS Appl. Mater. Inter.* **2010**, *2*, 474–483.
- (10) Takano, T.; Masunaga, H.; Fujiwara, A.; Okuzaki, H.; Sasaki, T. PEDOT Nanocrystal in Highly Conductive PEDOT:PSS Polymer Films. *Macromolecules* **2012**, *45*, 3859–3865.
- (11) Nardes, A. M.; Janssen, R. A. J.; Kemerink, M. A Morphological Model for the Solvent-Enhanced Conductivity of PEDOT:PSS Thin Films. *Adv. Funct. Mater.* **2008**, *18*, 865–871.

- (12) Xia, Y.; Sun, K.; Ouyang, J. Solution-Processed Metallic Conducting Polymer Films as Transparent Electrode of Optoelectronic Devices. *Adv. Mater.* **2012**, *24*, 2436–2440.
- (13) Alemu, D.; Wei, H. -Y.; Ho, K. -C.; Chu, C. -W. Highly Conductive PEDOT:PSS Electrode by Simple Film Treatment with Methanol for ITO-free Polymer Solar Cells. *Energy Environ. Sci.* **2012**, *5*, 9662.
- (14) Ding, Y.; Invernale, M. A.; Sotzing, G. A. Conductivity Trends of PEDOT-PSS Impregnated Fabric and the Effect of Conductivity on Electrochromic Textile. *ACS Appl. Inter. Mater.* **2010**, *2*, 1588.
- (15) Heuer, H. W.; Wehrmann, R.; Kirchmeyer, S. Electrochromic Window Based on Conducting Poly(3,4-ethylenedioxythiophene)-Poly(Styrene Sulfonate). *Adv. Funct. Mater.* **2002**, *12*, 89.
- (16) Cravino, A.; Schilinsky, P.; Brabec, C. J. Characterization of Organic Solar Cells: the Importance of Device Layout. *Adv. Funct. Mater.* **2007**, *17*, 3906–3910.
- (17) AGFA; http://www.agfa.com/docs/sp/sfc/Patterning_UV-lithografie.pdf, 2001; accessed Sept 3, 2012.
- (18) AGFA; http://www.agfa.com/docs/sp/sfc/jul05_application_PatterningUVlithografie.pdf, 2005; accessed Sept 3, 2012.
- (19) Hansen, T. S.; West, K.; Hassager, O.; Larsen, N. B. Direct Fast Patterning of Conductive Polymers Using Agarose Stamping. *Adv. Mater.* **2007**, *19*, 3261.
- (20) Hansen, T. S.; Hassager, O.; Larsen, N. B.; Clark, N. B. Micropatterning of a Stretchable Conductive Polymer using Inkjet Printing and Agarose Stamping. *Synth. Met.* **2007**, *157*, 961.
- (21) Yoshioka, Y.; Calvert, P. D.; Jabbour, G. E. Simple Modification of Sheet Resistivity of Conducting Polymeric Anodes via Combinatorial Ink-Jet Printing Techniques. *Macromol. Rapid Commun.* **2005**, *26*, 238.
- (22) Lind, J. U.; Acikgoz, C.; Daugaard, A. E.; Andresen, T. L.; Hvilsted, S.; Textor, M.; Larsen, N. B. Micropatterning of Functional Conductive Polymers with Multiple Surface Chemistries in Register. *Langmuir* **2012**, *28*, 6502.
- (23) DeLongchamp, D. M.; Vogt, B. D.; Brooks, C. M.; Kano, K.; Obrzut, J.; Richter, C. A.; Kirillov, O. A.; Lin, E. K. Influence of a Water Rinse on the Structure and Properties of Poly(3,4-ethylenedioxythiophene):Poly(styrene sulfonate) Films. *Langmuir* **2005**, *21*, 11480–11483.
- (24) Crank, J. *The Mathematics of Diffusion*; Oxford University Press: New York, 1980.
- (25) Obviously, somewhat higher values for D_{eff} are obtained if swelling of the HC PEDOT:PSS* layers is taken into account by choosing an increased value for l .
- (26) See for instance: Crank, J. *Diffusion in Polymers*; Academic Press Inc.: New York, 1968.
- (27) Stöcker, T.; Köhler, A.; Moos, R. Why Does the Electrical Conductivity in PEDOT:PSS Decrease with PSS Content? A Study Combining Thermoelectric Measurements with Impedance Spectroscopy. *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 976.
- (28) Cruz-Estrada, R. H.; Folkes, M. J. Structure Formation and Modelling of the Electrical Conductivity in SBS-polyaniline Blends, Part I: Percolation theory approach. *J. Mater. Sci. Lett.* **2002**, *21*, 1427.
- (29) Cruz-Estrada, R. H.; Folkes, M. J. Structure Formation and Modelling of the Electrical Conductivity in SBS-polyaniline Blends, Part II: Generalized effective media theories approach. *J. Mater. Sci. Lett.* **2002**, *21*, 1431.
- (30) McLachlan, D. S. An Equation for the Conductivity of Binary Mixtures with Anisotropic Grain Structures. *J. Phys. C: Solid State Phys.* **1987**, *20*, 865.
- (31) The PEDOT:PSS ratio in the untreated material is not explicitly given in this paper for reasons of confidentiality. It is however comparable to the ratio typically used in most HC PEDOT:PSS systems encountered in the literature.
- (32) See Bauhofer, W.; Kovacs, J. Z. A Review and Analysis of Electrical Percolation in Carbon Nanotube Polymer Composites. *Compos. Sci. Technol.* **2009**, *69*, 1486–1498.
- (33) Chen, N.; Hong, L. A study on Polypyrrole-coated Polystyrene Sulfonic Acid Microspheres – a Proton Electrolyte. *Eur. Polym. J.* **2001**, *37*, 1027.
- (34) Ouyang, J.; Xu, Q.; Chu, C. -W.; Yang, Y.; Li, G.; Shinar, J. On the Mechanism of Conductivity Enhancement in Poly(3,4-ethylenedioxythiophene):Poly(styrene sulfonate) Film Through Solvent Treatment. *Polymer* **2004**, *45*, 8443–8450.
- (35) Lorenz, C. D.; Ziff, R. M. Precise Determination of the Critical Percolation Threshold for the Three-dimensional “Swiss Cheese” Model Using a Growth Algorithm. *J. Chem. Phys.* **2001**, *114*, 3659.
- (36) Timpanaro, S.; Kemerink, M.; Touwslager, F. J.; de Kok, M. M.; Schrader, S. Morphology and Conductivity of PEDOT/PSS Films Studied by Scanning–Tunneling Microscopy. *Chem. Phys. Lett.* **2004**, *394*, 339–343.
- (37) van de Ruit, K.; Cohen, R. I.; Bollen, D.; van Mol, T.; Yerushalmi-Rozen, R.; Janssen, R. A. J.; Kemerink, M. Quasi-one Dimensional In-plane Conductivity in Filamentary Films of PEDOT:PSS. *Adv. Funct. Mater.* **2013**, DOI: 10.1002/adfm.201301174.
- (38) Carmona, F.; Prudhon, P.; Barreau, F. Percolation in Short Fibres Epoxy Resin Composites: Conductivity Behavior and Finite Size Effects Near Threshold. *Solid State Commun.* **1984**, *51*, 255–257.
- (39) Blaszkiewics, M.; McLachlan, D. S.; Newnham, R. E. The Volume Fraction and Temperature Dependence of the Resistivity in Carbon Black and Graphite Polymer Composites: an Effective Media-percolation Approach. *Polym. Eng. Sci.* **1992**, *32*, 421–425.
- (40) Mamunya, Ye. P.; Davydenko, V. V.; Pissis, P.; Lebedev, E. V. Electrical and Thermal Conductivity of Polymers Filled with Metal Powders. *Eur. Polym. J.* **2002**, *38*, 1887–1897.
- (41) Stauffer, D.; Aharony, A. *Introduction to Percolation Theory*, 2nd ed.; CRC Press: Boca Raton, FL, 1994.