Structural Control of Charge Storage Capacity to Achieve 100% Doping in Vapor Phase-Polymerized PEDOT/Tosylate

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ABSTRACT: Vapor phase polymerization (VPP) is used to fabricate a series of tosylate-doped poly(3,4-ethylenedioxythiophene) (PEDOT) electrodes on carbon paper. The series of VPP PEDOT/tosylate coatings has varying levels of crystallinity and electrical conductivity because of the use (or not) of nonionic triblock copolymers in the oxidant solution during synthesis. As a result, the impact of the structure on charge storage capacity is investigated using tetra-n-butylammonium hexafluorophosphate (0.1 M in acetonitrile). The ability to insert anions, and hence store charge, of the VPP PEDOT/tosylate is inversely related to its electrical conductivity. In the case of no nonionic triblock copolymer employed, the VPP PEDOT/tosylate achieves electrochemical doping levels of 1.0 charge per monomer or greater (≥100% doping level). Such high doping levels are demonstrated to be plausible by molecular dynamics simulations and density functional theory calculations. Experiments show that this high doping level is attainable when the PEDOT structure is weakly crystalline with (relatively) large crystallite domains.

1. INTRODUCTION

Whether in the context of large scale infrastructure electricity supply or for portable electronic devices, the ability to efficiently store energy and redploy it at a later time is becoming increasingly important.1,2 Electrochemical cells, such as supercapacitors3 and batteries,4 provide one way to address this energy storage need. Within such cells, an anode and cathode (two electrodes) come in contact with an electrolyte containing the charge carrying atoms or molecules and can be charged by applying an electrical potential across the cell (charging). This causes cations and anions to be physically stored within the anode and cathode, respectively, to compensate the charges on the electrodes. Upon discharging, the ions diffuse out of the electrodes and associate within the electrolyte, releasing a flow of current in the process to power the connected electrical circuit. Key performance parameters relate to how efficiently large amounts of charge can be stored within the electrodes. Research focuses on improved electrode materials that have increased charge storage capacity,5–7 primarily by increasing the electrode surface area in contact with the electrolyte.

Conducting polymers have gained interest as electrode materials in electrochemical devices,5,9 because of their ability to readily electrochemically exchange anions with the surrounding electrolyte. For example, as anions are inserted (referred to as doping/oxidizing in this case) or released, (dedoping/reducing) many conducting polymers undergo a change in optical properties (electrochromism).10,11 This behavior can be exploited to build devices that switch visual (even outside the visible spectrum) appearance for applications of small electrical potentials. The desire for large changes in optical states between doped and dedoped states necessitates the need for efficient storage and release of anions, that is, as high charge storage capacity as possible is desired. Similarly, conducting polymers have been tested in supercapacitors with a view to use their interaction with anions to store large amounts of charge.12–14

Central to achieving high-performance electrochemical devices is the need to understand what aspects of a conducting polymer lead to enhanced anion uptake (high doping levels). Of interest is the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT)—widely regarded as the prototypical conducting polymer showing high electrical conductivity15,16 and good air stability in its oxidized form.17,18 Recent studies have shown the use of the nonionic triblock copolymer polyethylene glycol/polydimethylsiloxane/polyethylene glycol (PEG/PDMS/PEG) in the synthesis of PEDOT doped with tosylate anions can improve its properties for use in a
symmetric supercapacitor and for oxygen reduction. The underlying mechanism of this improvement is not well understood and serves as a motivation for the study herein.

In this study, comparison is made between PEDOT/tosylate films prepared using vapor phase polymerization (VPP) (Figure 1) using two different triblock copolymers, polyethylene glycol/polypropylene glycol/polyethylene glycol (PEG/PPG/PEG) and PEG/PDMS/PEG, with a reference PEDOT/tosylate having no added triblock copolymer. These triblock copolymers are added to the oxidant solution used in the VPP process to synthesize thin films of the conducting polymer. The PEG/PPG/PEG is used as a benchmark additive that leads to enhancement of the properties of VPP PEDOT/tosylate. For ultimate use in an electrochemical device (such as a supercapacitor), the VPP PEDOT/tosylate is deposited onto a carbon paper substrate.

2. RESULTS AND DISCUSSION

Electrochemical oxidation and reduction of the different PEDOT/tosylate samples were compared using cyclic voltammetry (CV) in 0.1 M tetra-n-butylammonium hexafluorophosphate in acetonitrile (Figure 2). All samples show pseudocapacitive response which is typical for PEDOT (Figure 2a), with a doping onset potential of about −0.6 V versus Ag0/+, followed by a broad peak at about −0.2 V versus Ag0/+.

Figure 1. (a) VPP process where EDOT vapor condenses at the vapor-solution interface of the Fe(III)-based oxidant solution. This oxidant initiates the oxidative polymerization of the EDOT to generate (b) the PEDOT doped with tosylate anions.

Figure 2. (a) CV measurements of PEDOT/tosylate prepared using PEG/PPG/PEG, PEG/PDMS/PEG and no triblock copolymer in the oxidant solution, compared with the heat-treated PEDOT/tosylate variants, all deposited on carbon paper. The insets present the schematic of oxidized and reduced PEDOT, which is based on the calculations of the bond length alternation reported in ref 28. (b) Specific charge capacity determined from CV. (c) Doping level, as charges per monomer unit, obtained for the highly oxidized state (+1 V) at the maximum charge storage capacity. Blue: Condition A, PEDOT/tosylate−PEG/PPG/PEG; orange: Condition B, PEDOT/tosylate−PEG/PDMS/PEG; and gray: Condition C, PEDOT/tosylate; dashed lines in (a): heat-treated samples. For the grayscale version, A denotes Condition A, B denotes Condition B, and C denotes Condition C, with the subscript “hash” # denoting untreated and ht denoting heat-treated samples. Error bars indicate 95% confidence intervals.
At +1.0 V versus Ag⁰⁺⁺, there is some current contribution from overoxidation, which peaks at +1.6 V versus Ag⁰⁺⁺ if samples are scanned to such high potentials (Figure S1). Although this pseudocapacitive CV response is very similar for all samples, the magnitude of the current differs greatly. Figure 2a shows that the current per gram of PEDOT/tosylate present is the lowest for the PEDOT/tosylate−PEG/PPG/PEG, much larger for the PEDOT/tosylate−PEG/PDMS/PEG, and the largest for the PEDOT/tosylate in the absence of any triblock copolymer. In fact, there is an order of magnitude difference in the current observed for the PEG/PPG/PEG and no triblock copolymer samples. The capacitive contribution from the carbon paper substrate was negligible in this potential region (Figure S1). The cyclic voltammograms can be integrated to give a specific charge density in mA h/g for the different samples (Figure 2b, see details in the Experimental Section and Computational Methods section). This demonstrates that the absence of the triblock copolymer yields PEDOT/tosylate with a significantly higher charge storage capacity than when PEG/PPG/PEG or PEG/PDMS/PEG is employed in the oxidant solution. The specific charge values are in the range expected for conducting polymers (electrochemically prepared PEDOT ≈ 14 mA h/g, chemically prepared PEDOT/chloride ≈ 40 mA h/g, and electrochemically prepared polypyrrole ≈ 40 mA h/g)—noting that the as-prepared PEDOT/tosylate−PEG/PPG/PEG is low and PEDOT/tosylate only is relatively high. To understand this, the doping levels (oxidation levels) achieved at 1.0 V versus Ag⁰⁺⁺ (Figure 2c) can be calculated (see details in the Supporting Information) and are quite different between the different samples. The origin of these differences is discussed further below.

Figure 3 presents a range of analyses on the as-deposited samples of PEDOT/tosylate on the carbon paper. Scanning electron microscopy (SEM) images highlight that the current differs greatly. Figure 2a shows that the current per gram of PEDOT/tosylate present is the lowest for the PEDOT/tosylate−PEG/PPG/PEG, much larger for the PEDOT/tosylate−PEG/PDMS/PEG, and the largest for the PEDOT/tosylate in the absence of any triblock copolymer. In fact, there is an order of magnitude difference in the current observed for the PEG/PPG/PEG and no triblock copolymer samples. The capacitive contribution from the carbon paper substrate was negligible in this potential region (Figure S1). The cyclic voltammograms can be integrated to give a specific charge density in mA h/g for the different samples (Figure 2b, see details in the Experimental Section and Computational Methods section). This demonstrates that the absence of the triblock copolymer yields PEDOT/tosylate with a significantly higher charge storage capacity than when PEG/PPG/PEG or PEG/PDMS/PEG is employed in the oxidant solution. The specific charge values are in the range expected for conducting polymers (electrochemically prepared PEDOT ≈ 14 mA h/g, chemically prepared PEDOT/chloride ≈ 40 mA h/g, and electrochemically prepared polypyrrole ≈ 40 mA h/g)—noting that the as-prepared PEDOT/tosylate−PEG/PPG/PEG is low and PEDOT/tosylate only is relatively high. To understand this, the doping levels (oxidation levels) achieved at 1.0 V versus Ag⁰⁺⁺ (Figure 2c) can be calculated (see details in the Supporting Information) and are quite different between the different samples. The origin of these differences is discussed further below.

Figure 3 presents a range of analyses on the as-deposited samples of PEDOT/tosylate on the carbon paper. Scanning electron microscopy (SEM) images highlight that the PEDOT/tosylate−PEG/PPG/PEG is nonuniformly deposited over the substrate area (larger area images presented in Figure S2). The electrical conductivity measurements on the flat reference glass substrate samples (Figure 3d) indicate there is a change in contrast between the SEM images in Figure 3a−c: the highest conductivity sample, PEDOT/tosylate−PEG/PPG/PEG, has a comparable electrical conductivity, to the underlying carbon paper substrate (Toray carbon paper is approximately 170 S/cm). Whereas, in the case of the PEDOT/tosylate with no added triblock copolymer, the conductivity decreases by 2 orders of magnitude. In this case, the PEDOT/tosylate will be a poor conduit for the electrons, locally charging up the surface during the SEM imaging; the underlying carbon paper will dissipate this charge. The origins of the changing electrical conductivity arise from two sources: (i) the doping level of the as-deposited PEDOT/
tosylate, and (ii) the morphology and structure of the PEDOT chains. X-ray photoelectron spectroscopy (XPS) analysis (Figures 3e and S3) shows a change in the doping level as the triblock copolymer is changed from PEG/PPG/PEG to PEG/PDMS/PEG or is completely removed. The magnitude of this change in doping, however, is not sufficient to completely explain the differences in conductivity. X-ray diffractograms shown in Figure 3f show that the structure of the samples also changes. The PEDOT/tosylate−PEG/PPG/PEG displays the highest level of chain ordering [with diffraction peaks observed from both (100) and (200) planes] in combination with the highest as-deposited doping level—therefore the highest electrical conductivity within this set of samples.

Comparing the electrical conductivity and specific charge of the various as-deposited samples (Figure 4) shows an inverse relationship, that is, the lower the electrical conductivity of the as-deposited PEDOT/tosylate, the greater its charge storage capacity. The origins of this relationship are hypothesized to arise from the structure of the PEDOT itself (which then manifest in the electrical properties in question). The X-ray diffraction (XRD) analysis in Figure 3f shows that the degree of ordering the PEDOT/tosylate is different, and the full width at half-maximum of the primary peak shows that the crystallite size is also changed. In fact, the PEDOT/tosylate with no triblock copolymer has a relatively lower degree of ordering yet an increased crystallite size (ca. 25 nm) relative to the other PEDOT/tosylate samples that employ triblock copolymers (<10 nm) (Figure 4b). Heat treatment of PEDOT/tosylate−PEG/PPG/PEG after polymerization but prior to washing has been shown to modify the resultant properties (higher doping, lower conductivity, and greater robustness). In the study herein, this modification also showed an improvement in the charge storage capacity, presented in Figure 2. However, this did not positively translate to the other PEDOT samples. The use of heat treatment for the PEG/PDMS/PEG sample led to an increase in conductivity and decrease in charge storage capacity (Figure 4a), while the loss of charge storage capacity in the sample with no triblock copolymer was most significant with values decreasing from 130 to 24 mA h/g. The rationale here is that the different triblock copolymers impart different levels of stability to the polymer film’s properties during a moderate (70 °C) heat treatment step during fabrication. The PEG/PPEG/PPEG imparts stability to the polymer properties under heat treatment conditions, albeit for a higher conductivity/lower charge storage capacity to begin with. For PEG/PDMS/PEG, a much greater level of stability is seen, with an increase in electrical conductivity and decrease in charge storage capacity upon heat treatment. In the absence of any triblock copolymer, the electrical properties of the PEDOT/tosylate cannot survive the heat treatment process, with a dramatic drop in charge storage capacity.

The high doping level of 100%—reached with the cyclic voltammogram at +1.0 V versus Ag0/+ for PEDOT/tosylate...
synthesized without any triblock copolymer—signifies that each 3,4-ethylenedioxythiophene (EDOT) monomeric unit bears one positive charge, each compensated by one counterion. This is highly unusual for conducting polymers, which can typically only be charged to doping levels of 25−33% before undergoing overoxidation reactions that lead to degradation. Given the value is determined from the electrochemical experiment, it cannot be assigned to anions associated with cations (i.e., salt) as these anions would not contribute to the electrochemical charge stored. Similarly, the high charge per monomer only occurs for PEDOT without the triblock copolymer—therefore, coordination with the ethoxy groups cannot assist in such high levels of charge per monomer. It is also worth noting that these higher doping levels are not associated with an increased stable potential range, but rather with a higher capacitance. In other words, each oxidation step, introducing a positive charge on the PEDOT backbone, has only a small influence on the potential required for the next oxidation step, and thus allowing more charge to be stored in the same potential interval. This implies that the charges introduced on the PEDOT backbone are very efficiently shielded (minimizing the Coulombic interactions with the surrounding PEDOT charges) because in the fully charged state, every monomeric unit is positively charged, although this hypothesis requires further research, out of scope of this manuscript. In a previous study, we have also observed high capacitance and doping levels (up to 69%) for vapor phase-polymerized PEDOT/tosylate (employing a PEG/PDMS/PEG triblock copolymer) in ionic liquid-based supercapacitor cells, and we then hypothesized that the triblock copolymer provided such efficient shielding. However, the results presented herein show that even higher doping levels are obtained when the VPP process is performed without any triblock copolymer, showing that the triblock copolymer is not necessary for—but in fact detrimental to—obtaining high doping levels. Judging by the fact that no significant change occurs during consecutive CV cycles, when tosylate counterions are exchanged for hexafluorophosphate (from the supporting electrolyte), and also considering that the results are analogous to those of supercapacitor cells where dicyanamide anions were used, this effect appears rather general and not specific to this particular electrolyte or solvent.

To rationalize the apparent influence of the triblock copolymer, we present the following hypothesis. The study herein and previous reports have shown that the introduction of a triblock copolymer into the VPP process yields greater alignment of PEDOT chains within the film. Such proximity of chains should facilitate good interchain charge transport and thus higher charge mobility and higher electrical conductivity. At the same time, it is hypothesized that the local order/aggregate structures have greater alignment which imparts a certain “rigidity” to the chain packing structure. This rigidity restricts the chains from sufficiently separating to accommodate large numbers of anions from inserting/intercalating during the electrochemical oxidation. This draws comparison with paraffinic-like microstructures for polymer semiconductors. Conversely, in the absence of the triblock copolymer, the reduced chain alignment decreases the mobility and electrical conductivity (retards interchain hopping), while allowing the packing structure to “swell” to accommodate much larger numbers of anions during oxidation. Such a hypothesis puts the chain packing structure (not necessarily crystallinity though) as the central property that defines the trade-off between electrical conductivity and charge storage capacity (cf. the inverse relationship in Figure 4a).

Overoxidation limits the maximum positive potential that can be applied to the samples, and this usually means that at lower potentials, the conducting polymer will lose charge in a so-called self-discharge process. This was investigated by charging samples to 1.0 V versus Ag0/+ and then monitoring the spontaneous potential decrease during the self-discharge process (Figure S4). In all cases, the self-discharge rate was exponentially dependent on the potential, in agreement with previous observations. This indicates that self-discharge proceeds via an unstable intermediate reached through a higher oxidation state, which can also be observed by CV at 1.6 V versus Ag0/+ (Figure S1). Overoxidation thus does occur for these PEDOT/tosylate samples also and at a similar potential to what is commonly observed for conducting polymers, but the higher capacitance means that more charge can be stored in these samples before this overoxidation starts to contribute to any appreciable extent. Furthermore, calculations indicate that the PEDOT itself is not inherently unstable at high doping levels (vide infra), but the limitation lies in its vulnerability to nucleophilic attack by other species such as solvents, anions, dissolved oxygen, impurities, and so forth. It should thus be possible to improve the stability at high potentials by the proper choice of the electrolyte system and careful exclusion of oxygen and other impurities. Also, larger crystallite size seems to improve stability by limiting the solvent access to the bulk of the PEDOT, as observed for the no triblock copolymer samples.

To confirm the plausibility of such high doping levels for the PEDOT/tosylate without any triblock copolymer, a coarse grain molecular dynamics (MD) simulation and density functional theory (DFT) calculations on PEDOT/tosylate were made as a function of doping level (and hydration level). Noting here for simplicity that (i) tosylate ions are used to dope the PEDOT in these calculations to levels beyond those previously reported (>50% oxidation) and (ii) water is used as the solvent instead of acetonitrile. The simplified model is designed to give an indication of the likelihood that PEDOT can accommodate such high doping levels without degradation. Figure 4c–f shows the outcomes of the MD simulations—although it should be noted that the structure discussion to come may not exactly represent the structures formed using the VPP process. The snapshot in Figure 4c highlights the intercalation of tosylate ions between the PEDOT chains at a 100% doping level and a hydration level from 80% dried to 10%. The tosylate ions position at the same distance from the PEDOT as typically observed for the π−π stacking of PEDOT chains [the (010) plane] at lower doping levels. As the doping increases, there is a complete loss of the nearest neighbor π−π stacking of PEDOT (approx. at 75% doping in Figure 4d) and then loss of the stacking all together (200% doping). At a doping level of 100%, the packing appears as π−anion−π stacking of PEDOT−tosylate−PEDOT. The calculated radial distribution function as a function of doping level and hydration level is presented in Figure S5, along with a snapshot of the MD simulation for 100% doping and 80% hydration where the π−anion−π stacking is clearly evident. In this case, the 80% hydration level is presented to replicate the highly solvated case in the electrochemical measurements with acetonitrile in direct contact with the PEDOT/tosylate.
Note that formation of the intercalated structure can explain the inverse dependence between conductivity and charge storage capability. Recently, multiscale transport calculations were reported for PEDOT/tosylate relating its mobility to the material morphology.33,34 These studies outline the importance of the π-π connections between polymeric chains forming a percolative transport network through the whole sample, which represents a prerequisite for a high mobility of the polymeric films. When tosylate counterions intercalate between the polymeric chains in the samples with high doping levels, the π-π connections are apparently destroyed, which suppresses the charge carrier hopping between the chains and hence leads to the mobility decrease as compared to the moderately doped samples. This rationale is supported by previous work by Petsagkourakis et al. who positively correlated crystallinity with charge carrier mobility.35

DFT calculations (Figure 4e) show that the PEDOT chain is stable at 100% doping, with the conjugated backbone being positively charged within the middle of the chain. The carbon–carbon bond length within the middle of the PEDOT chain (Figure 4f) approaches a purely aromatic structure (benzene bond length ≈ 1.40 Å). The longest bond lengths near the end of the chain (1.46 Å) appear sp2–sp3 in character (ca. 1.47 Å). Such bonding character indicates probable stability of the PEDOT chain at such high doping levels.

3. CONCLUSIONS

In summary, a variety of PEDOT/tosylate films were prepared via VPP to study their charge storage capacity. Comparing the addition of different nonionic triblock copolymers (PEG/PPG/PEG and PEG/PDMS/PEG) reported in the literature with no triblock copolymer highlights that although they enhance the electrical conductivity, they adversely impact the charge storage capacity. Similarly, the use of post-VPP heat treatment has previously been reported as a useful means to enhance the properties of PEDOT/tosylate; however, this proved disadvantageous for charge storage. The absence of the triblock copolymer in the VPP process yielded PEDOT/tosylate after the VPP process is critical to defining the ultimate charge storage capacity. A larger charge storage capacity demonstrated herein will in turn result in more efficient energy storage devices.

4. EXPERIMENTAL SECTION AND COMPUTATIONAL METHODS

4.1. Materials. Fe(III) tosylate (Clevios CB54, 54 wt % in butanol) was obtained from Heraeus. The EDOT monomer PEG/PPG/PEG of Mw = 5800 g/mol (Pluronic P-123), acetonitrile, and tetra-n-butylammonium hexafluorophosphate were received from Sigma-Aldrich. PED/PDMES/PDMS (DBE-U12) was purchased from Gelset. Butanol and 100% undenatured ethanol were purchased from Chem-Supply. All chemicals were used without further purification. The choice of the molecular weight and structure of the PEG/PPG/PEG triblock is based on previous work for performance improvement of PEDOT/tosylate through higher levels of crystallinity.24 The basis for using the PEG/PDMS/PEG was previous work on PEDOT/tosylate in supercapacitors.12 The carbon paper substrates (Toray carbon paper, wet proofed with 40 wt % poly(tetrafluoroethylene) coating) were supplied by Fuel Cell Earth LLC. The glass substrates (76 × 51 × 1 mm borosilicate glass) were provided by ProSciTech.

4.2. Oxidant Solutions and PEDOT Fabrication. Three categories of oxidant solution were prepared as per the formulae mentioned in Table 1. The labeling of Condition A, B, and C refers to the use of PEG/PPG/PEG, PEG/PDMS/PEG, and no additive, in the oxidant solutions. The carbon paper substrates were cut into 20 × 25 mm size and attached on a glass slide as shown in Figure S6. The prepared oxidant solution was dip-coated on to the carbon paper as per the dip coating parameters given in the Table 2.

In the case of the glass reference substrate, the oxidant solutions were spin-coated (400B-6NPP, Laurel Technologies Inc.) at a speed of 1500 rpm for 25 s. Prior to the oxidant-coating step, the substrates were air plasma-treated (Diener, Plasma etcher NANO, Germany) for 2 min to remove contaminants and to increase the wetting of the oxidant solution. The oxidant-coated substrates were then placed on a hot plate at 70 °C for 1 min to evaporate the excess solvent. Samples were removed from the hot plate and transferred to the VPP chamber (Binder VD115) containing a Petri dish with 2 drops of the EDOT monomer. The chamber was evacuated to 45 mbar at room temperature (ca. 23 °C) and the Petri dish containing the EDOT heated to 35 °C. After 45 min, the samples were taken out from the chamber and immediately washed with ethanol to remove any remaining oxidant and unreacted monomer. This general procedure is presented in
the schematic of Figure 1, with samples labeled with the subscript #. A second set of samples were prepared, where the PEDOT/tosylate was heat-treated after the VPP process at 70 °C for 7 h before the ethanol washing step. Such samples are referred to as “heat treated” and labeled with the subscript “ht”.

4.3. Characterization. Elemental analysis of the PEDOT samples was carried out using XPS (SPECS SAGE, Phoibos 150-HSA) with a Mg anode (200 W power). The quantitative analysis (atomic percentage and doping level) of the XPS results were carried out using CasaXPS software. The doping level of each sample was analyzed using the methodology used by Bubnova et al.36 Two doublets were fitted to the spectra, with a spin-split, S 2P_{1/2} and S 2P_{3/2}, and with the energy splitting set at 1.2 eV (Figure S3). These doublets, (163.8 and 165 eV) and (167 and 168.2 eV), correspond to neutral PEDOT.

The samples were mounted on a Pt wire working electrode, the counter electrode was Pt coil. The electrolyte was thoroughly degassed with N2 and then kept under a N2 atmosphere throughout the experiments. The self-discharge rate was calculated as a function of potential as described previously.12

4.4. Simulation and Theoretical Calculations. A set of Martini coarse graining MD simulations were employed at different doping levels to study the interaction between PEDOT chains and tosylate anions at a variety of doping levels. These MD simulations extend to much higher doping (oxidation) levels beyond those reported previously (>33%).30

More details of CG simulations and PEDOT model are in our previous work.40 All MD simulations are performed by using the Gromacs package.41–43 Similarly, DFT calculations were made at doping levels of 100 and 200% to ascertain the electron density along a PEDOT chain at these extremely high doping levels.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02710.

Measured current density, lower magnification SEM images of PEDOT, XPS analysis, self-discharge measurements, radial distribution function, carbon paper substrates attached to rigid glass slides, and PEDOT mass loss (PDF)

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**Notes**

The authors declare no competing financial interest.

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rate of 0.1 V/s. From the CV data, the specific charge and doping level were determined by averaging the integrated current of the first oxidation and reduction sweeps (in order to avoid errors from polarization and instrument current bias) for 4–10 samples of each type and normalizing with the mass of PEDOT/tosylate as determined by TGA. Further details on the calculation of the doping level can be found in the Supporting Information. Self-discharge experiments were performed after CV by first sweeping the potential to 1.0 V versus Ag_0/+/ (0.1 V/s) and then keeping the potential constant at 1.0 V versus Ag_0/+ for 60 s and subsequently measuring the potential at an open circuit. The self-discharge rate was calculated as a function of potential as described previously.12
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