Electrochemical Variation of the Energy Level of Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate)

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The doping level of spin-coated poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDT:PSS) films was adjusted quantitatively by an electrochemical doping/dedoping process using *p*-toluenesulfonic acid in acetonitrile as supporting electrolyte. Higher oxidation states relative to as-prepared layers remain stable under dry condition, and the electrochemical treatment does not affect the surface morphology and homogeneity of the polymer film. The work function of PEDT:PSS increases with the doping level after adjusting the layer at electrode potentials higher than the value of the electrochemical equilibrium potential (E_{eq}) of as-prepared films. The ohmic behavior for hole-injection is nearly achieved at anode/NPB interfaces for a PEDT:PSS anode with very high doping level (E_{eq} of up to 0.59 V vs Ag/AgCl). This indicates a further reduction of the hole-injection barrier at the contact of polymeric anode/hole transport layers.

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDT) is a stable conjugated polymer, with high transparency in the doped (oxidized) state.[1–2] The blend of PEDT with poly(styrenesulfonate) (PSS) dispersed in water (PEDT:PSS) shows good film-forming properties[3–4] and has been commonly used as a buffer layer in organic devices such as polymeric light-emitting diodes (PLED) and solar cells. In PLED application, an ultrathin film of PEDT:PSS is inserted between indium–tin oxide (ITO) anode and the organic electroluminescent (EL) layer. A PEDT:PSS-covered ITO anode reduces the operating voltage and increases the device lifetime remarkably,[5–8] which was attributed to a lower hole injection barrier between ITO and the hole transport layer as well as a smoother surface than bare ITO. Usually, this layer is prepared by spin-coating of a PEDT:PSS dispersion. To optimize its electronic and optical properties, a controlled treatment of the dispersion or the produced layer is necessary. However, up to now there have been only a few reports on this strategy. For instance, a small amount of glycerol was added to PEDT:PSS (G-PEDT:PSS),[9] which allows the conductivity of PEDT:PSS to be dramatically enhanced. On the basis of this result, a PEDT:PSS-only anode has been used in OLED.[10] Here, we attempt to adjust the doping level of PEDT:PSS layers electrochemically in order to tune the hole-injection capacity of ITO/organic interfaces.

The doping level of the polymer anode is correlated with its electrochemical equilibrium potential (E_{eq}),[11] and an offset exists between E_{eq} and the work function ϕ[12], with the latter directly influencing the hole injection barrier. It is therefore possible to control ϕ of the anode directly by the adjustment of the doping level of the polymer. Electrochemical charge transfer is a convenient method to adjust the redox state of the polymer in an electrodeposition process,[11] and the potentiostatic doping of the polymer is usually used. Gross et al. demonstrated that the hole-injection barrier can be tuned continuously by modifying the doping level of poly(4,4′-dimethoxybithiophene) (PDBT)
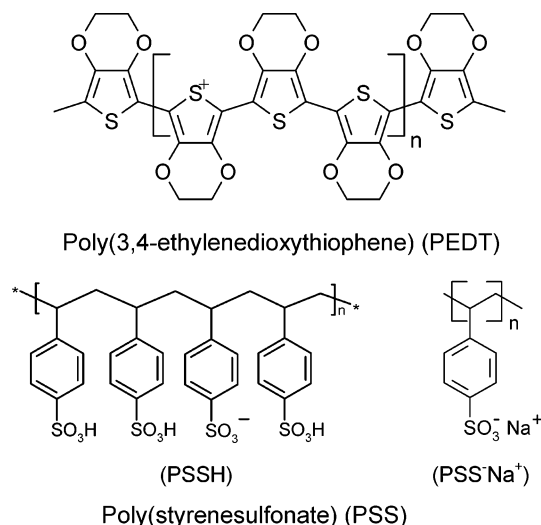
layer prepared electrochemically.[13] For the π-conjugated PEDT, this adjustment can be carried out without polymer degradation over a wide potential range from −0.6 to +1.4 V, demonstrating the wide range of the tunability of E_{eq}.[1,2] However, the layers formed by electropolymerization are usually not smooth enough, which will be disadvantageous for the performance and reliability of the device fabricated. In our case, smooth PEDT:PSS layers from a casting procedure were chosen and *p*-toluenesulfonic acid was used as supporting electrolyte to change the doping state of the polymer electrochemically. Our objective is to control and quantify the doping level and thus the value of ϕ of the PEDT:PSS layer in order to reach well-defined redox states under dry condition for use in OLEDs.

2. Experimental Section

The patterned ITO-coated glasses (Merck, $15\Omega \ \square^{-1}$) were cleaned extensively,[14] and then treated in oxygen plasma prior to use. The polymer films were prepared by spin-coating of an aqueous PEDT:PSS dispersion (Baytron P;[15] its chemical structure is shown in Figure 1) on ITO. Very homogeneous layers were formed due to good wetting of such an ITO surface. The thickness is about 60–150 nm as determined by atomic force microscope (AFM) measurements. Then the films were dried at 100 °C for 10 min in air. PEDT:PSS films prepared according to this procedure are referred as "as-prepared" below in contrast to the "treated" ones in the following sections.

Tuning of the doping level was carried out by the potentiostatic electrolysis at the applied potentials from −0.6 to +0.8 V in a one-compartment electrochemical cell. The electrolyte was water-free 0.1 M *p*-toluenesulfonic acid in acetonitrile. This acid was chosen due to its high structural similarity with the repeating unit of PSS as well as its higher mobility than PSS. The PEDT:PSS coated ITO anodes served as working electrodes; the reference and counter electrode was Ag/AgCl and Pt, respectively. All potentials given are referred to the potential of an aqueous Ag/AgCl electrode. The electrolyte was degassed from oxygen by nitrogen bubbling for 15 min and nitrogen atmosphere was maintained over the solution during the experiment. Thereafter, the films were rinsed carefully with

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17302 *J. Phys. Chem. B, Vol. 108, No. 45, 2004*

Zhang et al.

Poly(3,4-ethylenedioxythiophene) (PEDT)

(PSSH)   (PSS⁻Na⁺)

Poly(styrenesulfonate) (PSS)

Figure 1. Chemical structure of PEDT:PSS.

TABLE 1: Amount of Injected Charge Q and Variation of Doping Level $\Delta\delta$ for a 120 nm PEDT:PSS Layer (Area, 5 cm²; density, 1.5 g/cm⁻³) Adjusting at Different Electrode Potentials (vs Aqueous Ag/AgCl Electrode)[a]

applied potential (V)	Q (mC)	$\Delta\delta$ (10^{-2})
none	0.0	0.0
(as-prepared)		
0.77	1.98	7.91
0.67	1.14	4.55
0.57	0.712	2.84
0.47	0.382	1.53
0.26	−0.30	−1.20
0.17	−0.632	−2.52
−0.18	−4.93[b]	−19.7[c]
−0.48	−15.30[b]	−61.1[c]

[a] The sequence of potential steps applied follows the pathway: +0.47 V → ... → +0.77 V → +0.26 V → ... → −0.48 V. The effect of double-layer capacitance on the injection current was neglected. [b] A part of the cathodic current stems from a reduction process of the ITO substrate by negative potential ($\leq$ −0.18 V). [c] Not reliable values of the doping level.

TABLE 2: Electrochemical Equilibrium Potentials E_{eq} of a PEDT:PSS Layer Relevant to $\Delta\delta$ Values Shown in Table 1 after Adjustment at Different Applied Potentials (vs Aqueous Ag/AgCl Electrode)

applied potential (V)	E_{eq}^{a}(V)	E_{eq}^{b}(V)
none	0.37	0.37
(as-prepared)		
0.77	0.68	0.59
0.67	0.57	0.51
0.57	0.52	0.45
0.47	0.41	
0.26	0.27	0.27
0.17	0.23	0.22
−0.18	−0.01	0.09
−0.48	−0.05	0.02

[a] Measured in the solution (20 min after the modification by positive potential and 5 min after the modification by negative potential, respectively). [b] Measured after the modified layers were rinsed by acetonitrile and dried.

acetonitrile and dried in a stream of pure N₂. The electrochemical equilibrium potential E_{eq} was determined from the value of open circuit potential (OCP) measured after the above-mentioned procedure.

The absorption spectra were measured in situ at relevant E_{eq} values with a diode array UV−vis−near-IR spectrophotometer (J&M, Analytische Mess- und Regeltechnik GmbH, Aalen, Germany). X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI 5600I spectrometer equipped with monochromatized Al Kα source, and ultraviolet photoelectron spectroscopy (UPS) measurement was carried out with He I ($h\nu$ = 21.2 eV) radiation. For the determination of work function by UPS, the samples were biased at −5.0 V so that the inelastic secondary electron cutoff can be determined.

3. Results and Discussion

3.1. Variation of the Doping Level. The cyclic voltammograms of "as-prepared" PEDT:PSS films show an oxidation peak potential of PEDT of ca. 0.35 V, which is very similar to that for PEDT electrodeposited from an aqueous electrolyte. The films display a reproducible redox behavior in the electrolyte and remains electroactive after continuous cycles between −0.2 and +0.7 V, indicating high electrochemical stability.

When an electrode potential is applied to the working electrode, an anodic or cathodic current occurs in dependence of the value of the potential. The amount of the charge within the polymer was thus changed, which should be accompanied by the injection of Tos⁻ anions or the migration of H⁺ ions out of the polymer during the doping, as well as the injection of H⁺ ions into the layer during the dedoping, respectively. The nominal doping level can be defined as

$$\delta = \frac{\text{molar number of charge injected}}{\text{molar number of EDT}} \quad (1)$$

Since PEDT:PSS is highly p-doped with an oxidation level of 33%,[15] in our case the amount of charge (positive and negative) injected during the redox process, should correspond to the variation of doping level $\Delta\delta$ in the polymer. With the known amount of PEDT:PSS deposited on ITO, the number of PEDT repeating units can be calculated (overall molar ratio of PEDT to PSS repeating units is 0.82[15]). Hence the change in doping level can be quantitatively determined. Table 1 lists the amount of injected charge and relevant $\Delta\delta$ value for a 120 nm

thick PEDT:PSS layer at different electrode potentials. The doping level increases monotonically with applied positive potential.

To validate the above introduced $\Delta\delta$, we correlate its value with a "true" quantification of the doping level by measuring the electrochemical equilibrium potential E_{eq}. Table 2 gives a series of E_{eq} values of the layer after the redox processes. It indicates that the doping level of PEDT:PSS layer can be modified further despite its compact morphology, and also suggests that the amount of the charge injected is indeed a good measure of the doping state of the polymer. As shown in Figure 2, the E_{eq} value increases approximately logarithmically with the amount of injected charge. The higher oxidation state (e.g., E_{eq} of 0.68 V) relative to the unmodified layer (E_{eq} of 0.37 V) is very stable, which is manifested by only a slight drop of E_{eq} as the modification process is interrupted by disconnecting the electrochemical cell. Such a high oxidation state also changes little at the dry state in air (a slight drop to 0.59 V of E_{eq}). This stabilization of increased doping of PEDT:PSS is critical for any device preparation.

In contrast, the reduced state is more difficult to obtain. The applied potential of up to −0.5 V leads only to an E_{eq} value of 0 V (after drying). Also, the dedoped layer shows a rapid increase of open circuit potential in the electrolyte after interrupting the reduction process. This is attributed to the very low reduction potential of PEDT (−0.5 V).[16] A trace amount
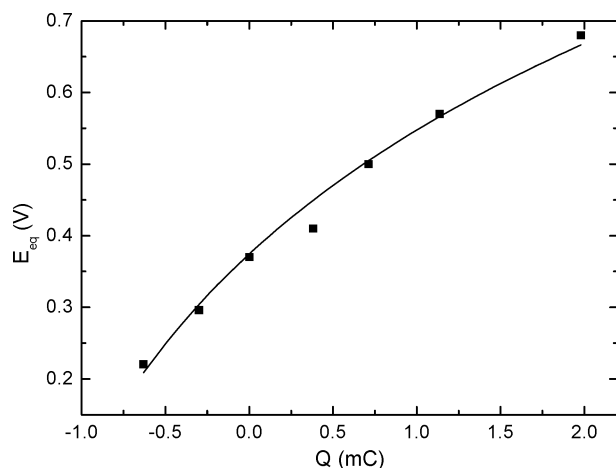
Spin-Coated PEDT:PSS

J. Phys. Chem. B, Vol. 108, No. 45, 2004 **17303**

Figure 2. E_{eq} ($E_{eq}{}^a$ in Table 2) change of PEDT:PSS film (with a thickness of 120 nm and the area of 5 cm^2) as a function of the amount of charge Q injected during electrochemical modification. The data were not shown for the dedoping at high negative potential (≤ -0.18 V) due to the large instability of the E_{eq} value and the derivation on calculation of Q (large part of cathodic current comes from the redox process of ITO substrate).
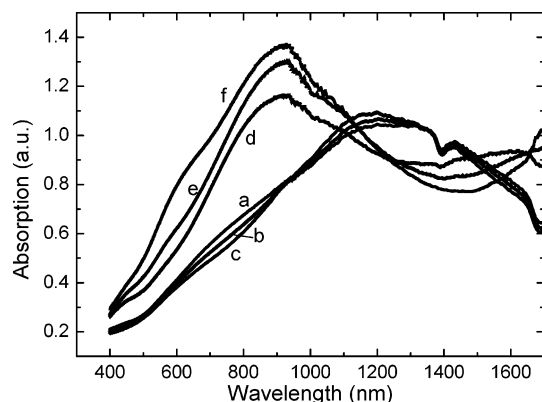

Figure 3. In situ UV–vis–near-IR absorption spectra of 240 nm PEDT:PSS on ITO as a function of the electrode potential: (a) as-prepared; (b) +0.60 V; (c) +0.80 V; (d) 0 V; (e) −0.3 V; (f) −0.5 V.

of O$_2$ from the electrolyte or air can oxidize the layer. In addition, if the layer is reduced at a large negative potential (≤ -0.48 V) at first and then oxidized at the potential above 0.37 V (E_{eq} of as-prepared layer), the doping level is always lower than that for the as-prepared film. It suggests the possibility that a degradation process of the chemical structure in PEDT:PSS occurs during the dedoping process.

The change of surface morphology of PEDT:PSS films during electrochemical treatment is an important issue to consider. SEM observation shows that no apparent change in morphology takes place during doping and dedoping processes. The surface is very smooth with a roughness of 2–3 nm from AFM measurement, nearly the same as that for the as-prepared layer. Only little small cracks are found at the boundary of the film after long-time reduction for up to 400 s, which is attributed to the erosion of the underlying ITO by the acidic electrolyte. In general, this indicates that the electrochemical treatment does not affect the homogeneity of the polymer films.

3.2. UV–Vis–Near-IR Spectra. Figure 3 shows a series of UV–vis–near-IR absorption spectra for PEDT:PSS films treated at different electrode potentials. The absorption below 1000 nm decays especially for the feature centered around 890 nm that is assumed to be the band of polaron pairs.[17] Meanwhile the band centered around 1200 nm enhances gradually with the
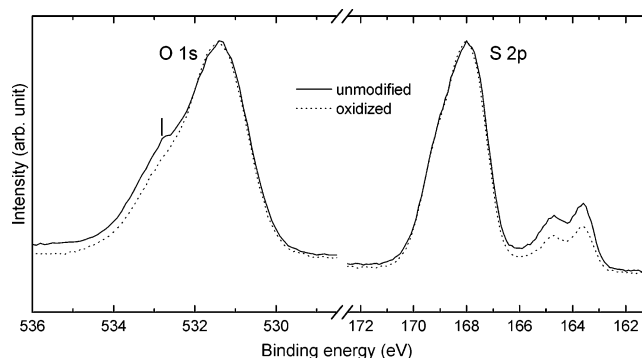
increase of positive potential, which is ascribed to bipolaron subgap states.[18] The number of bipolaron states increases while the number of polaron states decreases with doping level, which indicates that the transition from polaron pairs to bipolarons occurs during the doping process. The variation of absorption corresponds to that of E_{eq} shown in Table 2.

It is to be pointed out that the absorption band at a higher oxidation state varies only a little as compared to that for the as-prepared layer (slight enhancement of bipolaron band relative to the latter), because the oxidation level for as-prepared film is already high. On the other hand, the infrared bands are still present and the absorption associated with π–π* transition (band at 580 nm) remains very weak when a high negative potential is applied. This indicates that the "reduced" PEDT is not entirely neutral, similar to the case of aqueous PEDT electrodeposited.[19] A possible reason is suggested which could cause such a feature: existence of some amount of charged PEDT after the reduction, which originates from the compact structure of PEDT:PSS layer.

3.3. XPS and UPS Results. XPS spectra were measured to investigate the chemical changes of PEDT:PSS during the electrochemical modification process. For as-prepared layers, a strong Na 1s peak is found, indicating a large amount of sodium (roughly one sodium atom per four sulfur atoms from quantitative analysis) in the near surface region. However, Na 1s emission disappears completely after electrochemical treatment. Furthermore, the absence of sodium is also found if the as-prepared layer is immersed in pure acetonitrile for 10 min. This indicates that sodium can be completely exchanged by the solvent before electrolysis (the electrolyte has to be degassed for 10 min). Therefore, Na$^+$ ions are not responsible for the doping/dedoping process.

Figure 4 (right part) shows the S 2p core-level spectra of PEDT:PSS as-prepared and after the doping. For the as-prepared film, the lower binding energy (BE) emission peaks at 163.4 and 164.7 eV, can be assigned to the sulfur atoms in PEDT.[20–21] Moreover, it shows an asymmetric tail on higher BE side. This arises from the presence of positive charges (p-doped) in monomer units of PEDT chain, which are delocalized. The S 2p emission with higher BE near 168 eV is assigned to sulfur atoms in PSS, which according to the analysis by Greczynski[20] is a combinational contribution from PSSH and PSS$^-$Na$^+$ species in PSS chains. For the samples with further doping, the line shape of S 2p remains similar to that for the as-prepared layer. However, the intensity of PEDT component relative to that of PSS is reduced, which can be attributed to the injection of tosylate anions from the electrolyte into the near-surface region. Moreover, the S 2p peak at 168 eV becomes more well-resolved and shifts slightly toward higher BE. This is attributed
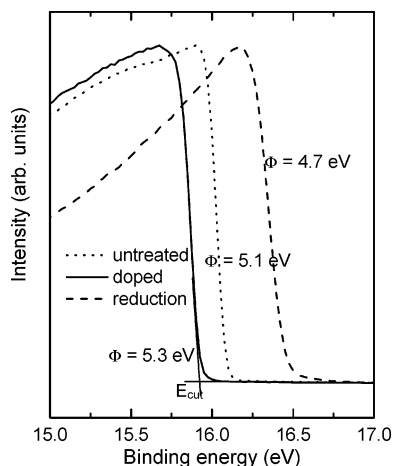

Figure 4. S 2p and O 1s core-level spectra of PEDT:PSS from as-prepared and after electrochemical doping at 0.77 V.

17304 *J. Phys. Chem. B, Vol. 108, No. 45, 2004*

Zhang et al.

Figure 5. Inelastic secondary electron cutoff's (shown as E_{cut}) in UPS spectra of PEDT:PSS from as-prepared as well as those after electrochemical doping (at the potential of 0.77 V, E_{eq} of 0.59V) and dedoping (at 0 V in a glovebox, E_{eq} of 0.05V).

to the removal of sodium, by which PSS^-Na^+ is converted into the sulfonic acid form (PSSH) so that most of the PSS component arises from PSSH species. On the other hand, the relative intensity of the PEDT component changes only slightly after the reduction process (not shown), indicating that no expulsion of PSS^- anions into the electrolyte takes place during the process.

The variation of O 1s spectra (left part in Figure 4) after electrochemical treatment is consistent with that of the S 2p emission. By spectra deconvolution, the oxygen component (at 532.8 eV), assigned to the oxygen atom in PEDT, is found to decrease relative to the PSS component at lower BE (531.7 eV) after the doping, which originates from the penetration of Tos^- anions. Meanwhile the lower BE component shifts toward higher binding energy. This is correlated with the conversion of PSS^-Na^+ into PSSH in the polymer.

From the XPS observations and the other results shown above, some comments will be given on the microscopic process involved in the electrochemical modification of PEDT:PSS films. Upon doping, Tos^- anions penetrate into polymer layer to compensate the enhanced positive charge on the PEDT chains. On the other hand, the cathodic current during the dedoping should originate from the injection of H^+ ions from the electrolyte rather than the diffusion of PSS^- chains out of the layer on account of its large size. This is verified by the modification of PEDT:PSS using $N(B_u)_4PF_6$ as supporting electrolyte. During the doping, the value of the anodic current is nearly the same as that in toluenesulfonic acid solution at a given potential. However, the cathodic current is reduced by a factor of 2 during the dedoping, because $N(B_u)_4^+$ is a less mobile ion in this case. Its diffusion is more difficult than that of H^+ ions due to its relatively large size as well as the close-packed PEDT:PSS structure.

In the UPS spectra of the layers before and after electrochemical treatment, a finite density of states at the Fermi edge is detected, which is a direct confirmation of the metallic nature of PEDT:PSS. The work function ϕ of the sample can be obtained by[22-23]

$$\phi = h\nu - \Delta E \tag{2}$$

$h\nu$ is the photon energy and the spectrum width ΔE is determined from the distance between the inelastic secondary-electron emission cutoff (E_{cut}) and Fermi edge. Figure 5 shows the emission cutoffs for as-prepared sample as well as oxida-
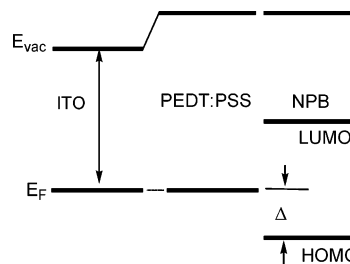

Figure 6. Schematic energy level diagram for a ITO/PEDT:PSS/NPB system. The barrier for hole injection is denoted by $\triangle$.

tively and reductively treated films, respectively. The different cutoff energies indicate the variation of the work function upon the adjustment. The work function of the as-prepared layer is 5.1 eV, in good agreement with the value given in the literature.[24,25] The work function ϕ for the oxidized sample (E_{eq} of 0.59 V) is enhanced by 0.2 eV while the ϕ decreases by 0.4 eV for the reduced layer (E_{eq} of 0.05 V), which is in good agreement with the change of E_{eq} values. This unambiguously demonstrated that the work function can be tuned by an electrochemical adjustment of the oxidation level in the PEDT: PSS layer.

3.4. Energy Level Alignment. The work function of PEDT: PSS is independent of that of the underlying ITO substrate upon comparing our UPS result with those in the literature.[24-25] This is because the density of charge carriers in highly doped PEDT: PSS (conductivity of ca. 10^{-1} S·cm^{-1}) is high enough to allow the equilibration of the Fermi level (E_F) between the polymer and ITO substrate by means of interfacial charge transfer. Thus, PEDT:PSS always aligns to E_F of ITO with a potential drop at the interface, which equals to the work function difference as illustrated in Figure 6. The change of work function by the modification of the doping level in the polymer does not influence the alignment of the Fermi level but only the interfacial potential drop. Figure 6 shows the energy level diagram at the interface between PEDT:PSS and a hole transport layer NPB. The separation between the E_F in the polymer and the HOMO level of NPB is the energy barrier for hole-injection. As verified by Mäkinen et al. from UPS measurements,[24] the interfacial dipole effect may be negligible at the PEDT:PSS/NPB interface, and thus the vacuum level of PEDT:PSS aligns with that of NPB; i.e., the hole-injection barrier is simply equal to the difference between the HOMO level of NPB and work function of the polymer. Since work function is enhanced by electrochemical doping, the hole injection barrier should be reduced with the increase of the doping level of PEDT:PSS. For the polymer with a high E_{eq} of 0.59 V, the barrier will then be very small (0.2 eV, the HOMO value of NPB is 5.5 eV) and an ohmic contact is almost achieved.

Hole-only devices were prepared to study the influence of electrochemical doping on the hole-injection. A 60 nm PEDT: PSS layer on ITO oxidized at 0.77 V (E_{eq} of 0.59 V) acts as an anode. The device structure is ITO/polymer/150 nm NPB/Ag. Figure 7 shows the current density−voltage (J−V) characteristic of such a device in a log−log plot. Power law dependence is found above the bias of 1.5 V: $J \propto V^{1.93}$, approaching the trap free space-charge-limited (TFSCL) current:[26,27] $J_{SCL} = {}^9/_8\epsilon_o\epsilon\mu V^2/d^3$ (where ϵ is the relative permittivity, and d is NPB thickness). The inset of Figure 7 gives the injection efficiency of such a device, which is defined as the ratio of the measured current and TFSCL current.[28] The mobility μ is assumed to be 4×10^{-4} cm^2/V·s for NPB.[29] The value of injection efficiency is in the range of 0.2−0.3, nearly 3 orders of magnitude larger than that for a ITO/NPB interface.[14] It indicates that the injection is
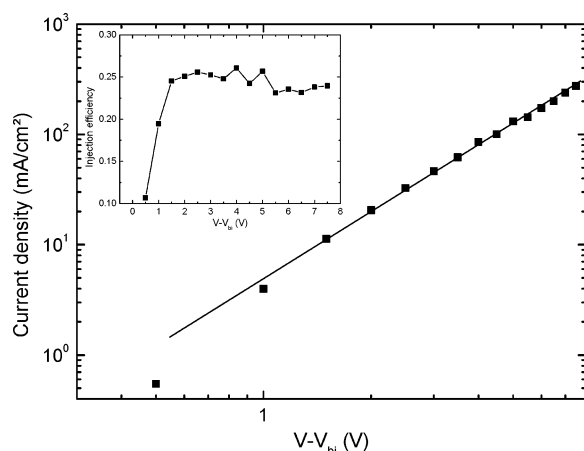
Spin-Coated PEDT:PSS

J. Phys. Chem. B, Vol. 108, No. 45, 2004 **17305**

Figure 7. $J-V$ characteristic of hole- only ITO/PEDT:PSS/NPB/Ag device in log−log plot. Polymer anode was doped further at the potential of 0.77V. The solid line shows the fitting of experimental data. Inset: injection efficiency of the device. The built-in-potential V_{bi} equals to the difference of work function between polymeric anode (5.3 eV) and Ag cathode (4.3 eV), with a value of 1.0 eV.

close to ohmic at such a polymer anode/NPB interface due to high ϕ up to 5.3 V of PEDT:PSS. The deviation from ideal TFSCL behavior may originate from insufficient purity of NPB material (unsublimed), in which the mobility will be much reduced.

As an efficient method for optimizing the properties of a conducting polymer, electrochemistry has several advantages: (1) It is a well-introduced procedure, and it is more convenient than other methods, e.g., a chemical oxidation/reduction process. (2) The doping level can be adjusted in infinitesimally small steps by simply changing the applied potential of the working electrode, and thus optimized hole injection conditions can be easily achieved. (3) Electrochemical treatment using a small counterion is valid for the compact polymer from the casting process. It does also not alter and roughen the morphology of the polymer surface, which is crucial for device fabrication. The method can be applied to other π-conjugated polymers in general, which serve as carrier injection contact in OLED devices.

4. Conclusions

We demonstrated that the doping level of compact PEDT: PSS films can be well adjusted by controlling the amount of charge injected during electrochemical doping/dedoping processes using toluenesulfonic acid. The change of the redox state leads to a variation of the work function of the layer. The increase of the oxidation level by electrochemical doping causes an enhancement of the work function of PEDT:PSS, which reduces the hole injection barrier at a polymer anode/small molecular NPB interface. $I-V$ characteristics of the hole-only device, with a PEDT:PSS anode doped at 0.77 V, have given an indirect but unambiguous evidence for the claim that without further doping the hole-injection is not so efficient from the PEDT:PSS layer to the organics and a considerably larger barrier exists, e.g., as seen by Kim et al.[10] This demonstrates that electrochemical treatment is an effective process to optimize

energy levels of a polymeric anode. In further investigation,[30] we have found that the OLEDs using electrochemically doped PEDT:PSS/ITO anodes show a significant reduction of operating voltage and improved device performance consistent with an increase of doping level of the polymer.

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