Investigating Work Function Tunable Hole-Injection/Transport Layers of Electrodeposited Polycarbazole Network Thin Films

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Received: May 12, 2004; In Final Form: August 26, 2004

Electrochemical doping properties and morphology changes of electropolymerized poly(*N*-vinylcarbazole) (PVK) thin films were investigated toward improved hole-injection/transport properties in polymer light emitting diode (PLED) devices. The conjugated network polycarbazole thin films (resulting from a poly(*N*-carbazole) (PCz) network) were prepared by electrodeposition of PVK and/or *N*-vinylcarbazole comonomer via precursor route and were investigated in situ by electrochemical-surface plasmon resonance spectroscopy (EC-SPS). Distinct doping-dedoping properties and morphology transitions were observed with different compositions of PVK and Cz. By electrochemical doping of the cross-linked conjugated polycarbazole units, the electrochemical equilibrium potential (E_{eq}), which correlates to Fermi level (E_f) or the work function (ϕ_w) of the film, was adjusted in the vicinity of the anode electrode. The conjugated network PCz films were then used as a hole-injection/transport layer in a two layer device. Remarkable enhancement of PLED properties was observed when optimal electrochemical doping was done with the films. Important insight was gained on charge transport phenomena between polymer materials and conducting oxide substrates.

Introduction

Controlling and achieving balanced charge injection and transport at the electrode/organic interface is one of most important factors for improved organic light emitting diode (OLED) device performance. This is usually achieved by fabricating an additional hole-injection layer and hole-transport layer between the anode and the electroluminescent (EL) active layer in a multilayer OLED device. This extra hole-injection layer lowers the hole-injection barrier, $\varphi_{\rm h}$, between the indium tin oxide (ITO) anode and the hole-transport layer, and the holetransport layer transports the holes effectively while it blocks the electron transport from the light emitting layer. A number of approaches using π -conjugated polymers as the hole-injection layer have been reported.^{1–7} For processing these hole-injection and hole-transport layers, many deposition techniques have been employed, e.g., spin coating, electropolymerization,^{6,8,9} layerby-layer techniques,^{4,5} and so forth. In these materials, smoothness, homogeneity, and charge mobility are very important. This is especially the case where a combination of film deposition techniques is used and where multilayer integrity is important for these "sandwich devices". Although electropolymerization is a very simple and convenient technique to deposit π -conjugated polymers, previous studies involving direct electropolymerization of monomers on a conducting substrate have shown relatively rough morphologies and poor electroactivity. They are due to a variety of factors, including changes in solubility between monomer and polymer, a rapid propagation process, and changes in the ion transport properties of the electrodeposited film. Thus, though a number of investigations have focused on the electrical and charge transport properties of these electrodeposited materials, very little focus has been

given on their optimized morphology and optical properties as ultrathin films for OLED devices.

In a recent work by Dunsch and co-workers, they reported that the work function of a π -conjugated polymer hole-injection layer could be tuned by electrochemical-doping after film deposition.^{6,7} They demonstrated that the electrochemical equilibrium potential can be controlled, i.e., electrochemical doping level directly corresponds to the work function of the electroactive conjugated polymer thin films. Meerholz and co-workers reported that the work function of the electropolymerized PEDOT thin films can be controllably adjusted within a fairly large energy window of more than 1 eV by electrochemical doping¹⁰ whereas the work function of the spin coated PEDOT: PSS films can be varied by about 0.6 eV.¹¹ In principle, by employing an electrochemically active smooth polymer film as a hole injection layer, the work function tuning methods can be employed to match a wide range of EL materials and the common ITO anode.

Recently, we have reported a novel method of depositing high optical quality ultrathin films of conjugated polymers on a flat conducting substrate.¹² We have investigated this "precursor polymer" route by depositing and patterning films using electrochemical methods. A polymer precursor is first synthesized chemically and by design contains pendant electroactive monomer units. The precursor is then electropolymerized on the conducting substrate to form an insoluble cross-linked network of conjugated polymers (oligomers). The network structure is a consequence of both inter- and intramolecular polymerization reaction resulting in a cross-linked insoluble film.

In this work, we investigated the properties of poly(*N*-vinylcarbazole) (PVK), which can be applied as a hole-transport layer, ¹³ as well as a precursor polymer. Figure 1 shows our strategy to use the precursor PVK route as both a hole-injection layer and hole-transport layer. First, PVK thin films were electrodeposited onto the ITO surface. This precursor route

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Figure 1. Strategy to use the precursor PVK route as both the hole-injection layer and hole-transport layer.

allows the PVK thin films to form conjugated network films with polycarbazole (PCz) units. By utilizing an electrochemically active π -conjugated network film, we can control the work function of the PCz thin film adjacent to the electrode, through electrochemical doping. Therefore, these films can be used as both a hole-injection layer and hole-transport layer through optimal electrochemical doping.

To understand the correlation and control of electrochemical and optical properties of conjugated network PCz thin films, in situ electrochemical-surface plasmon spectroscopy (EC-SPS)¹⁴ was used. By simultaneous electrochemical investigations with EC-SPS and the electrochemical quartz crystal microbalance (EC-QCM) method, the dielectric constant and/or film thickness changes during electrodeposition were also monitored in situ. The results showed that electrochemical behavior, i.e., redox properties, can be directly correlated with the changes in the optical parameters and morphology transitions. Atomic force microscopy (AFM) was used to investigate the surface roughness and morphology correlated with the EC-SPS. Finally, the polymer light-emitting diode (PLED) properties using conjugated network PCz thin films as the hole-injection/transport layer was investigated and optimized.

Experimental Section

Materials. Poly(*N*-vinylcarbazole) (PVK) (M_w 69 000) and *N*-vinylcarbazole monomer were purchased and used as received from Aldrich. NMR was used to confirm purity. The synthesis procedure for the polyfluorene was done according to a previous publication and the purity was verified by NMR and elemental analysis.¹⁵

Electrochemistry. All potentiostatic and cyclic voltammetry measurements were carried out using a one-compartment, threeelectrode cell driven by an EG&G PAR Potentiostat (Model 263A) or an AMEL INSTRUMENTS general purpose Potentiostat (Model 2049). In all the measurements, the working electrodes consisted of Au films (thickness \sim 50 nm) vacuum evaporated onto a LaSFN9 glass substrate. The counter electrode was a platinum wire and the reference an Ag/Ag⁺ electrode.

The PVK was electrodeposited on a conducting substrate under cyclic voltammetry (CV) conditions. This was done by preparing solutions of the PVK polymer where the polymer deposits at the electrode surface during the electropolymerization/cross-linking process forming a film.¹³ Note that the term electropolymerization and cross-linking (even electro-crosslinking) can be interchangeably used because the pendant electroactive monomer can react both *intermolecularly* and *intramolecularly* forming conjugated PCz species of various chain lengths and network.^{12,13} Vinylcarbazole monomer units were also mixed with the PVK solution at different molar composition ratios. Electrodeposition in a three-electrode cell was carried out in a THF solution containing the PVK and Cz comonomer, 0.1 lithium perchloride (LiClO₄). This was performed by sweeping the potential from -0.2 to +1.1 V vs Ag/Ag⁺ (0.01 M in acetonitrile) reference electrode at rates of 20 mV/s.

Atomic Force Microscopy (AFM). Atomic force microscopic (AFM) images were taken in air and ambient conditions by tapping mode using a Nanoscope II, Digital Instrument system equipped with a $10 \times 10 \,\mu$ m scanner and a silicon nitride tip.

Electrochemical-Surface Plasmon Resonance Spectroscopy (EC-SPS) Measurement. The surface plasmon resonance (SPR) setup is combined with a three-electrode electrochemical cell in a Kretschmann configuration for the excitation of surface plasmons. Details of this setup can be found elsewhere.¹⁶ Surface plasmons are excited by reflecting p-polarized laser light off the Au-coated base of the prism. The excitation source employed was He–Ne laser: $\lambda = 632.8$ nm. Kinetic measurements were performed to monitor the formation of the film and the oxidation/reduction and doping/de-doping properties of deposited polycarbazole thin film via reflectivity changes as a function of time. Angular measurements were also performed by scanning an incident angle range while the potential was held constant. For these experiments, the gold film thickness (\sim 47 nm) was chosen for optimum excitation of the surface plasmons. The electrode surface area was 0.785 cm².

Polymer Light Emitting Diode Measurements. The demonstrated PLED device was composed of an ITO anode, the electrodeposited conjugated PCz network thin film (ca. 50 nm), a light emitting layer of the polyfluorene derivative (ca. 50 nm in thickness) spin cast from a solution of toluene; and finally aluminum (ca. 25 nm) was evaporated on the top as a cathode. The base pressure in the evaporation chamber was lower than 1.0×10^{-6} Torr. Current–voltage (*I*–*V*) curves were measured with a Keithley 236 programmable source meter. Luminancevoltage (*L*–*V*) properties were measured with an Ocean Optics S-2000 spectrometer combined with the source meter.

Results and Discussion

Electropolymerization and In-Situ EC-SPS Experiment. The conjugated polymer network film was electrodeposited on a flat gold electrode substrate using CV conditions. The electrodeposition was done with a scan rate of 20 mV/s from -0.2 to +1.1 V. The CVs obtained from different concentrations of the polymer are shown in Figure 2. For all the CV traces, the current starts increasing at around 0.7 V on the first anodic



Figure 2. Cyclic voltammograms from -0.2 V to $_+1.1$ V up to 6 cycles during electrodeposition of different ratios of monomers and precursor polymers in the THF containing 0.1 M LiClO₄.

scan. In the first cathodic scan, a reduction peak, corresponding to the de-doping from the deposited film, was clearly seen for the pure PVK. On the other hand, the de-doping peak was not clearly observed in the case of electropolymerization of vinyl Cz monomer. This indicates that the electroactive monomer unit was oxidized in all cases, but the film was efficiently deposited only when the precursor PVK was present. These trends were observed with subsequent cycles too. As the cycling number increased, the doping—dedoping current increased clearly when the PVK precursor was present, whereas no obvious doping dedoping peak was seen in the case of vinyl Cz monomer electropolymerizations. It is reasonable that the PVK precursor polymer is more electrochemically active when depositing it on the electrode surface compared to the vinyl Cz monomer. This is because, for a highly conjugated polycarbazole polymer



Figure 3. Potential ramp and SPR kinetic curve during electrodeposition of different ratios of monomers and precursor polymers in the THF containing 0.1 M LiClO₄.

to form, a reasonable amount of carbazole oxidative monomer species (radical cations) has to form simultaneously. Likewise, Cz electropolymerization can be complicated because it is difficult to control the polymer microstructure due to the possibility of polymerization of vinyl groups in the monomer.¹⁷ Also, solubility is a problem with a growing polycarbazole linear chain. In the case of the PVK, the polymer backbone helps the electrodeposition due to the improved adhesion strength onto the surface.¹⁰ Also the carbazole monomer tethered to the polymer backbone lowers the activation energy of cross-linking of the electroactive unit. The polymer backbones serve to improve monomer availability (not dependent on monomer diffusion or transport) and interfacial transition from precursor to cross-linked films. Again, it is noted that intermolecular and intramolecular cross-linking results in an insoluble and highly stable conjugated PCz network film. This stability is further confirmed by the reversibility in the CV experiments with the monomer/PVK precursor free solution.

To confirm the effective deposition of PVK precursor polymer (growth kinetics of the network film), we measured the electrochemical/optical properties by simultaneous EC-SPS.¹² Figure 3 shows SPS electrodeposition kinetic curves for different ratios of Cz monomer and PVK polymer in THF containing 0.1 M LiClO₄, e.g., 0:100, 20:80, 40:60, 60:40, 100:0, Cz monomer: PVK polymer percentage ratio, respectively. The data were recorded as a function of time (up to 2 cycles). As shown in this figure, the increase of the reflectivity was observed in all the ratios. This indicates that thin films were deposited onto the Au substrates by potential cycling. As expected in the CV experiments, the SPR curves show that the film thickness increases with increasing ratio of PVK, indicating the influence of the PVK precursor toward thicker films. The current efficiency during the electrodeposition (Table 1) shows that the PVK precursor can be effectively deposited linearly onto the

TABLE 1: Reflectivity (R) and Amount of Charge (Q) during Electrodeposition, and Current Efficiency (dR/dQ) after 2 Potential Cycles

	0	20	40	60	80	100
reflectivity	0.34	0.455	0.633	0.681	0.728	0.879
$Q (\text{mC/cm}^2)$	1.23	1.59	1.36	1.64	1.72	1.00
efficiency (dR/dQ)	2.76	2.86	4.65	4.15	4.23	8.79

electrode surface. These experiments indicate that the amount of oxidation of electroactive units is similar in extent for all the ratios but can only be easily deposited onto the electrode surface if the PVK precursor is present. Besides the increase of the reflectivity at oxidation potential above 0.7 V, the increase of the reflectivity was also observed at lower potential (< 0.4 V) corresponding to the de-doping potential. The increase of the reflectivity at lower potential was also seen with all the ratios of the PVK precursor. This indicates that the dielectric constant or thickness change was amplified by doping/de-doping in these films.^{12a} This is very important especially for the adjustment of the work function of the conjugated PCz film for the holeinjection/transport layers.

Morphology Studies by AFM. The morphologies of the deposited film after electropolymerization were studied by AFM. Figure 4 shows AFM images of four different ratios of Cz monomer and PVK polymer. These films were deposited up to 6 potential cycles from -0.2 to +1.1 V. RMS values were summarized in Table 2. These RMS values show that the deposited films have relatively smooth microscopic surfaces in

TABLE 2: RMS Values Obtained from AFM Images

	(a) 0% PVK	(b) 40%	(c) 60%	(d) 100% PVK
RMS	3.0 nm	7.8 nm	11.5 nm	5.7 nm

each deposition ratio. By comparison of AFM images, smaller spots were observed in the Cz film deposition, showing mostly the ITO substrate (striated patterns). This trend was observed consistently by AFM imaging on several spots of the electrode. As has been investigated in EC-SPS measurements, because Cz monomer was not efficiently deposited due to poor solubility or adhesion strength, only some aggregated oligomers or poorly cross-linked polycarbazole precipitates are expected to adhere onto the surface. This was observed even when a higher oxidation potential (1.3 V) was applied for the electropolymerization process. When the PVK was present for co-electrodeposition with the carbazole (beginning at 40%), a more globular morphological feature and larger domains was observed on the film. This also corresponded to an increase of the film roughness, as evidenced in the 60% composition, but a smoother film was achieved with 100% PVK. These trends were also observed when the applied potential range for the CV was higher (-0.2 to +1.3 V).

Doping-Dedoping Property. As mentioned above, the electrochemical equilibrium doping level directly corresponds to the work function of the conjugated film. To investigate the electrochemical tunability of the work function of the electropolymerized PCz films, we measured the doping-dedoping



Figure 4. AFM images of the film deposited onto ITO glass substrates from a solution of several different ratios of monomers and precursor polymers (after 6 potential cycles from -0.2 to +1.1 V): (a) 100% Cz monomer; (b) 40% PVK precursor:60% Cz monomer; (c) 60% PVK precursor:40% Cz monomer; (d) 100% PVK precursor.



Figure 5. (a) Reflectivity transitions of film switched sequentially between the doped state and de-doped state in monomer free acetonitrile solution containing 0.1 M LiClO₄ ((i) 100% PVK, (ii) 60% PVK:40% Cz, (iii) 100% Cz). (b) Frequency transitions of film switched sequentially between the doped state and de-doped state in monomer free acetonitrile solution containing 0.1 M LiClO₄. (c) Determined real part, ϵ' , and imaginary part, ϵ'' , of dielectric constants as a function of potential at 632.8 nm.

properties of electrodeposited film in monomer free solvent. After the electropolymerization, the films were rinsed with THF, and then they were measured in monomer free acetonitrile solution containing 0.1 M LiClO₄. Figure 5a shows the EC-SPS doping-dedoping properties of deposited thin films from PVK (i), PVK:Cz = 60:40 (ii), and Cz (iii), and Figure 5b shows EC-QCM doping-dedoping properties. These films were deposited to have almost the same thickness (\sim 80 nm) by monitoring the SPR kinetic curves and QCM. This figure clearly shows that the optical and acoustic response of the polymerized thin films due to electrochemical doping depends on the ratio of the PVK and Cz. Both reflectivity and mass of PVK quickly changed when the potential was switched to both negative and positive potentials, and they were stable both in EC-SPS and EC-QCM experiments at constant potentials whereas Cz shows instability in EC-QCM measurements. This indicates that the work function of PVK can be tuned stably in this potential window. In the EQCM measurement, Sauerbrey equation was used to estimate the thickness change of the film on the

assumption of a mass density of 1.3 g/cm³.^{18,19} By using the thickness values obtained from EQCM measurements, we estimated the change of dielectric constants from the Fresnel calculation with angular measurements (Supporting Information). As can be seen in Figure 5c, the larger change in the real part of the dielectric constants were obtained if the PVK precursor is present in the film electrodeposition. As shown in the AFM experiments, the electrodeposition of 100% PVK precursor showed a smoother surface than co-electrodeposion of PVK and Cz; hence we believe that this larger optical change with doping/de-doping is not due to a porous structure but is primarily due to the formation of a cross-linked PCz network system and its effect on the dielectric constant. Furthermore, the large imaginary part, ϵ'' , of the dielectric constant, which can interrupt the light emission from the EL layer, was not observed unlike some electrochromic conjugated polymers show large color change after the electrochemical doping.

PLED Properties. Because the cross-linked conjugated PCz can be effectively deposited with high optical quality and high



Figure 6. Current–voltage and luminance–voltage properties of the ITO/PVK/polyfluorene/Al hole-only PLED device at several different doping levels of the conjugated PVK layer. PVK films were doped or dedoped in monomer free THF solution containing 0.1 M LiClO₄ at -0.5, -0.2, +0.3, and +0.7 V (vs Ag/AgCl) for 5 min, respectively.

electrochemical tunability (compared to the polycarbazole film electropolymerized directly from Cz monomer), we tried to use the cross-linked conjugated PCz thin film as a hole-injection/ transport layer. The cross-linked conjugated PCz thin film was electrodeposited onto the ITO surface, and then the work function was tuned between -4.0 and -5.0 eV by the electrochemical doping in monomer free solution with LiClO₄ as supporting salt. The equilibrium open circuit potentials after each doping for 5 min was read from the potentiostat, and the equilibrium potential 0 V (vs Ag/AgCl) can be assumed to have the work function of 4.5 eV.6 Polyfluorene was spin-coated onto conjugated PCz film as the electroluminescent active layer. Then the PLED device was completed by evaporation of the aluminum (~25 nm) as an upper cathode electrode. Note that in most PLED device fabrication procedures, preventing dissolution of the polymer hole injecting layer during spin-coating of the electroluminescent layer is a problem, especially if their solubilities are similar. Figure 6a,b shows the current-voltage and luminance-voltage properties, respectively, with the doping levels of cross-linked conjugated PCz thin films. As shown in these figures, we found that the PLED property shows a big difference with electrochemical doping of the cross-linked conjugated PCz thin films. In the voltage-current properties, it is clearly seen that the current is higher with the doping level. On the other hand, in the voltage-luminance properties, electrochemical doping at +0.3 V showed the highest luminance. This luminance was comparable to the PEDOT:PSS holeinjection layer when we used spin coated PEDOT:PSS as holeinjection layer.²⁰ A proposed mechanism is drawn in Figure 7. In the case of dedoped state of PCz films (dedoped at -0.5



Figure 7. Schematic drawing of the proposed mechanism of the holeinjection/transport.

and -0.2 V), the work function was tuned to about 4.0-4.2eV, which was estimated by the equilibrium electrochemical potential. In this case, holes are hardly injected into PCz films due to the large difference between the two work functions of ITO and PCz, i.e., built-in potential, eV_{bi} , and they are also hardly transported into polyfluorene films due to the neutral state (insulating state) of conjugated network PCz film.⁷ Hence, both current and luminance values are lower than the doped state. In the case of the doping at +0.7 V, the work function was adjusted around 5.0 eV, and the holes are easily injected into network PCz films due to a lowered built-in potential, $eV_{\rm bi}$.²¹ They are also easily transported into the polyfluorene layer due to the higher conductivity (semiconducting state). Therefore, the current at 0.7 V was highest in the tested system. This corresponds to a reported theoretical study, i.e., ohmic contact can be obtained when the built-in potential $eV_{\rm b}$ is smaller than 0.3 eV.²² However, due to the high doping level, many electrons are injected from the polyfluorene layer into the cross-linked network PCz films (i.e., electrons cannot be confined in the emitting layer). Hence the luminance was less than the doping level at +0.3 V. In the case of the doping level at +0.3 V, the electron can be blocked more than at +0.7 V, whereas holes are still effectively injected and transported. Therefore, even though the current was less than that at 0.7 V, the luminance was actually the highest in this system.

Conclusion

In this investigation, we have gained unique insight in the work-function tuning and charge carrier transport properties of a cross-linked electropolymerized hole-injecting/transport layer. The electrodeposition properties of poly(N-vinylcarbazole) (PVK) were investigated in situ by cyclic voltammetry and surface plasmon resonance spectroscopy. The PVK was efficiently electrodeposited as a "precursor route" to form a conjugated PCz polymer network which can be doped or dedoped. It was found that the conjugated network PCz thin film is more stable and has tunability of the work function via electrochemical methods. Using EC-SPS, EC-QCM, and AFM techniques, the influence of carbazole and PVK composition in the electrochemical, optical and morphological properties of the film was determined. The performance of the PLED device was remarkably enhanced by controlling the doping level of conjugated PCz thin films which functions as a hole-injection/ transport layer.

Acknowledgment. We acknowledge support from various funding agencies that made this work possible: NSF-DMR-99-082010, NSF INT-99-80398, Robert A. Welch Foundation (E-1551), NSF-CTS (0330127), and NSF-CHE-0304807. We are grateful to Dr. J. Lübben for helpful discussions in EQCM

experiments. A.B. acknowledges the Max-Planck Society and the Alexander von Humboldt Foundation for a postdoctoral fellowship.

Supporting Information Available: Figures of L-V properties of ITO/PEDOT:PSS/PFO/AC structure and comparison of luminance at 9 V. This material is available free of charge via the Internet at http://pubs.acs.org.

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