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A facile synthesis of sulfonated poly(diphenylamine) and the application as a novel hole injection layer in polymer light emitting diodes

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Abstract

Water-soluble sulfonated poly(diphenylamine) (SPDPA) was synthesized and applied as a hole injection layer (HIL). It was characterized in terms of ^{1}H NMR, ^{13}C NMR, elemental analysis (EA), UV−vis, Raman, ultraviolet photoelectron spectroscopies (UPS) and TGA thermal stability measurement. The high transparency in visible region and acceptable conductivity were beneficial as HIL material. The topographic image obtained from Atomic Force Microscope shows that the surface of SPDPA-coated indium tin oxide (ITO) is smoother than that of bare ITO. Raman spectra indicate that SPDPA possesses the higher oxidation and doping level due to SO_3H group on the phenyl ring, rendering SPDPA the higher work function with 0.35 eV than PDPA from UPS spectra. The electroluminescence efficiency of polymer light emitting diode using poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene) (MEH−PPV) as an active layer and SPDPA as HIL can be reached 2.0 cd/A, showing the slightly better performance than that using PEDOT:PSS as HIL.

Keywords: Sulfonated poly(diphenylamine); Hole injection layer; Polymer light emitting diode

1. Introduction

Polymer light emitting diodes (PLEDs) were attracting great attention as a potential flat panel display due to outstanding advantages, such as easily fabricating and processing flexible display. However, PLEDs possess inherently adverse properties, for instance, mismatch of energy level between conventional electrode and emissive layer. Therefore, many researchers have reported utilizing hole injection layer (HIL) or hole transporting layer (HTL) to achieve efficient charge injection and improve the quantum efficiency [1−5]. Yang and Heeger [1] utilized metallic salt form of polyaniline (PANI) doped with camphor sulfonic acid (CSA) as HIL. Further reports [6,7] indicated that the work function and the conductivity of PANI could be altered by varying dopants and the doping ratio, affecting the device performance. In fact, polyethylene dioxythiophene−polystyrene sulphonate (PEDOT:PSS) was commonly used as HIL, due to its superior properties, such as water soluble, environmentally stable, high transparency and great hole-injecting ability [8]. Nevertheless, phase segregation has been a problem in this system [9]. So far, PANI has been rarely employed as HIL because it had the problem of solubility and processability. Besides, the derivative, sulfonated PANI, is also not a proper candidate for HIL because the strong visible light region absorption causes EL spectrum of emissive layer inevitably shifts [10]; and high conductivity (10^{-1}−10^{-2} S/cm) causes crosstalk in the passive matrix display device.

Recently, our group reported that diphenylamine (DPA) was polymerized into PDPA through oxidative coupling method in a 3 N methanesulfonic acid solution [11]. To be mentioned, the mechanism of PDPA polymerization is different from that of other aniline derivatives, which occurs

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through a 4–4′ phenyl–phenyl coupling instead of N–C coupling in other substituted anilines. As a consequence, PDPA combines the chemical structure of PANI and poly (*p*-phenylene), which can improve solubility and processability. Besides, PDPA can enhance hole drift mobility due to bearing arylamine moieties. In this work, we synthesized SPDPA by employing a facile process for sulfonation of PDPA. The properties of SPDPA are wide divergent with those of PDPA, such as outstanding water solubility, moderate conductivity, thermal stability and optical behavior. SPDPA was then successfully used as HIL in PLEDs for the improvement of EL efficiency.

2. Experimental section

2.1. Materials

Reagent grade diphenylamine (DPA; Riedel-deHaën), ammonium peroxydisulfate (APS; J.T. Baker), sodium hydroxide pellets (Riedel-deHaën) were used without any further treatment. Sulfuric acid (Riedel-deHaën), acetone (Riedel-deHaën), ammonia (Fluka) and *N*,*N*′-dimethylformamide (DMF; Fluka) were used as-received.

2.2. Synthesis

2.2.1. Polymerization of diphenylamine

Poly(diphenylamine) (PDPA) was prepared by the chemical oxidation method. Diphenylamine (3.4 g, 0.04 mol), 2 M H_2SO_4 solution (300 mL) and acetone (200 mL) were placed into a 1 L round-bottom reactor. The system was subjected to intensive magnetic stirring, cooled to 5 °C, and then APS (4.5 g, 0.04 mol) solution in 30 mL of 2 M H_2SO_4 was dropwise added into the reactor. The solution color changed from colorless to green, indicating polymerization of DPA. The reaction mixture was stirred continuingly for at least 16 h and then green precipitate was obtained. The crude product was filtered and washed with a large amount of deionized water until the filtrate was colorless. Then, the H_2SO_4-doped PDPA was dedoped with 1 N ammonia aqueous solution for 24 h. PDPA was filtered and washed until no colored supernatant was observed. Furthermore, PDPA was dispersed in acetone and was centrifuged at 5000 rpm for 15 min. The precipitate was washed with acetone several times to remove the unreacted monomer and oligomer. The gray neutralized PDPA powder was dried under vacuum at room temperature for at least 24 h. ^{1}H NMR (DMSO-d_6, 500 MHz; ppm): δ 6.81 (t, 2H, $J = 7.8$ Hz), 7.10 (m, 8H), 7.23 (t, 4H, $J = 7.8$ Hz), 7.48 (d, 4H, $J = 7.8$ Hz), 8.20 (s, 2H). ^{13}C NMR (DMSO-d_6, 125 Hz; ppm): δ 117.29, 118.12, 126.69, 129.35, 131.69, 131.89, 142.17, 143.56. FT-IR (film, cm^{-1}): 3388, 1595, 1504, 1319, 825, 748. Elemental analysis, found: C, 83.64; H, 5.65; N, 8.42.

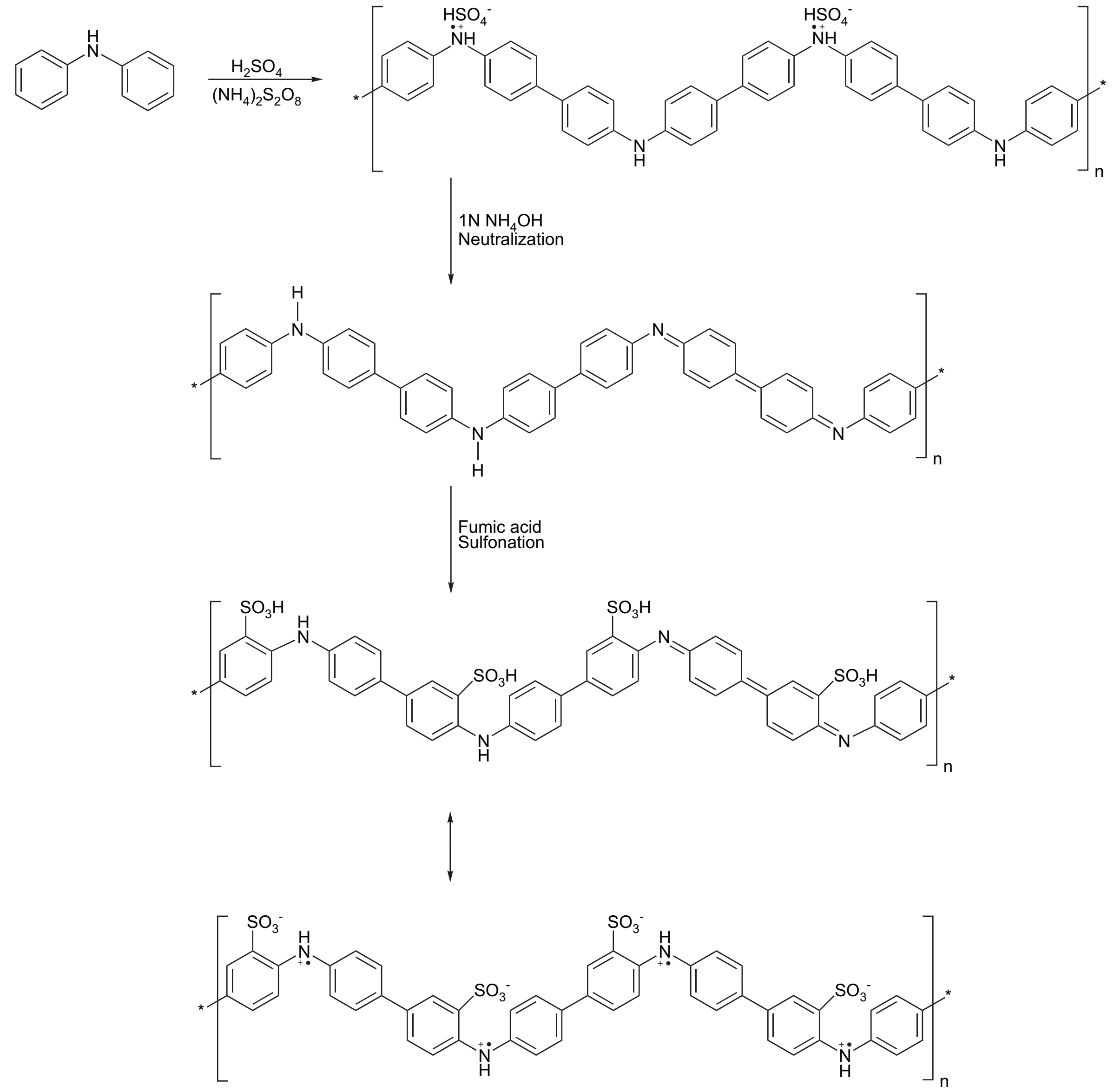
2.2.2. Preparation of sulfonated poly(diphenylamine)

According to the report about sulfonation of PANI described by Yue et al. [12], neutralized PDPA (0.5 g) was sulfonated by dissolving in 40 mL of fuming sulfonic acid with constant stirring at 5 °C for 1 h. The solution was added to 500 mL of acetone and then green product precipitated, the temperature being held at 10 °C. The green powder was washed sufficiently with acetone, collected by centrifugation and then dried under vacuum. Afterward, the SPDPA aqueous solution was purified to remove excess acid by dialysis with semipermeable membrane (Spectra/Por Membrane, MWCO:3500) in deionized water. Finally, the resultant product was dried under vacuum and the water-soluble product SPDPA was obtained. FT-IR (film, cm^{-1}): 3360, 1595, 1497, 1319, 1163, 1032 (S=O), 821, 690 (C–S). Elemental analysis, found: C, 44.74; H, 5.11; N, 4.51; S, 10.47.

2.2.3. Chemical characterization of neutralized PDPA and SPDPA

NMR experiments were performed on the Bruker AMX-400 spectrometer with ^{1}H resonance frequencies at 400.0 MHz. The neutralized PDPA sample was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6). ^{13}C NMR spectra of neutralized PDPA and SPDPA were obtained on the Bruker AMX-500 spectrometer with resonance frequencies at 125.0 MHz. The neutralized PDPA and SPDPA samples were dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) and deuterium oxide (D_2O), respectively. FT-IR measurements were carried out on Nicolet-550 Fourier Transfer Infrared Spectrometer, and the sample pellets were prepared by mixing powders and KBr. The elemental analysis (EA) was carried out in Heraus CHNS-Rapid elemental analyzer. The molecular weight and polydispersities of SPDPA were determined through gel permeation chromatography (GPC) at 50 °C using DMF as the eluent and polystyrene for calibration of the molecular weight. The thermogravimetric analysis (TGA) measurement was carried out on Perkin–Elmer Thermal Gravimetric Analysis-7/DX. The sample was preheated at 100 °C for 30 min to remove excess H_2O before measurement. The TGA experiment was performed under a nitrogen stream, and the temperature scan was from 40 to 800 °C with a heating rate of 10 °C/min. The pH value and UV–vis absorption were measured in HANNA instrument pH 211 Microprocessor and Shimadzu UV-2101 UV–vis spectrophotometer, respectively.

The characterization of polymer films was carried out in the following instruments. The electrical conductivities were measured by standard four-probe method. Atomic force microscopy (AFM) was performed with a NanoScope IIIa (Digital Instruments Inc.) run in the tapping mode. Raman scattering study was performed on a Jobin Yvon LabRAM HR Spectrometer using 633 nm irradiation as the photon source. The ultraviolet photoemission spectroscopy (UPS) experiments were carried out in VG CLAM4, whose illumination was non-monochromatic He(I) UV source (21.2 eV). The total energy resolution of the measurement was 0.38 eV. Overall process was performed in multi-chamber ultrahigh vacuum (UHV) system, including main UPS analysis chamber base ($P_{\text{base}} \sim 8 \times 10^{-10}$ Torr) and the preparation chamber ($P_{\text{base}} \sim 9 \times 10^{-10}$ Torr).



Scheme 1. Synthetic route to sulfonated poly(diphenyl amine).

2.2.4. Fabrication and characterization of the EL device

The purified SPDPA and neutralized PDPA were dissolved in deionized water and DMF with about 15 mg/mL concentration, respectively. The reference hole injecting material was prepared by using commercial PEDOT (Baytron-P AI 4083).

Devices fabricated on ITO glass substrates with surface sheet resistance $<15\ \Omega$ per square were supplied by RITEK Corporation. ITO glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone and isopropyl alcohol sequentially. ITO was treated in an UV/O_3 photoreactor before casting a HIL on ITO substrate. The HIL was spin-coated to modify the ITO surface and then baked at 150 °C for 30 min. Then, poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene) (MEH–PPV) was dissolved in cyclohexanol (10 mg/mL) and coated as active layer, whose thickness was measured to be about 70 nm by ellipsometry (Ulvac ESM-1) and baked at 65 °C for 30 min under an inert nitrogen atmosphere. Metal cathodes were applied by vacuum evaporation and consist of Ca and Al at a pressure of $\sim 10^{-6}$ Torr. The active pixel area of the device is $0.06\ cm^2$. The current density–brightness–voltage (*J*–*V*–*L*) characteristics of devices were measured with Keithley 2400 source measure units and Keithley 2000 digital multimeter along with a silicon photodiode calibrated by Minolta LS-100 luminous meter.

3. Results and discussion

3.1. Chemical characterization of neutralized PDPA and SPDPA

Scheme 1 outlines the synthetic route for SPDPA via oxidative coupling. Due to its diphenyl structure, the polymerization mechanism of DPA is different from other aniline derivatives, being envisaged to occur through 4–4′ phenyl–phenyl coupling [13]. This coupling mechanism will give rise to dimerization of DPA and low-molecular-weight oligomers, because stabilization of radical center upon conjugation with the polaron structure of the growing chain in the course of reaction occurs shortly after the formation of oligomers [14]. Consequently, the molecular weight is supposed to be not high. Due to the steric strain effect, 4–4′ phenyl–phenyl coupling causes adjacent phenyl rings of PDPA polymer backbone to be nonplanar, leading to diminish of the hydrogen bonding interaction of the inter-amino moieties. The results render PDPA soluble and processable easily. In order to obtain the appropriate conductivity for HIL, neutralized PDPA was converted to SPDPA by sulfonation using fumic acid.

The resonance peaks between $\delta = 6.8$ and 7.8 ppm in the ^{1}H NMR spectrum of neutralized PDPA as-synthesized (Fig. 1(a)) are assigned to double-substituted phenyl protons of the PDPA backbone [15]. The peak at 8.2 ppm is attributed to the amine group. The narrow peaks imply that PDPA as-synthesized involves the dimer, oligomer and polymer. In order to separate the polymer from the dimer and oligomer, the neutralized PDPA as-synthesized was dispersed in acetone to remove the low-molecular-weight products for the purified PDPA with high molecular weight (denoted as neutralized PDPA). After the separation, the acetone-dissoluble fraction and neutralized PDPA are characterized by ^{1}H NMR as shown in Fig. 1(b) and (c), respectively. Clearly, the acetone-dissoluble fraction should be the DPA dimer or oligomer because the ^{1}H NMR spectrum is identical to that of the DPA dimer. The resonance peaks of purified PDPA are much broader than those of the DPA dimer because the chain entanglement is greater as increasing the molecular weight, for which the correlation time of polymer in the solvent is much longer and hence the broader resonance peaks. However, neutralized PDPA turns into near insulator without measurable conductivity. The semi-conductivity characteristics are necessary for being a HIL. To tackle this problem, purified PDPA was converted into SPDPA via sulfonation. In Fig. 1(d), SPDPA spectrum shows a hump between 5 and 9 ppm and the resonance peaks for the phenyl protons are not resolved. SPDPA has one charge distributed over every two aromatic rings due to doping effect and one charge gives rise to a specific chemical shift. This charge distribution results in a large chemical shift anisotropy. It also indicates that the charges are more delocalized in the SPDPA backbone than in neutralized PDPA [16]. Therefore, SPDPA has the higher conductivity than neutralized PDPA. This has been verified by conductivity measurements. The conductivity of SPDPA film coated on a glass plate is about 10^{-4} S/cm. This moderate conductivity can prevent crosstalk for the further PLED application. The ^{13}C NMR spectrum of SPDPA (Fig. 2(b)), similar to its proton spectrum, exhibits large chemical shift anisotropy for aromatic carbons. However, three resolved broad peaks shown in the spectrum correspond to the carbons of the substituted phenyl rings. The chemical shifts of the three broader peaks are similar to the carbons of PDPA (Fig. 2(a)); however, the resolution is too low to be assigned. Besides, phenyl C-2 attached SO_3H substituent could be assigned to around 140 ppm. The results

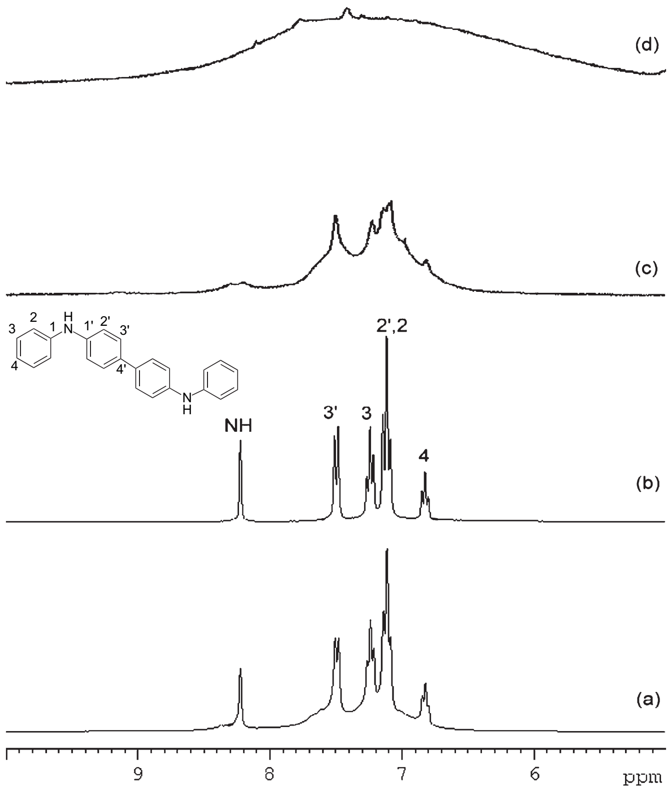


Fig. 1. ^{1}H NMR spectra of (a) neutralized PDPA as-synthesized in DMSO-d_6, (b) the acetone-dissoluble PDPA in DMSO-d_6, (c) neutralized PDPA (purified) in DMSO-d_6 and (d) SPDPA in D_2O.

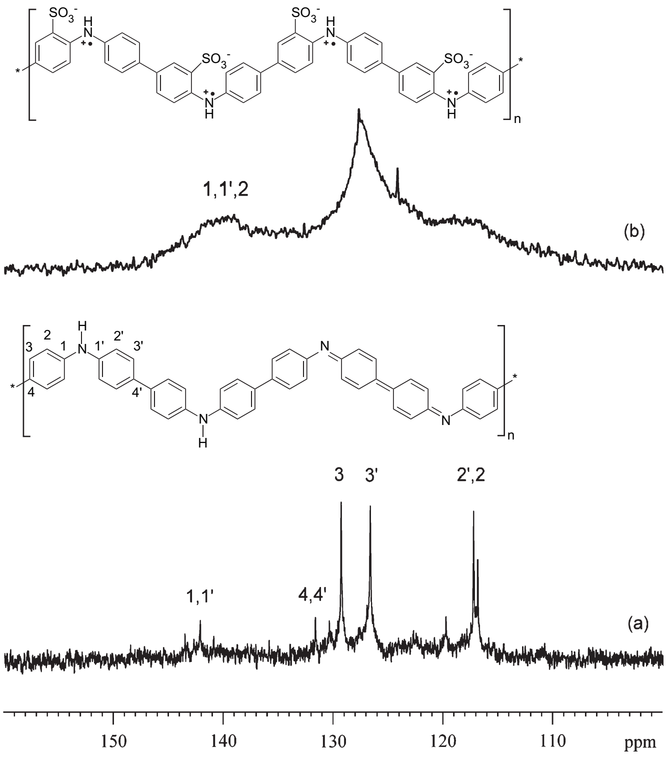


Fig. 2. ^{13}C NMR spectra of (a) neutralized PDPA (purified) in DMSO-d_6 and (b) SPDPA in D_2O.

indicate that SO_3H groups are bonded to the polymer chains with the self-doping effect. The elemental analysis reveals the S/N atomic ratio of 1.01 for SPDPA, suggesting that one SO_3H group is attached to every phenyl rings. The number-average molecular weights and polydispersity index of SPDPA were determined as 3.84×10^4 and 1.64, respectively, by GPC against polystyrene as standard.

The solubility of SPDPA in water is good because of the SO_3H group in the polymer chain. To cast a very smooth film as the hole injection layer, we dissolved SPDPA in water with [SPDPA] = 15 mg/mL, and then spin-coated it on ITO substrate. Fig. 3 shows AFM topographic images of bare ITO (a) and SPDPA coated on the ITO surface (b). The root-mean-square (RMS) roughness of bare ITO and the ITO/SPDPA film is 1.945 and 0.885 nm, respectively. The smoother surface of ITO via SPDPA modification is a good advantage for the application to HIL. On the other hand, the pH value of SPDPA in aqueous solution is ca. 2 at [SPDPA] = 15 mg/mL. The higher pH of SPDPA than PEDOT:PSS is also an advantage for HIL, circumventing ITO etched problem due to acidity.

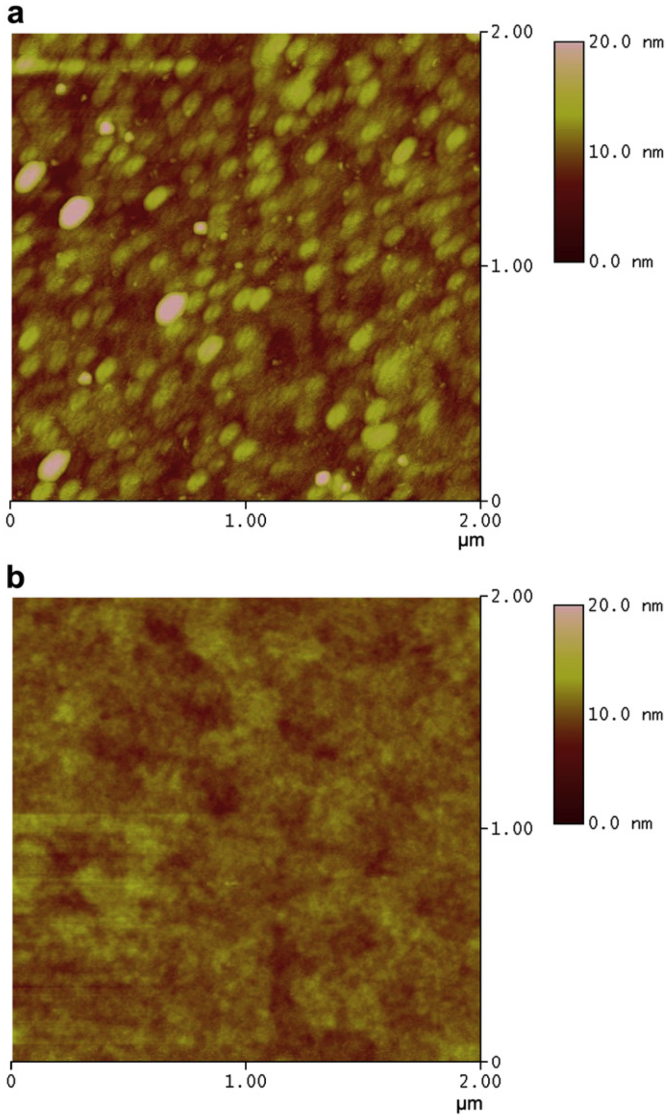


Fig. 3. AFM topographic images of (a) bare ITO and (b) SPDPA coated on ITO substrates.

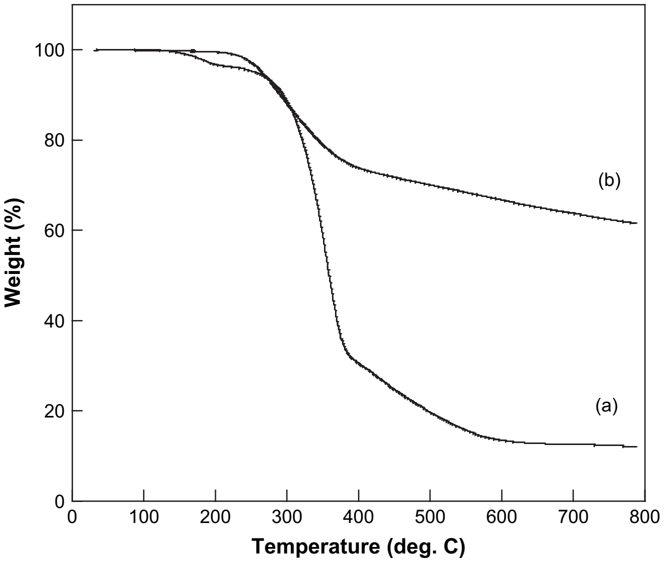


Fig. 4. Thermogravimetric analysis of (a) neutralized PDPA and (b) SPDPA.

The thermal stability should be considered because joule heat is produced upon operating PLED device. The TGA thermogram of neutralized PDPA and SPDPA is shown in Fig. 4. The neutralized PDPA showed three-stage weight changes at temperature around 130, 250 and 380 °C. These steps could be assigned for the volatilization of low-molecular-weight fragments, decomposition of main chains, and complete degradation of the polymer matrix [17]. The TGA curve of SPDPA presents different characteristic weight loss against heating. The weight loss at about 230 °C is owing to the removal of sulfonic acid groups from phenyl ring. Due to the self-doped structure, the polymer might crosslink in the heating process [18]; thus, SPDPA is much more stable than neutralized PDPA.

3.2. Optical properties

The transmittance of SPDPA coated on ITO (bare ITO is used as the standard) shown in Fig. 5(a) exhibits high transparency in the visible region. In comparison with other PANI derivatives, SPDPA reveals puny absorption in visible region, suggesting that SPDPA is a proper material for acting as a transparent HIL. Fig. 5(b) shows the normalized UV–vis spectra for neutralized PDPA, H_2SO_4–PDPA (dissolved in DMF), and SPDPA (dissolved in aqueous solution). For neutralized PDPA, strong absorption rising at 350 nm is attributed to the π–π^* transition of benzenoid rings. Another at about 620 nm is assigned to the polaron *N*,*N*-diphenylbenzidine radical cation ($DPB^{\bullet +}$). This relies on the external acid dopant which removes one electron from nitrogen of the DPA unit [22]. The spectrum of SPDPA shows two absorption bands at 330 and 640 nm, which have been assigned to the foregoing characteristic peaks. The blue shift of the π–π^* transition

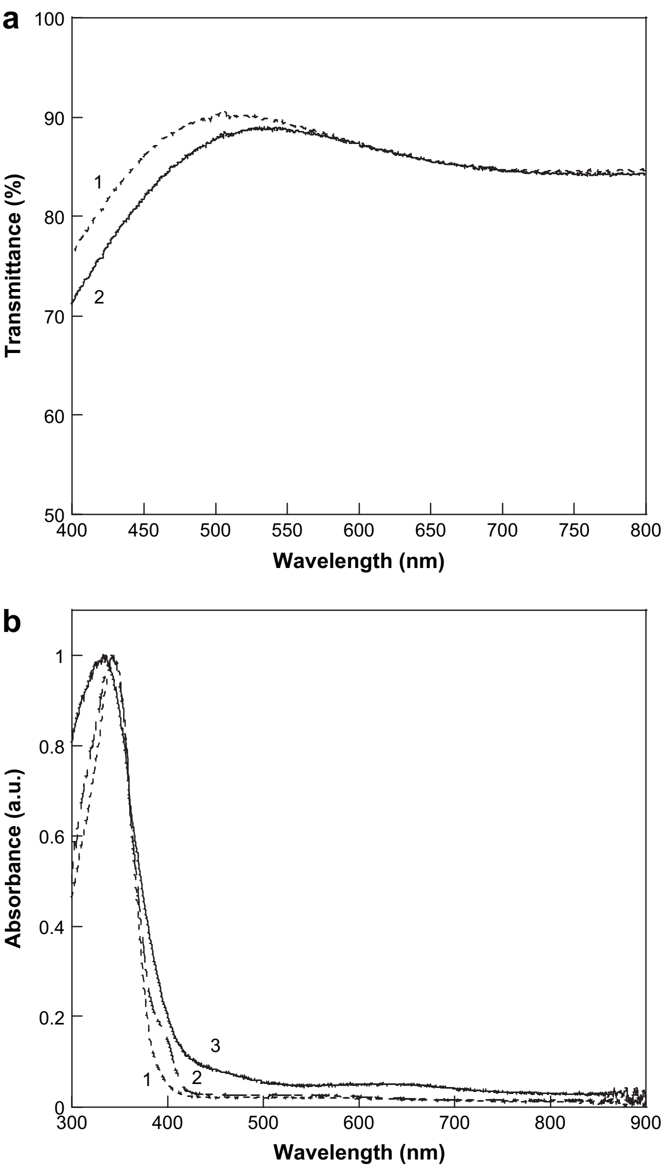


Fig. 5. (a) Transmittance spectra of bare ITO glass (----) and SPDPA coated on ITO glass (—); and (b) normalized solution UV–vis spectra of neutralized PDPA in DMF (----), H_2SO_4–PDPA in DMF (– —) and SPDPA in H_2O (—).

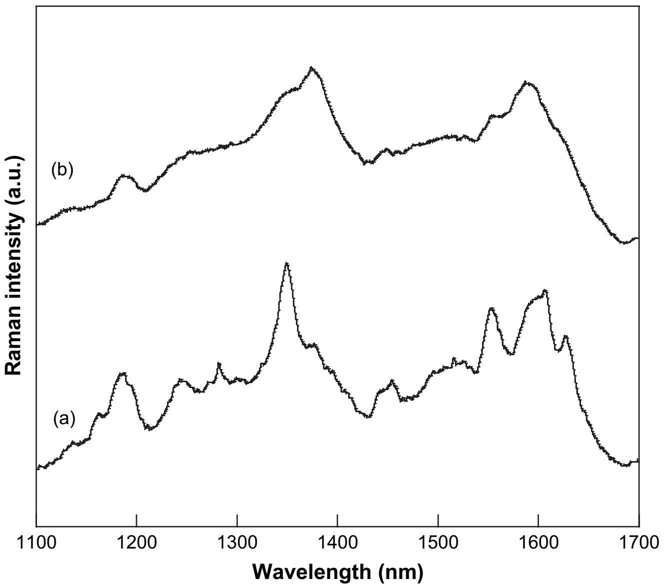


Fig. 6. Raman spectra of (a) neutralized PDPA and (b) SPDPA with 633 nm exciting radiation.

(330 vs. 350 nm) and the red shift of polaron band transition (640 vs. 620 nm) implied that SPDPA possessed the shorter conjugated length than PDPA, being attributable to the larger torsion angle of polymer chain due to the steric repulsion between the SO_3H groups and hydrogen on the adjacent phenyl rings [13]. On the other hand, the band gap of conjugated polymer would be increased due to the blue shift of the $\pi-\pi^*$ transition, which simultaneously shakes energy level shifts of molecular orbitals (HOMO and LUMO included). Besides, it is observed that the conductivity decreases from 10^{-3} (the doped PDPA) to 10^{-4} S/cm (SPDPA), being attributable to the decrease in free carrier density. The free carriers could be hindered from transporting due to the strong electron-withdrawing groups on the conjugated chain. Recent report demonstrated that the positions of molecular orbitals in PANI, relative to the Fermi level, were shifted toward smaller binding energy with UPS measurement by doping an electron acceptor such as halogens [19]. Besides, the related report revealed that the oxidation level of PEDOT:PSS was increased by utilizing electrochemical doping and the work function of PEDOT:PSS was immediately enhanced, which would assist anode in hole injection ability [20]. As for SPDPA, the energy level is supposed to be shifted toward higher work function upon inserting electron-withdrawing SO_3H group.

The Raman spectra of neutralized PDPA and SPDPA are shown in Fig. 6. The Raman bands of neutralized PDPA (spectrum (a)) can be assigned as follows: 1180 (C–H in-plane stretching), 1351 (C–C inter-ring stretching), 1583 and 1620 cm^{-1} (C–C ring stretching) [21]. In contrast to neutralized PDPA, the C–C inter-ring stretching band at 1351 cm^{-1} is diminished and a band at 1375 cm^{-1} appears in the spectrum for SPDPA. The change had been assigned to the increasing ratio of diphenoquinone diimine (dications' segment) to diphenosemiquinone diamine (radical cations' segment) in PDPA–CSA system. For SPDPA the prominent bands at 1175, 1375, and 1583 cm^{-1} are characteristic for dications. The results reveal that SPDPA is subjected to relatively high oxidation state and doping level because the electron-withdrawing SO_3H group is directly bonded on polymer backbone.

In order to confirm the variation of work function due to the SO_3H group bonded on polymer chain, the valence band spectra of neutralized PDPA and SPDPA are measured by UPS in UHV environment (Fig. 7). Fig. 7(a) reveals the highest occupied molecular orbitals (HOMOs) of neutralized PDPA and SPDPA. The features of HOMO of SPDPA are distinct from those of neutralized PDPA due to highly doping effect of the SO_3H group on the amino group, rendering the polymeric characteristics transition from semiconducting state into metallic state [22]. Simultaneously, the position shifts of HOMO of SPDPA tend to higher binding energy with the

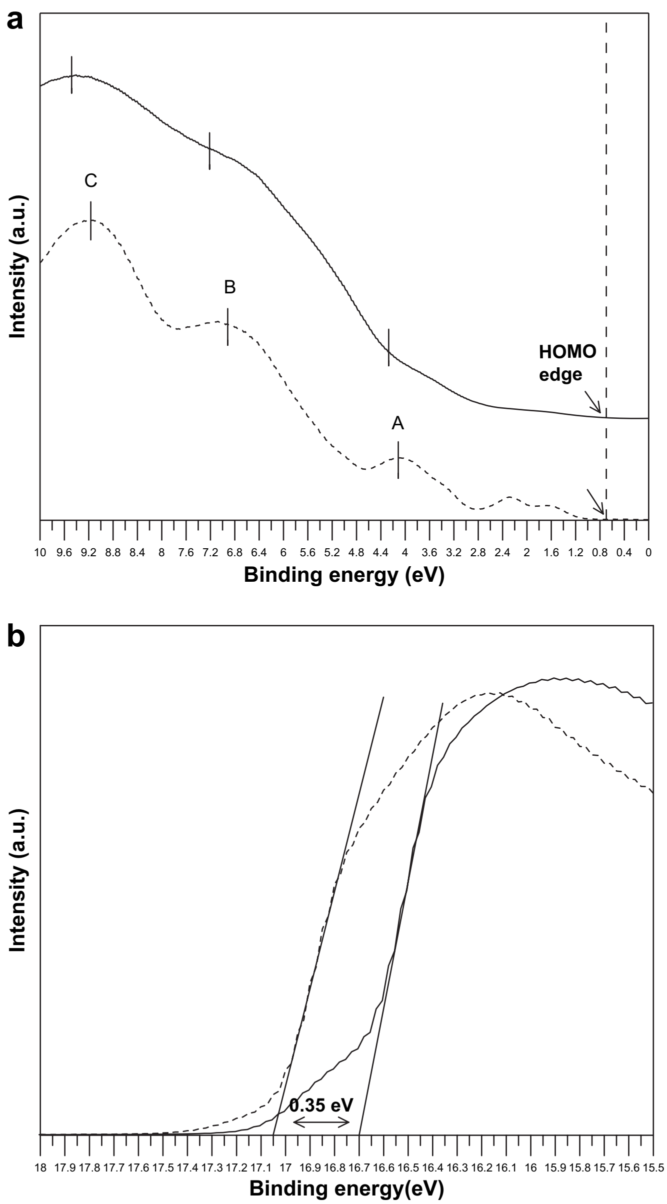


Fig. 7. UPS spectra of neutralized PDPA (---) and SPDPA (—) using He(I) UV source (21.2 eV); (a) valence bands/HOMO region and (b) secondary cutoff region.

doping electron-withdrawing (acceptor) groups [19]. The work function Φ of the sample can be obtained by [20,23]

$$\Phi = h\nu - \Delta E$$

$h\nu$ is the photon energy (~21.2 eV) and the spectrum width ΔE is determined from the distance between the inelastic secondary electron emission cutoff (Fig. 7(b)) and HOMO edge. Clearly, the enhancement of work function from 4.85 to 5.2 eV can be obtained.

3.3. Performance of the electroluminescence device

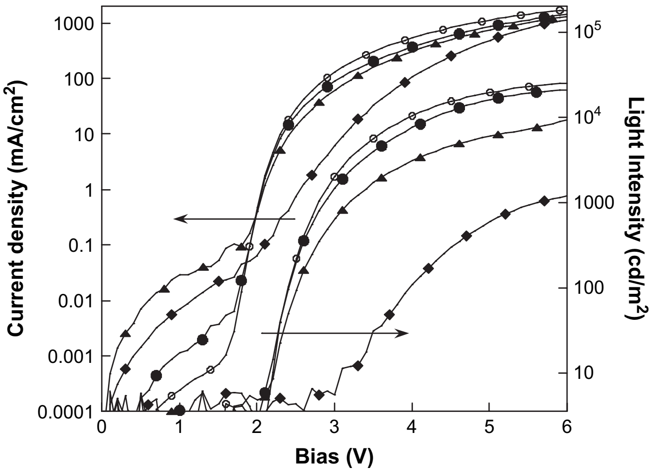


Fig. 8. J–V–L curve of the devices with (○) ITO/SPDPA, (●) ITO/PEDOT:PSS, (▲) UV–ozone-treated ITO and (◆) ITO/neutralized PDPA as anode.

Fig. 8 presents the J–L–V curve for devices by employing UV–ozone-treated ITO, ITO/SPDPA, ITO/neutralized PDPA and ITO/PEDOT:PSS as anode, MEH–PPV as EL and the Ca/Al as cathode. The device with SPDPA as HIL shows smaller leakage than the device with UV–ozone-treated ITO, and it suggests that the SPDPA-modified ITO prevents the occurrence of pinhole. The J–V curves show that the device with SPDPA exhibits higher injection current than those with UV–ozone-treated ITO and neutralized PDPA, indicating that the barrier height is smaller at the interface between SPDPA and MEH–PPV. It is obvious that the ITO/SPDPA device can enhance luminescence and EL efficiency, but ITO/neutralized PDPA device presents contrary results. Because PEDOT:PSS (10^{-3} S/cm) holds higher conductivity than SPDPA (10^{-4} S/cm), the relatively high current density of the device based on PEDOT:PSS could be measured. Fig. 9 shows EL efficiency with the current density for the devices

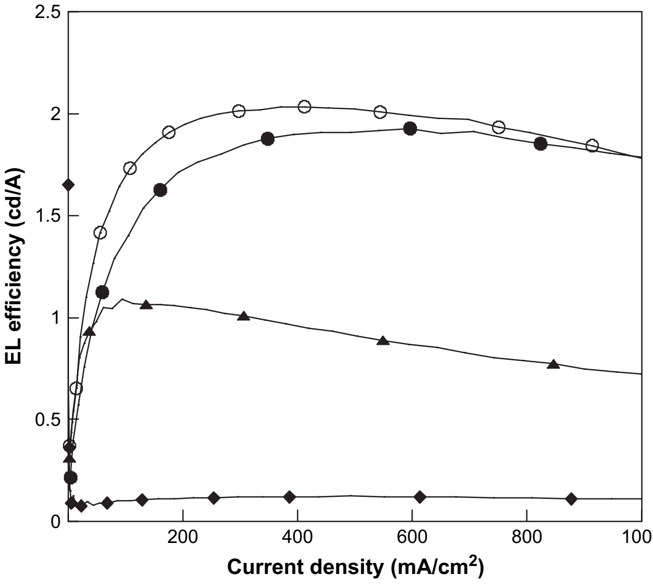


Fig. 9. Current density–EL efficiency characteristics of (○) ITO/SPDPA, (●) ITO/PEDOT:PSS (▲) UV–ozone-treated ITO, and (◆) ITO/neutralized PDPA as anode.

with different HILs. The maximum efficiency is ca. 2.0, 1.9, 0.12 and 1.1 cd/A for the device based on SPDPA, PEDOT:PSS, neutralized PDPA and UV–ozone-treated ITO, respectively. Thus, the performance of PLED with SPDPA as HIL is better than that of neutralized PDPA. The EL efficiency with SPDPA is superior to that with commercial PEDOT:PSS, which is attributable to hole–electron recombination more balanced in the emissive layer.

4. Conclusions

We have synthesized SPDPA simply by sulfonation of neutralized PDPA. The chemical structure of SPDPA was characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis. SPDPA could be dissolved in water as well as in polar organic solvents, and thus has a wide window of processability. The water-cast SPDPA film showed a very smooth surface, a moderate conductivity (10^{-4} S/cm) and high transparency in the visible region. With introduction of the SO_3H group into the polymer chain, SPDPA owns the following peculiar properties: (1) the lower conductivity as a result of the shorter conjugated length than PDPA doped form; (2) high oxidation state and doping level due to the SO_3H group directly bonding on polymer backbone; (3) the higher work function due to highly doping effect of the SO_3H group on amino group. The EL device with SPDPA as HIL exhibited significant enhancement in brightness and EL efficiency. On the basis of the above characteristics, we expect that SPDPA is a promising candidate polymer for being used as the hole injection layer in electroluminescence devices.

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