

Electrical Properties of Poly(*p*-phenylene vinylene) Films with an Incorporation of Platinum Metal Nanoparticles

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ABSTRACT: The effects of platinum metal nanoparticles on a conjugated polymer were investigated by monitoring the electronic structures and measuring the electrical properties of poly(*p*-phenylene vinylene) (PPV) and PPV/Pt nanocomposites films. Enhanced current density in PPV/Pt nanocomposite films was obtained by the incorporation of Pt nanoparticles into the conjugated polymer PPV. This

result agrees well with our observation of an increase in the electron affinity and an increase in roughness with increasing Pt nanoparticle content. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 811–815, 2011

Key words: conjugated polymers; metal-polymer complexes; nanotechnology; thin films; XPS

INTRODUCTION

Organic/inorganic nanocomposites have been increasingly studied because of their enhanced optical and electronic properties.¹ For example, incorporation of CdSe nanoparticles into a conjugated polymer, such as poly[2-methoxy-5-9(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), can result in the improved optical and electronic properties.^{2,3} Also, incorporation of metal nanoparticles into a conjugated polymer, devices based on conjugated polymer leads to enhancement of electrical properties and stability.⁴ Although this improvement has been obtained in conjugated polymer/nanoparticle composite, our understanding of the effects of nanoparticles on the performance of devices based on conjugated polymer is far from complete.⁵ Poly(*p*-phenylene vinylene) (PPV) and its derivatives usually have low efficiencies because injection of holes is much more favorable than injection of electrons. The hole mobility in PPV is 200 times higher than the electron mobility.⁶ Therefore, to enhance the properties of devices based on PPV, the charge injection into, as well as carrier transport within the emitting layer should be balanced by chemical modi-

fication of PPV.⁷ In this work, we focused on the enhancement of the current density for PPV/Pt nanocomposites. We examined factors that affect carrier injection and mobility by observing the energy structure and morphologies of composite films.

EXPERIMENTAL DETAILS

PPV was prepared via a sulfonium precursor route.⁵ The starting materials of the monomer were α,α' -dichloro-*p*-xylene and tetrahydrothiophene (THT). The monomer was polymerized using an equal molar quantity of NaOH. The reaction was terminated by adding an excess amount of dilute HCl to neutralize the unreacted NaOH. The product was then purified by dialysis using a cellulose tube. The purified solution was spin-coated onto a clean indium tin oxide (ITO) coated glass substrate and then converted to PPV film by thermal conversion under vacuum at 200°C for 4 h.⁵ The thickness of the films was controlled around 150 nm thick.

Platinum nanoparticles were prepared by citrate reduction. $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ and trisodium citrate were purchased from Aldrich. $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ (0.2 mM) and trisodium citrate (0.2 mM) were dissolved in 100 mL water. The colloidal solution was irradiated with a 1000 W mercury arc lamp ($\lambda = 365$ nm) at room temperature.⁸

The PPV/Pt nanocomposite films were prepared by mixing Pt nanoparticles and PPV precursors. The PPV/Pt nanocomposite films were prepared by spin coating in the same manner as for the PPV.

Current-voltage (I-V) experiments were performed on PPV and PPV/Pt nanocomposite films. For measurement, PPV and PPV/Pt nanocomposite films

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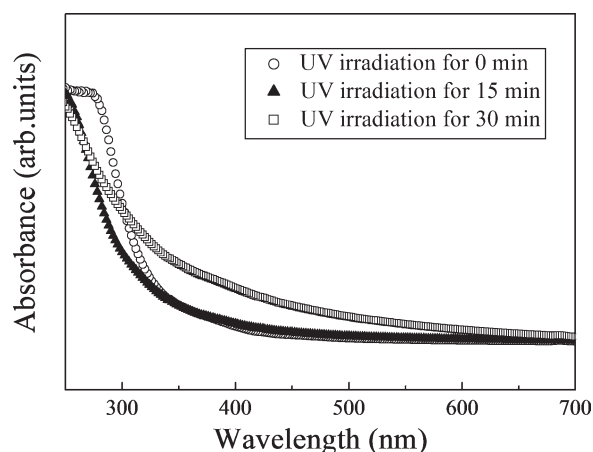


Figure 1 UV-vis absorption spectra of Pt colloidal solutions with different UV exposure times.

were deposited on an ITO-coated substrate and a 200-nm thick aluminum electrode was formed by thermal evaporation.⁵ Atomic force microscopy (AFM) was used to monitor the surface morphology of the PPV and PPV/Pt nanocomposite films. Optical absorption measurements were performed using a UV-vis spectrophotometer. Also, ultraviolet photoelectron spectroscopy (UPS) with He I (21.22 eV) radiation was effectuated in the 8A2 beam line of the Pohang Accelerator Laboratory. To provide evidence of presence of Pt nanoparticles in PPV matrix, X-ray photoelectron spectroscopy (XPS) was used with an Al K α monochromatic source.

RESULTS AND DISCUSSION

The UV-vis absorption spectra were monitored during the synthesis of Pt nanoparticles and the results are given in Figure 1. In case of nonirradiated Pt colloidal solution, a peak of the [PtCl₆]²⁻ was observed. When the UV-irradiation time was 30 min, the peak completely disappeared, i.e., [PtCl₆]²⁻ was decomposed, suggesting that the Pt nanoparticles were formed.⁹ The size of the Pt nanoparticles prepared in this experiment was about 5.5 nm.¹⁰ Figure 2 shows the UV-vis absorption spectra of PPV and PPV/Pt nanocomposite films. The spectra of PPV nanocomposite were blue-shifted from the PPV, this result indicated that nanocomposite films have wider band gap than PPV. Also, an incorporation of metal nanoparticles generally hinders the chain for-

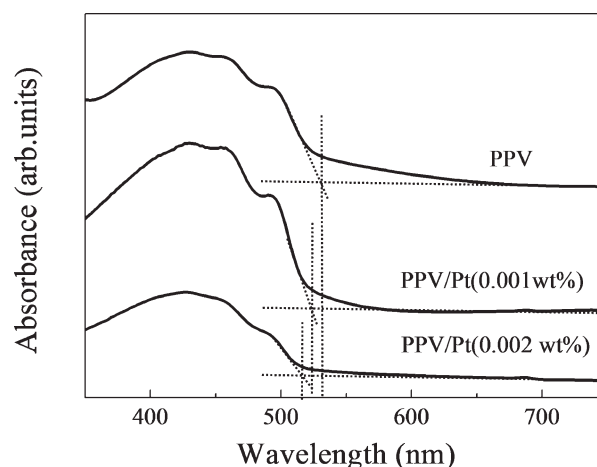


Figure 2 UV-vis absorption spectra of PPV and PPV/Pt (0.001 and 0.002 wt %) nanocomposite films.

mation and results in a slight shortening of the chain length.¹¹ The onset point of the absorption of PPV appeared at 531.56 nm and continuously decreased with increasing Pt nanoparticles: 521.32 nm and 514.04 nm for 0.001 wt % and 0.002 wt % of Pt nanoparticles incorporation, respectively. These values are given as absorption edge in Table I and with the absorption edge, we can calculate the optical band gap energy, E_g .¹² The photoluminescence (PL) spectra of the PPV and PPV/Pt (0.001 wt %) nanocomposite films are given in Figure 3. When the Pt nanoparticle is incorporated into PPV film, PPV/Pt (0.001 wt %) nanocomposite film showed blue-shifted spectrum when comparing with that of PPV film. The blue shift of the spectrum with incorporation of Pt nanoparticles is well matched with the results observed in the UV-vis absorption spectra. However, the presence and chemical state of Pt nanoparticles in PPV were directly confirmed by XPS analyses. Figure 4 shows the Pt 4f spectra of PPV and PPV/Pt nanocomposite films with Pt nanoparticle contents of 0.001 and 0.002 wt %. Naturally, the intensity of Pt 4f peak increased with increasing Pt nanoparticle content.

Figure 5 schematically shows the locations of occupied and unoccupied electronic energy level near the Fermi level, E_F . Definition of the energy gap (E_g), the ionization potential (IP), and the electron affinity (EA) are shown.¹³ These energy levels are important for the performance of an OLED because they determine the carrier tunneling barrier

TABLE I
Energy Positions of PPV and PPV Nanocomposite Films as Measured by Using UPS and UV-Vis Spectroscopy

	E_{cutoff} (eV)	HOMO (eV)	IP (eV)	Absorption edge (nm)	E_g (eV)	EA (eV)
PPV	16.47	0.88	5.63	531.56	2.34	3.29
PPV/Pt (0.001 wt %)	16.76	1.23	5.69	521.32	2.36	3.33
PPV/Pt (0.002 wt %)	16.78	1.30	5.74	514.04	2.38	3.36

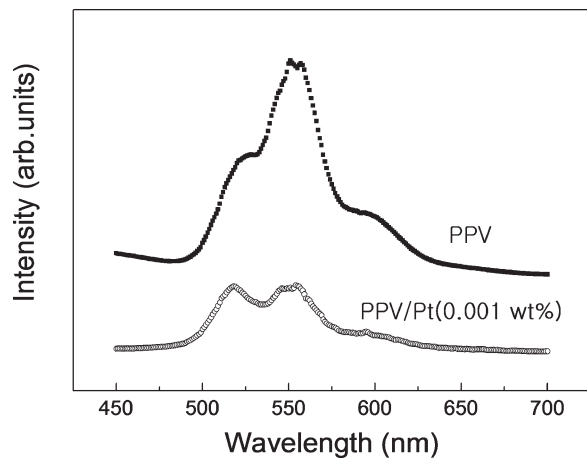


Figure 3 PL spectra of PPV and PPV/Pt (0.001 wt %) nanocomposite films.

height that electrons and holes injected from electrode to emissive layer. The injection of holes and electrons depends on the relative barrier heights, IP and EA, respectively. Figure 6(a) shows a typical He I UPS spectrum of a PPV film on an ITO-coated glass substrate. We calculated the energy levels from the UPS and UV-vis absorption spectra. The location of the Fermi level relative to the vacuum level, $E_{vac} - E_F$, can be determined from the following formula:¹⁴

$$hv = |E_{cutoff}| + E_{vac} - E_F \quad (1)$$

where $|E_{cutoff}|$ is the location of the inelastic cutoff point and hv is the incident photon energy. For PPV film, the incident photon energy is 21.22 eV and $E_{vac} - E_F$ was calculated as 4.75 eV from inelastic cut-

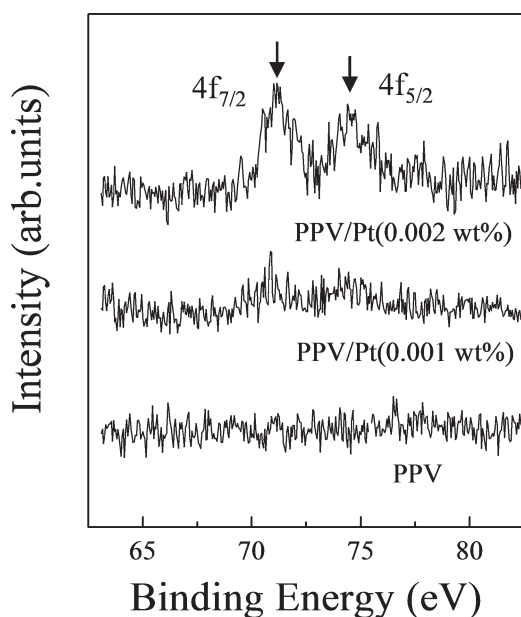


Figure 4 Pt 4f XPS spectra of PPV and PPV/Pt (0.001 and 0.002 wt %) nanocomposite films.

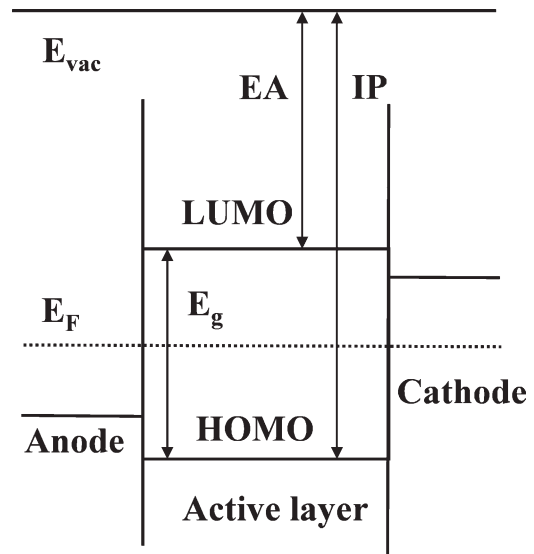


Figure 5 Schematic diagram of various energy levels near the valence region.

off point in Figure 6(a). The IP is the location of the highest occupied molecular orbital (HOMO) relative to E_{vac} and it is the sum of $|E_{vac} - E_F|$ and

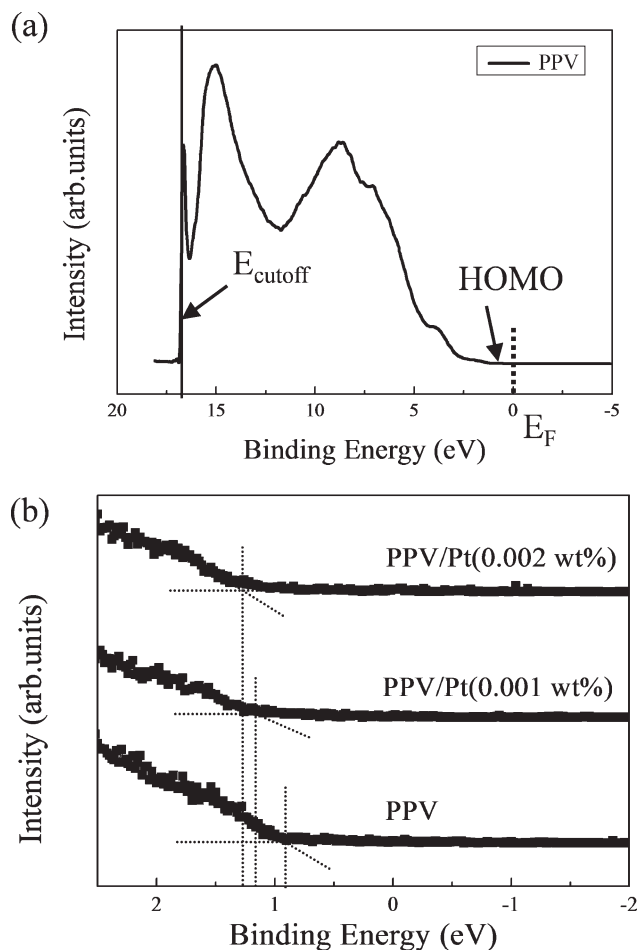


Figure 6 (a) He I UPS spectrum of PPV film and (b) the enlarged HOMO region of PPV and PPV/Pt (0.001 and 0.002 wt %) nanocomposite films.

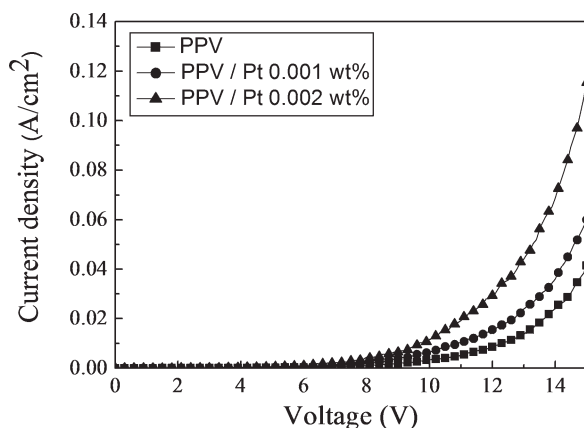


Figure 7 Current-voltage curves for PPV and PPV/Pt (0.001 and 0.002 wt %) nanocomposite films.

$|HOMO - E_F|$. From the UPS spectrum, the IP was calculated to be 5.63 eV for the case of PPV and this also corresponds to $EA + E_g$ because EA is the location of the lowest unoccupied molecular orbital (LUMO), relative to the vacuum level. Because UPS only probes occupied states, LUMO cannot be determined from the UPS spectrum. We utilized the energy band gap, E_g , determined from UV-vis absorption measurements as neglecting exciton binding energy and relaxation effects.^{13,14} Using $E_g = 2.34$ eV that calculated from UV-vis absorption spectrum for PPV, we obtained $EA = 3.29$ eV. The relative HOMO shifted to high-binding energies with increasing Pt nanoparticle contents as shown in Figure 6(b). In the same manner, the energy levels were determined for the PPV and PPV/Pt nanocomposite films and are summarized in Table I. Although the band gap of the nanocomposites slightly increased with increasing Pt nanoparticle contents, we obtained increased EA values due to a shift HOMO to high-binding energy. These results indicate that the electrons are more easily injected from Al electrode to emissive layer and transported in nanocomposite films. In other words, energy barrier of the nanocomposites was lower than that of PPV.

Figure 7 shows the current density of PPV and PPV/Pt nanocomposite films. We obtained enhanced current density in PPV nanocomposite films by incorporation of Pt nanoparticles into the conjugated polymer PPV. This result agrees well with our observation of an increase in EA with increasing Pt nanoparticle content.

To check whether there is an effect of surface morphology of the films on their electrical properties, AFM images were taken at $5 \mu\text{m} \times 5 \mu\text{m}$ to demonstrate the variation of morphology with increasing Pt nanoparticle content and shown in Figure 8. The roughness value of the PPV film surface was 0.37 nm. Meanwhile, the roughness values of PPV/Pt (0.001 wt %) and PPV/Pt(0.002 wt %) nanocompo-

site films were 0.44 nm and 0.80 nm, respectively. The surface of the nanocomposite films was slightly rougher than PPV film due to the presence of Pt nanoparticles. A rougher cathode interface may give rise to an increase in the surface area, i.e., effective contacting area with electrode. Finally, electron injection increased with resulting enhancement of current density.¹ This enhancement of current in our nanocomposite films is similar to those reported in the literature.^{1,5,15}

CONCLUSIONS

Focusing on electron energy band structure, morphology, and chemical structure of PPV and PPV/Pt nanocomposite films, we have demonstrated that the incorporation of Pt nanoparticles has an influence on

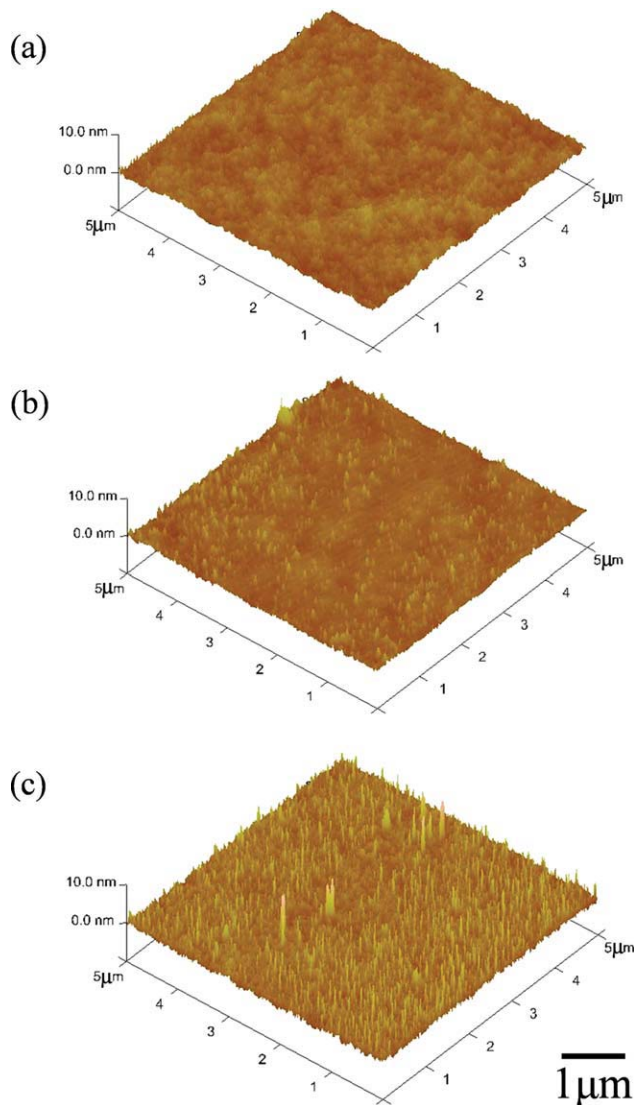


Figure 8 AFM images of (a) PPV film and PPV/Pt nanocomposite films with (b) 0.001 wt % Pt and (c) 0.002 wt % Pt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electrical properties. Incorporation of Pt nanoparticles in PPV resulted in an increase of current density. The UPS spectra show that the Pt nanoparticles modify the electron energy band structure: an increase of EA with increasing Pt nanoparticle content. The current density enhancement of the PPV/Pt nanocomposite was also slightly influenced by the roughened morphology of the composite resulting from the presence of Pt nanoparticles in the PPV/Pt film.

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