Increasing the work function of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) by ultraviolet irradiation

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The effects of ultraviolet (UV) irradiation on the work function of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) have been investigated in this study. Spectroscopic methods [x-ray photoelectron spectroscopy and Raman spectroscopy (532 nm excitation)] and electrical conductivity measurements were used to characterize the electrical conducting polymer PEDOT:PSS prepared by UV irradiation. The authors found that UV irradiation could lead to an increase in the work function and the enhancement of electrical conductivity of PEDOT:PSS, resulting from a decrease in the number of the charge-trapping-related defects and the formation of linear or expanded-coil conformation. © 2007 American Institute of Physics.

Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) has become one of the most widely studied conducting polymers in both academic and industry due to its several advantages such as high work function, high conductivity, high stability in the oxidized state, and the ability to incorporate water-soluble polyelectrolyte dopants.1–7 PEDOT:PSS was also used as an antistatic function, high conductivity, high stability in the oxidized industry due to its several advantages such as high work function and electrical conductivity measurements were used to characterize the electrical conducting polymer PEDOT:PSS prepared by UV irradiation. The authors found that UV irradiation could lead to an increase in the work function and the enhancement of electrical conductivity of PEDOT:PSS, resulting from a decrease in the number of the charge-trapping-related defects and the formation of linear or expanded-coil conformation. © 2007 American Institute of Physics.

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In this study, we found that UV irradiation could lead to an increase in the work function and the enhancement of electrical conductivity of PEDOT:PSS, resulting from a decrease in the number of the charge-trapping-related defects and the formation of linear or expanded-coil conformation.

A glass substrate was first cleaned by ultrasonic agitation in ethanol and subsequently in acetone followed by mechanical scrubbing in de-ionized water using a detergent. The samples were then cleaned in an ultrasonic bath using a water solution of the same detergent and rinsed several times by ultrasonic agitation in water. Then, PEDOT:PSS was deposited on glass surfaces by spin coating. Next, the PEDOT:PSS films were baked at 150 °C for 30 min. In our experiments, the PEDOT:PSS/glass sample was irradiated for 30 min by a UV light source (output power density of 460 μW/cm²) with emission centered at 365 nm (referred to as UV-irradiated PEDOT:PSS). The effect of the conformation of the PEDOT chains in the PEDOT:PSS film before and after UV irradiation was studied by Raman spectroscopy. X-ray photoelectron spectroscopy (XPS) was employed to examine the work function of PEDOT:PSS with or without UV irradiation. We used a monochromatic Al $K\alpha$ source for XPS analysis. The incident photon energy was calibrated with the core-level spectrum of Au 4f. Work function is determined by the difference between photon energy (Al $K\alpha$, 1486.6 eV) and the high binding energy cutoff (secondary edge).15,16 The high binding energy cutoff was determined by extrapolating two solid lines from the background and straight cutoff in the spectra.17

Figure 1 shows the XPS spectra region for the high binding energy cutoff. We find that the binding energy cutoff for PEDOT:PSS films with UV irradiation shifted to a lower binding energy by 0.25 eV with respect to the binding energy cutoff for PEDOT:PSS films without UV irradiation. This means that the work function of PEDOT:PSS films with UV light source (output power density of 460 μW/cm²) with emission centered at 365 nm (referred to as UV-irradiated PEDOT:PSS).

![FIG. 1. XPS spectra region for the high binding energy cutoff.](image-url)

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UV irradiation is higher by 0.25 eV than that of PEDOT:PSS films without UV irradiation.

Figure 2 shows Raman spectra of PEDOT:PSS films with and without UV irradiation under 532 nm semiconductor laser excitation. In Fig. 2, the band between 1400 and 1500 cm\(^{-1}\) corresponds to the stretching vibration of \(C\alpha=C\beta\) on the five-member ring of PEDOT (Refs. 18 and 19) and the band is observed to move towards lower wave numbers and becomes narrow. This means that the resonant structure of PEDOT chain changes from a benzoid to a quinoid structure. The benzoid structure may be the favorite structure for a coil conformation, while the quinoid structure may be the favorite structure for a linear or expanded-coil structure.\(^{20}\) Thus, we deduce that the coil conformation turns into linear or expanded-coil conformation, resulting in a marked increase in the work function of PEDOT:PSS.

The current-voltage \((I-V)\) curves for indium tin oxide (ITO)/PEDOT:PSS (350 nm)/Au devices are shown in Fig. 3. \(I-V\) characteristics of the devices were measured with a Keithley model 4200-SCS/F semiconductor characterization system. PEDOT:PSS was deposited on ITO surfaces by spin coating. Next, the PEDOT:PSS films were baked at 150 °C for 30 min. Au was used as the electrode, vacuum evaporated on top of the PEDOT:PSS films. The area of each ITO/PEDOT:PSS/Au device was 1 \(\times\) 1 cm\(^2\). The area of each Au electrode was 0.2 \(\times\) 0.8 cm\(^2\). The structure of the devices was shown in the inset of Fig. 3. The linear \(I-V\) curves are found in Fig. 3, because the work function of Au or ITO is close to that of PEDOT:PSS. The ITO/PEDOT:PSS/Au device without UV irradiation shows a linear \(I-V\) behavior with total resistance \((R_T)\) of 30.2 \(\Omega\), and the ITO/PEDOT:PSS/Au device following UV irradiation shows a linear \(I-V\) behavior with \(R_T\) of 26.20 \(\Omega\). According to the results shown in Figs. 1–3, we suggest that UV irradiation may lead to the formation of linear or expanded-coil conformation, resulting in an increase in the work function and the enhancement of the electrical conductivity of PEDOT:PSS.

In order to observe the change of the charge-detrapping current, the gap spacing between the Au contact pads was designed to be 1.5 cm. The large gap spacing between the Au contact pads may lead to an increase in the total resistance and a reduction in the total current. Thus, the change of the charge-detrapping current can be clearly observed. Smith and Forrest\(^{21}\) stated that the charge-detrapping current was found in the high-resistivity PEDOT:PSS film, meaning that the charge-detrapping current is extremely low. Brütting et al.\(^{22}\) suggested that due to the large sample resistance and trapped charges in the metal/poly-(p-phenylene-vinylene)/metal device there is an offset in the current zero crossing. Figure 4 shows \(I-V\) curves measured without and with an additional delay of 1 s for Au/PEDOT:PSS/Au devices. The voltage was incremented in steps of 10 mV from 10 to –10 V. The area of each Au/PEDOT:PSS/Au device was 2.54 \(\times\) 2.54 cm\(^2\). The area of each Au electrode was 0.52 \(\times\) 2.54 cm\(^2\). The structure of the devices was shown in the inset of Fig. 4. In Figs. 4(a) and 4(b), we find that the current measured without an additional delay of 1 s drops to zero at \(V=0.68\) V \((V=0.40\) V\) for the Au/PEDOT:PSS/Au devices without (with) UV irradiation and the residual current \((I_r)\) at 0 V for the Au/PEDOT:PSS/Au devices with UV irradiation is lower than that at 0 V for the Au/PEDOT:PSS/Au devices without UV irradiation. \(I-V\) measurements show that the device characteristics in negative bias direction and at low positive bias are influenced by charges trapped within the organic layers.\(^{22}\) Smith and Forrest\(^{20}\) and Forrest\(^{21}\) suggested that due to the large sample resistance and trapped charges in the metal/poly-(p-phenylene-vinylene)/metal device there is an offset in the current zero crossing.
Forrest\textsuperscript{21} suggested that the offset and $I_\text{c}$ is due to charge detrapping from the PEDOT:PSS film. Nguyen \textit{et al.}\textsuperscript{23} suggested that the similar $I$-$V$ characteristic is caused by recharging of deep traps for holes based on the simulated potential and concentration profiles. Thus, we deduce that UV irradiation may simultaneously lead to a decrease in the number of the charge-trapping-related defects, resulting in an increase in the work function and the conductivity of PEDOT:PSS films. In Figs. 4(c) and 4(d), we find that the current measured with an additional delay of 1 s drops to zero at $V$ = 0.30 V ($V$ = 0.11 V) for the Au/PEDOT:PSS/Au devices without (with) UV irradiation. In addition, we find that the $I_\text{c}$ measured with an additional delay of 1 s at 0 V for the Au/PEDOT:PSS/Au devices without or with UV irradiation is lower than that measured without an additional delay of 1 s at 0 V for the Au/PEDOT:PSS/Au devices without or with UV irradiation, meaning the presence of trapped charges in the device, which can require high time constants for the device to reach equilibrium.

In summary, the effects of UV irradiation on the work function of PEDOT:PSS films have been investigated in this study. From the Raman spectroscopy, XPS, and electrical conductivity measurements, it is suggested that the coil conformation turns into linear or expanded-coil conformation and the number of the charge-trapping-related defects is reduced, after UV irradiation, resulting in an increase in the work function and the conductivity of PEDOT:PSS films. The UV irradiation yields work-function shifts as high as 0.25 eV compared to the PEDOT:PSS sample without UV irradiation, which could be useful for the enhancement of the hole injection in OLEDs.

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\textsuperscript{17}J. Ouyang, Q. Xu, C. W. Chu, Y. Yang, G. Li, and J. Shinar, Polymer \textbf{45}, 8443 (2004).