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Study of Ultrathin Films of P3HT/PCBM by Means of Highly Sensitive Absorption Spectroscopy

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Ultrathin films of P3HT and P3HT/PCBM prepared on glass and ITO glass substrates by spin-coating were studied by means of highly sensitive absorption spectroscopy. For pristine P3HT films, we discuss the morphology and electronic structure at the interface between the substrate and the P3HT layer. For P3HT/PCBM films, we found that phase separation could be controlled by changing the concentration of the solutions used to prepare the films.

Interest in organic photovoltaic (OPV) cells as a new type of solar cell is increasing. Of the various proposed designs, one of the most successful is the bulk heterojunction (BHJ)-type solar cell.[1,2] Mixtures of poly(3-hexylthiophene) and [6,6]phenyl C_{61}-butyric acid methyl ester (P3HT and PCBM, respectively) have been used to prepare prototype BHJ cells. The two materials are dissolved in organic solvents, and a cast film is prepared by spin-coating. Phase-separated films are produced instantaneously, and the interface between the P3HT and PCBM phases acts as a p–n junction in the bulk. Nanoscale phase separation is a key factor for the realization of high-performance solar cells, and therefore various methods for controlling the nanostructure, for example, annealing the films after preparation[1,2] and changing the solvent properties,[3] have been investigated.

The nanostructure of BHJ solar cells has been studied by means of various experimental techniques, such as electron microscopy and atomic force microscopy.[1,2] Such studies have revealed that phase separation is a key factor in controlling cell performance, and therefore optimization of the size of the segregated phases has been examined. In addition to optimization of the two-dimensional structure, optimization of the depth profile of the films is also important for controlling device performance, but evaluation of the depth profile is difficult experimentally. Recently, the depth profile of the chemical composition of P3HT/PCBM was studied by means of time-of-flight secondary-ion mass spectrometry (TOF-SIMS) with gradient shaving preparation,[4] and the results indicated that the depth profile was not ideal.

The morphology and electronic structure at the interface between the organic material and the electrode also affect device performance. Organic molecules at the surface, morphology and their electronic structure are affected by interaction with the substrates.[5] To study such properties at the interface, ultrathin films prepared on the metal surface have been studied. Although various techniques can be applied in principle, only a limited number of techniques, such as photoelectron spectroscopy[5] and nonlinear laser spectroscopy,[6] have been used in practice because high sensitivity is required if reliable signals from ultrathin films are to be obtained.

Conventional absorption spectroscopy is a potentially powerful tool to evaluate the concentration and electronic structure of molecules. However, in reality, the method is difficult to use for the study of ultrathin films because of its low sensitivity. A conventional absorption spectrometer requires an absorbance of 10^{-2} for measurement of highly accurate spectra. Thus, a monolayer film with a density of $10^{14}\,\mathrm{cm}^{-2}$ can barely be detected, even for a molecule with a large molar absorption coefficient ($\varepsilon > 10^4\,\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$).

Although sensitivity can be improved by the use of special optical systems, such as optical waveguide systems[7] and cavity ring-down systems,[8] high sensitivity can also be achieved with a conventional single-path optical geometry. With this geometry, the concentration of a sample can be directly determined from the observed absorbance. Kotani and co-workers reported that absorbance intensities of $<10^{-4}$ can be detected by means of a simple absorption spectrometer with a stabilized light source and a precise digital voltmeter.[9] Yamamoto et al. constructed a highly sensitive absorption spectrometer capable of detecting a very weak absorbance ($<10^{-5}$). With this spectrometer, the intensity of the probe light is measured by means of photon-counting, and therefore fluctuation of signals from the amplifier is effectively eliminated.[10]

Here we studied the morphology and electronic structure of ultrathin films of P3HT and P3HT/PCBM prepared on a glass slide and an indium tin oxide (ITO) glass plate by means of a highly sensitive absorption spectrometer that was recently developed in our group.

P3HT and PCBM were purchased from Rieke and Solenne, respectively. Films of P3HT were prepared on glass slides and ITO glass (Nippon Sheet Glass) by means of spin-coating from chlorobenzene solutions of P3HT at 2000 rpm for 60 s. The concentrations of P3HT in the solutions were varied from 0.07 to 7 $\mathrm{mg\,mL^{-1}}$. In addition, we prepared P3HT/PCBM films from mixed solutions P3HT/PCBM $= (100\,\mathrm{mg} + 200\,\mathrm{mg})/\mathrm{mL}$.

Absorption spectra were measured with a homemade highly sensitive absorption spectrometer, which is similar to that reported by Kotani and co-workers.[9] A 100-W halogen lamp was used as the light source. Monochromatic light obtained with a monochromator (Acton, SP-2150i) was transmitted through the sample situated on a linear stage controlled with a computer, and the transmitted light was detected with a photodiode (Thorlab inc., DET100A/M) after being dispersed with a monochromator (Acton, SP-150-M). Photocurrent from the detector was measured with a digital multimeter (Keithley, 2010) and data accumulated with a computer. Spin-coated film was wiped off the left half of a plate, and the clean half of the plate was used as the reference for absorption measurements. The sample was moved in and out of the light beam by means of the linear stage (at a frequency of 0.5 Hz), and the photocurrents from the

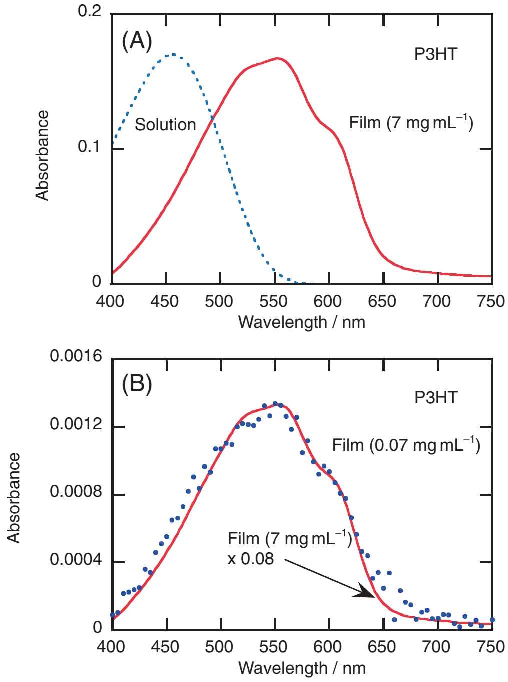

Figure 1. Absorption spectra of (A) a P3HT solution and a thick P3HT film and (B) thick and ultrathin P3HT films.

sample and the reference were detected. After accumulations, high sensitivity (absorbance 10^{-4}) was realized. All measurements were carried out at room temperature.

Comparison of the absorption spectrum of P3HT in chlorobenzene solution and the spectrum of a thick P3HT film prepared on a glass slide from a 7 mg mL^{-1} solution of P3HT in chlorobenzene clearly shows that the absorption band shifted toward longer wavelength upon film formation (Figure 1A). Previous studies[1–3] suggest that this red-shift is due to the electron delocalization induced by the stacking of the thiophene moieties and that the spectral shape is sensitive to film morphology. However, the exact origin of the shift is still under debate. Comparison of the absorption spectrum of the thick P3HT film with that of an ultrathin P3HT film prepared on a glass slide from a 0.07 mg mL^{-1} solution in chlorobenzene clearly indicates that the spectral shape of the ultrathin film was similar to that of the thick film (Figure 1B).

The absorption coefficient of 60-nm-thick P3HT films at 532 nm has been estimated to be 90000 cm^{-1}, calculated from the 0.5 absorbance of the films.[11] Using this coefficient, we estimated the average thickness of the ultrathin P3HT film to be 0.16 nm, which is thinner than the thickness of a π orbital in a benzene ring (about 0.35 nm). This indicates that the P3HT molecules were situated on the surface almost individually if the molecules were homogeneously dispersed on the surface and the polymer chain was not entangled. The fact that the spectral shape of the ultrathin film differed from that of P3HT dispersed in solution (Figure 1) suggests that the thiophene moieties were well-stacked in the film. The spectral shapes of the thick and ultrathin films were the same (Figure 1B). This similarity indicates that the nanoscale packing structures of these films were similar to each other. Thus, it is likely that the submonolayer film was composed of P3HT nanoparticles on the surface rather than entanglement with itself of an individual polymer molecule on the surface.

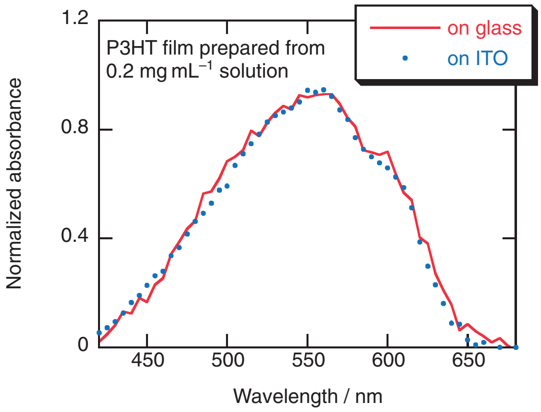

Figure 2. Absorption spectra (normalized at the peak) of P3HT thin films prepared from 0.2 mg mL^{-1} solutions on a glass plate and an ITO glass plate.

Absorption spectra can provide information not only about the morphology of P3HT films but also about surrounding conditions. For example, the spectra reflect interactions with the surface of electrodes, such as metal and ITO electrodes, because the spectra can change if charge-transfer interactions between P3HT films and ITO electrode are significant. Therefore, measurements of absorption spectra of thin films directly attached to electrodes are useful. Figure 2 shows the absorption spectra (normalized at the peak) of thin films prepared from 0.2 mg mL^{-1} P3HT solutions on a glass slide and on an ITO glass plate. The average thickness of these films was estimated to be about 0.5 nm, which suggests the formation of a monolayer in average. Because the absorption spectra of P3HT films reflect both morphology and electronic structure, information about the interaction between ITO and the P3HT films can be obtained from the absorption spectra of such thin films. The obvious similarity in spectral shape for the two substrates clearly indicates that the electronic interaction between P3HT and the ITO surface was negligible. Although these spectra were normalized at the peak, the fact that the observed absorbances were nearly the same suggests that the morphology of the films was not affected by changing the substrate from a glass slide to an ITO glass plate.

For application in BHJ-type solar cells, films of P3HT mixed with PCBM have been used. As mentioned above, nanoscale phase separation is essential for high solar cell performance. The spin-coating method has been widely used to prepare BHJ films, and variation of the preparation conditions has been examined as a means for controlling the morphology of the films. We examined here the effect of the concentration of the solution used to prepare the films on the morphology. P3HT/PCBM films were prepared from solution (P3HT/PCBM = (100 mg + 200 mg)/mL) and from solutions diluted by 1/3, 1/10, 1/30, and 1/100 with chlorobenzene. Figure 3 shows the normalized absorption spectra, indicating that the spectral shape was affected by solution concentration. As mentioned above, individual P3HT molecules in solution absorb at around 450 nm, whereas aggregates in thick films absorb at around 550 nm. The spectra shown in Figure 3 can be reproduced roughly using

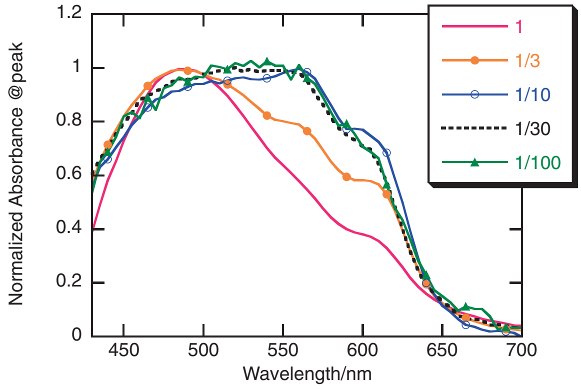

Figure 3. Absorption spectra of P3HT/PCBM films prepared from solution with concentration of P3HT/PCBM = (100 mg + 200 mg)/mL and from solutions diluted by 1/3, 1/10, 1/30, and 1/100 with chlorobenzene.

these two spectra. In the spectra, the contribution of PCBM is unimportant because of its small absorption coefficient in this wavelength range.[1–3] The film prepared from a concentrated solution absorbed relatively strongly at around 480 nm, which suggests that the P3HT molecules were well dispersed in the PCBM matrix, namely, phase separation was poor. The peaks for the films prepared from diluted solutions were at longer wavelength than those of films prepared from the concentrated solutions. This result suggests that P3HT molecules were well segregated from the PCBM matrix and that they formed aggregates in the films.

The spectra shown in Figure 3 indicate that the morphology of P3HT/PCBM films could be controlled by changing the concentration of the solution used to prepare the films. Although the films were rather thin for practical use, this concentration effect may be useful for furthering our understanding of the mechanism of phase separation during BHJ-film formation.

The absorbances of these films were roughly proportional to the concentrations of the preparation solutions. This suggests that the thickness of the solution remaining on the glass slide during spin coating was not affected by the concentration of the solution. Thus, solid films were formed by vaporization of the solution on the glass slide. Because the speed of solid film formation is limited by solubility, the film-formation speed for the concentrated solutions was faster than that for the dilute solutions. Thus, the morphology of the film prepared from the concentrated solutions was likely not to have been well segregated, because of the high speed of film formation. In contrast, a well-segregated structure can be expected for films prepared from dilute solutions, owing to the slow speed of film formation.

In summary, we described a highly sensitive absorption spectroscopy method for evaluation of the morphology and electronic state of ultrathin films of P3HT and P3HT/PCBM prepared by spin-coating. We found that the ultrathin film of P3HT consisted of small aggregates on the surface and that there was no significant interaction between the film and the ITO. We also found that phase separation during preparation of P3HT/PCBM films by spin coating could be controlled by changing the concentration of the preparation solution.

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