Enhancement of out-of-plane mobility in P3HT film: Face-on orientation produced by rubbing

The orientation of a conjugated polymer in a thin film affects the optical and electrical properties of the film. The control of the orientation is important to investigate the optoelectronic properties of conjugated polymers and produce functional polymer films. The increase in the use of conjugated polymers in a wide range of applications such as sensors, solar cells, and LEDs has motivated a number of attempts to investigate oriented polymer films. Poly(3-hexylthiophene) (P3HT) is a prototypical conjugated polymer associated with organic solar cells fabricated via solution processes. The anisotropic features of light absorption, light emission, and carrier transport have been reported for oriented P3HT films. The rubbing technique is a method employed to align molecules and has been applied to the preparation of oriented P3HT films [1]. The carrier mobilities in a P3HT film before and after rubbing have been reported as the in-plane mobility, i.e., carrier transport occurs parallel to the substrate [1].

Out-of-plane mobility is crucial for the performance of solar cells and LEDs, because the carriers migrate along the direction normal to the substrate of solar cells and LEDs. An increase in the power conversion efficiency of a solar cell employing rubbed P3HT film has been reported [2]. To further improve the performance of solar cells, it is important to investigate the carrier transport and film structure after rubbing. We have investigated the out-of-plane mobility and structure of thin films of P3HT [3], Si-nanocrystal/P3HT [4], and MEH-PPV [5]. In these studies, the out-of-plane mobility was measured using the time-of-flight (TOF) method, while the structure was examined using two-dimensional grazing-incidence X-ray diffraction (2D-GIXD). Here, we introduce recent results for the out-of-plane mobility and structure of a P3HT film after rubbing [3]. The orientation, molecular structure, and morphology after rubbing were investigated using polarized absorption, Raman spectroscopy, and microscopy. The structure change in the out-of-plane direction was investigated using 2D-GIXD.

2D-GIXD measurements of P3HT films before and after rubbing were conducted at beamline **BL19B2** with an X-ray energy of 12.39 keV (λ = 1 Å). The X-ray was irradiated at an incident angle of 0.12° in the direction parallel to the rubbing direction. The scattered X-ray was recorded using a 2D image detector (Dectris, Pilatus 300K).

Figure 1 shows the typically obtained 2D-GIXD patterns of P3HT films before and after rubbing. The (010) peak emerges in the out-of-plane (q_z) direction after rubbing, whereas it is in the in-plane direction (q_{xy}) before rubbing. Since the (010) peak corresponds to the π-π stacking of P3HT, the GIXD result indicates an increase in the out-of-plane π-π stacking, i.e., the face-on orientation. The increase in the face-on orientation can contribute to increasing the out-of-plane mobility because the carriers migrate in the film along the π-π stacking direction.

Figure 2(a) shows the time profile of the TOF signal for holes migrating along the out-of-plane direction in the P3HT film after rubbing. The out-of-plane hole mobility is obtained by analyzing the TOF profile and is enhanced up to eightfold after rubbing. Thus, the rubbing produces a film in which holes efficiently migrate in the out-of-plane direction. After rubbing, the face-on orientation is formed in the out-of-plane direction, as shown in Fig. 2(b). In addition, the in-plane anisotropy of the surface morphology is produced by rubbing, as shown in Fig. 2(c). Figure 2(d) shows the electronic absorption spectra of the π-π* transition of P3HT in the film after rubbing. The anisotropic absorbance indicates the orientation of P3HT molecules in the direction parallel to the rubbing

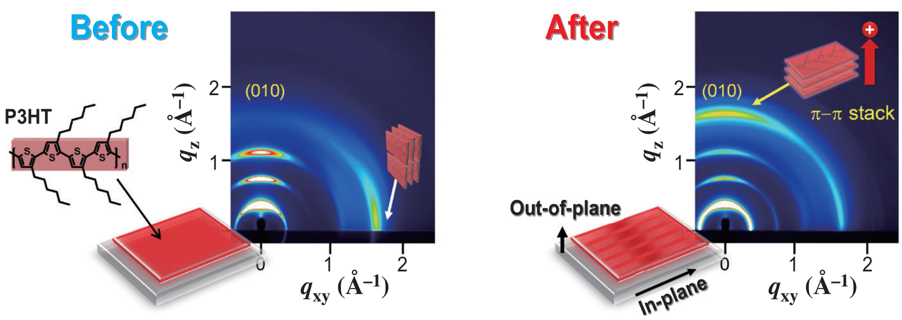

Fig. 1. 2D-GIXD patterns for P3HT films before and after rubbing.

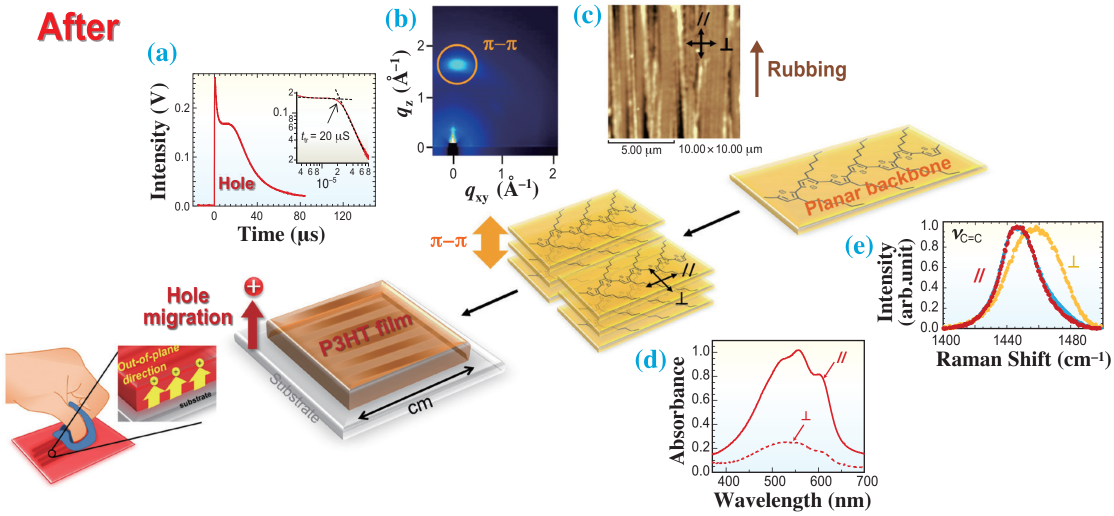

Fig. 2. Hole transport and structure of P3HT film after rubbing. **(a)** TOF, **(b)** GIXD, **(c)** AFM, **(d)** absorption spectra, and **(e)** Raman spectra results. [3]

direction. The degree of aggregation is obtained by analyzing the spectral profile and is enhanced after rubbing. Figure 2(e) shows the Raman spectra of the P3HT film after rubbing. The Raman result reveals an increase in the degree of planarity of the P3HT backbone structure. Thus, the rubbing enhances the out-of-plane mobility, face-on orientation, aggregation, and molecular planarity.

Figure 3 shows the enhancement factors (EFs) of mobility and aggregation resulting from rubbing. The EFs were obtained by using P3HTs different regioregularity (RR). All of the EF values are greater than 1, indicating the enhanced mobility and aggregation in all films with different RR values. These EFs reveal that slight aggregation (EF_{agg} = 1.2) results in a significant mobility enhancement (EF_{μ} = 8). A lower-RR film produces a larger EF. In particular, the hole mobility of the film with a low RR (91%) became almost equal to that of the film with a high RR (98%).

In summary, the eightfold enhancement of the out-of-plane hole mobility was achieved by rubbing. After the rubbing, the π-π stacking of P3HT was formed in the out-of-plane direction, whereas the P3HT backbone was oriented in the in-plane direction. Aggregation and planarity were enhanced by rubbing and facilitated carrier migration in a P3HT thin film [3]. These results are useful for further developing polymer-based devices.

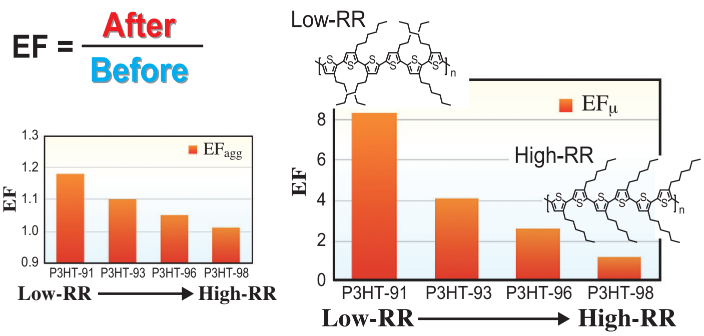

Fig. 3. EF of aggregation (EF_{agg}) and EF of mobility (EF_{μ}) as a function of RR. [3]

Daisuke Kajiya[a], Tomoyuki Koganezawa[b]
and Ken-ichi Saitow[a,c,*]

[a] Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University
[b] Japan Synchrotron Radiation Research Institute (JASRI)
[c] Graduate School of Science, Hiroshima University

*E-mail: saitow@hiroshima-u.ac.jp

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