Study of charge carrier transport in active layer P3HT:ZnO:PCBM hybrid solar cells measured by muon spin relaxation[†]

L. Safriani,^{*1} Risdiana,^{*1} A. Bahtiar,^{*1} A. Aprilia,^{*1} and I. Watanabe^{*2}

Recently, many researchers have been making an effort to obtain high performance of solar cells by modifying the active material of the solar cell. Conjugated polymers are promising active materials. Much attention has been paid to polythiophene and its derivatives owing to their chemical and thermal stability in addition to their potential to absorb the solar spectrum in solar cells. Poly(3-hexylthiophene) (P3HT), a derivative of poly(3-alkylthiophene), presents the highest hole mobility,¹⁾ thus attracting researchers'attention.

Hybrid solar cells that combine organic and inorganic materials have been developed to increase the performance of solar cells. P3HT having the highest hole mobility, when combined with inorganic materials with the highest electron mobility, shows promise for better performance. Zinc oxide (ZnO) is an inorganic material that has high electron mobility and is easy to prepare. In bulk heterojunction systems of solar cells, ZnO behaves as an electron acceptor to dissociate excitons formed in P3HT. For practical application to solar cells, ZnO nanoparticles are prepared to resolve the problem associated with the small diffusion range of P3HT.²⁾ Fullerene and its derivative [6,6]-phenyl C61 butyric acid methyl ester (PCBM) are well-known acceptor materials for polymer solar cells owing to their ability to transfer excitons from polymers within 45 fs.³⁾

In previous studies, ZF- and longitudinal-field (LF)- μ SR measurements were performed on samples of P3HT⁴⁾ and P3HT:ZnO.⁵⁾ For both the samples, it was found that charge carrier transport changes from intra-chain to inter-chain diffusion. For P3HT:ZnO, one-dimensional intra-chain diffusion was observed at low temperatures, while three-dimensional inter-chain diffusion was observed at high temperatures.⁵⁾ The addition of PCBM into the P3HT:ZnO blend increased the charge transfer from P3HT to ZnO and also reduced the aggregation of ZnO nanoparticles.

To clarify the charge carrier dynamics in a bulk ternary system of hybrid materials, we measured charge carrier transport using LF-µSR in the P3HT:ZnO blend by adding a fullerene derivative (PCBM).

Figure 1 shows the LF dependence of the raw asymmetry at 15 K and 25 K. The initial asymmetry increases with increasing LF field owing to the repolarization of the muonium state.⁶⁾ The raw asymmetries at 15 K and 25 K show a clear dependence on field and temperature.



Fig. 1. The asymmetry data of P3HT:ZnO:PCBM at 15 K and 25 K for various longitudinal magnetic fields.

Figure 2 shows the LF dependence of λ_1 in P3HT:ZnO:PCBM, where λ_1 is the depolarization rate associated with the fast component. At 15K, the relationship $\lambda \sim H^{-0.5}$ is observed clearly, which indicate that onedimensional intra-chain diffusion occurs in this system. Compared with the μ SR data for P3HT that show a 25K,³⁾ crossover at the data dimensional for P3HT:ZnO:PCBM show the dimensional crossover from one-dimensional to three-dimensional apparently at a lower temperature. We cannot explain the experimental results immediately, but they are likely related to the advantageous properties of ZnO nanoparticles that facilitate electron transfer.



Fig. 2. The longitudinal-field dependence of the relaxation rate λ_1 of P3HT:ZnO:PCBM at 15 K and 25 K.

With increasing temperature, the charge carrier transfer changes from intra-chain to inter-chain diffusion. One-dimensional intra-chain diffusion is observed in the samples at temperatures below 15K, while three-dimensional inter-chain diffusion is observed at temperatures above 25 K.

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^{*1} Department of Physics, Padjadjaran University

^{*2} RIKEN Nishina Center