2O08

分子動力学シミュレーションによるイオン液体中における フラーレンの結晶成長に関する研究

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【Introduction】

Ionic liquids-mediated vacuum deposition technique has been introduced to achieve high quality crystal growth of fullerene (C_{60}) for organic solar cell application [1]. For realizing high performance solar cell devices, improvement of C_{60} crystallization process is needed. Thin-film ionic liquids (IL) are predicted as suitable solvent media to improve crystallization process of C_{60}. One important aspect in the crystallization process of C_{60} in thin-film IL is diffusion of C_{60}. Understanding the diffusion of C_{60} in thin-film IL by simulation is important for the improvement of the methods since it is difficult to observe molecular level phenomena by experiment. Thus, we study the diffusion of C_{60} in thin-film IL on a graphite substrate by coarse-grained molecular dynamic simulation.

【Method】

All simulations were performed by coarse-grained molecular dynamics simulation at 400 K in the NVT ensemble. We used 2 fs timestep for 1 ns calculation and 400 ps for the relaxation time. Periodic boundary condition and Ewald method were applied in three dimensions. We used 1-butyl-3 methylimidazolium tetra fluoroborate ([Bmim][BF_4]) IL, where $[Bmim]^+$ is the cation and $[BF_4]^-$ is the anion. Density in the simulation cell was determined directly from experiment [2]. Details of coarse-grained models are shown in Figure 1 and all parameters were taken from ref. [3-4].

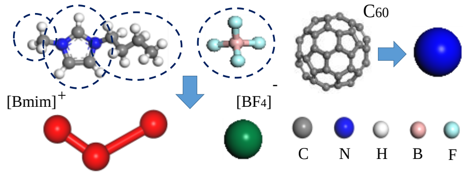

Figure 1 Coarse-grained model.

Table 1 Cation and anion diffusion coefficient of bulk IL without C_{60} calculated in this work compared to the experiment [3].

Diffusion Cofficient (10^{-10} $m^2 \cdot s^{-1}$)	This Work	Experiment
$[Bmim]^+$	3.17	2.75
$[BF_4]^-$	3.39	2.93

【Results】

At first, to confirm the accuracy of our models, we calculate the diffusion coefficient of cation $[Bmim]^+$ and anion $[BF_4]^-$ in IL system without C_{60}. In Table 1, our simulation shows that the diffusion coefficient of cation and anion are 3.17 10^{-10} $m^2 \cdot s^{-1}$ and 3.39 10^{-10} $m^2 \cdot s^{-1}$, respectively. These values are in good agreement with experimental results [3]. Therefore, our simulations are accurate for simulating IL systems. At the next step, we simulate thin-film IL on the graphite substrate as shown in Figure 2a. We observe a layered structure in IL near the substrate and this is also in good agreement with experimental observation [5]. The generation of the layered structure is caused by van der Walls interaction between IL and the substrate. Figure 2b shows the distribution of anion in z direction. There are three peaks at 0.4, 1.1, and 1.6 nm. The substrate affects the structure of IL and its effect almost disappears at 2.2 nm. To reveal the diffusion of C_{60} in thin-film IL, we investigate the diffusion coefficient of C_{60} in different thin-film thickness and compare it with C_{60} in bulk IL systems. Figure 3a shows the simulation of C_{60} in 2 nm thin-film IL case. Figure 3b shows that the diffusion coefficient increases with an increase in thin-film thickness. At 4 nm, the diffusion is almost same as that in the bulk. We suggest that in 2 nm systems case, C_{60} movement is limited because IL is still confined by the substrate as shows in Figure 2b. When the thin-film thickness increases, the confined effect from the substrate fades away, and the upper parts of IL are move more freely. We show the layered structure of thin-film IL near the substrate and reveal that the structure of 2 nm thin-film decreases the diffusion of C_{60}.

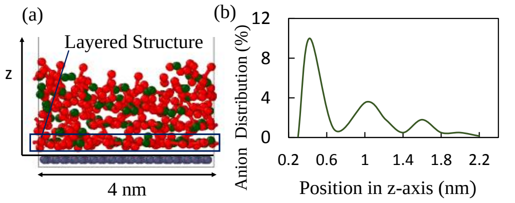

Figure 2 (a) Thin-film IL with graphite substrate and (b) distribution of anion along z direction.

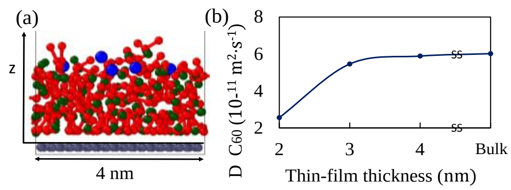

Figure 3 (a) C_{60} in 2nm thin-film IL with a graphite substrate and (b) diffusion coefficient of C_{60} in different thickness thin-film IL.

【References】

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