Suppression of Exciton Dissociation in the Fullerenephthalocyanine/Oxide System

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1 Introduction

Organic solar cells are one of ubiquitous renewable energy generators and are essential for realizing sustainable society. Phthalocyanine and fullerene are often used as electron donor and acceptor molecules, respectively, in organic solar cells. Both molecules absorb visible and ultraviolet lights to generate excitons, which, then, dissociate into free carriers at the donor/acceptor heterojunction, leaving the holes and the electrons in the phthalocyanine and fullerene phases, respectively [1]. On the other hand, our preceding study [2] has indicated that photogenerated excitons in monolayer-thick copper phthalocyanine (CuPc) and C60 layers on a TiO2 substrate stacked in this order, i.e., CuPc/C60/TiO2, behave differently; the excitons in both CuPc and C60 layers undergo dissociation by transferring their electrons to TiO2, leaving the holes in both CuPc and C60 layers. Such carrier dynamics in the CuPc/C60/TiO2 system is reasonable because the energy levels of the valence and conduction bands line up downwardly from CuPc to C60 and to TiO2 [2]. These preceding studies imply that the carrier dynamics is affected by the dimension of the composite materials.

Our aim in the present study is to assess the effect of stacking order of CuPc and C60 on the carrier dynamics and to verify the importance of the composite structure in the organic solar cells. For this purpose, we fabricated a C60/CuPc/TiO2 system with monolayer thicknesses of both C60 and CuPc layers and photoexcited carrier dynamics were examined by time-resolved X-ray photoelectron spectroscopy (TR-XPS). Conventional XPS measurements were also performed to determine the energy level structure of the layered system. It is found that the CuPc layer acts as a barrier for the electron transfer from C60 to TiO2 so that exciton dissociation of C60 is significantly suppressed [3].

2 Experiment

TR-XPS measurements were carried out at beamline (BL) 07LSU of SPring-8 utilizing a laser-pump/synchrotron-radiation-probe technique. The pump laser had a pulse duration of 60 fs and its energy was 3.11 eV. The synchrotron radiation pulses were provided by an F-mode operation of the storage ring. Energy and time resolutions were 0.7 eV and 50 ps, respectively.

XPS measurements were performed at BL-3B and 13B. The overall energy resolution of the measurement systems depended on the photon energy (hν); they were typically 0.25 eV at hν = 60 eV at BL-3B and 0.05 eV at hν = 100 eV at BL-13B.

C60 and CuPc was evaporated on a rutile TiO2(110) surface in ultrahigh vacuum conditions while keeping the substrate at 300 K. Thicknesses of the molecular layers were accessed by the intensity decrease of photoemission signals or Auger electron signals of the substrate.

For more details of the experimental procedure, see our latest work [3].

3 Results and Discussion

Fig. 1 compares valence-band spectra of the C60/CuPc/TiO2 and CuPc/C60/TiO2 systems. The highest occupied molecular orbital (HOMO) levels of CuPc and C60 are 0.7 and 1.6 eV, respectively, for CuPc/C60/TiO2, whereas those for C60/CuPc/TiO2 are 1.1 and 2.3 eV. Since the energy gap between the HOMO and the lowest unoccupied molecular orbital (LUMO) levels of C60 is 1.9 eV, the LUMO of C60 in the C60/CuPc/TiO2 system should be 0.4 eV below the Fermi level. A finite density of states at the Fermi level in
Fig. 2: C 1s spectra of the C$_{60}$/CuPc/TiO$_2$ system acquired with (top) and without (bottom) the pump laser. The power density of the pump laser was 0.39 mJ cm$^{-2}$ per pulse and the spectrum was measured at the delay time of 10 ns. Energies of the pump and probe lights were 3.11 and 385 eV, respectively.

Fig. 3 shows a delay time dependence of the C$_{60}$ C 1s peak shift for C$_{60}$/CuPc/TiO$_2$. For comparison, experimental data obtained from the CuPc/C$_{60}$/TiO$_2$ system is also shown in Fig. 3b [2]. For both systems, the C$_{60}$ peaks move toward the higher binding energies upon laser irradiation by 10–15 meV at most and the magnitude of the shift is diminished gradually at the delay times longer than 100 ns. On the other hand, a clear difference is seen in the delay times below 1 ns: no change in the peak shift is induced in the curve for CuPc/C$_{60}$/TiO$_2$, while the shift energy increases for C$_{60}$/CuPc/TiO$_2$. Solid lines in Fig. 3 are results of least-squares fitting using the sum of exponential functions [3]. For the curve of C$_{60}$/CuPc/TiO$_2$, the initial increase is reproduced by an exponential function with a time constant of 0.8 ns. Under the assumption that the magnitude of the shift reflects the number of the cationized molecules, C$_{60}$ is cationized with the reaction rate of 0.8 ns in C$_{60}$/CuPc/TiO$_2$, whereas C$_{60}$ cationization should be much faster (less than the time resolution of the system, 50 ps) in CuPc/C$_{60}$/TiO$_2$ because the initial enhancement of the energy shift is not observed at > 0.1 ns.

The slow accumulation of cationic C$_{60}$ in C$_{60}$/CuPc/TiO$_2$ is considered to result from slow dissociation of the photogenerated exciton in C$_{60}$ by suppression of the electron transfer from C$_{60}$ to TiO$_2$. Obstruction of electron transfer is apparently caused by insertion of the CuPc layer between C$_{60}$ and TiO$_2$. In the CuPc/C$_{60}$/TiO$_2$ system, the LUMO of C$_{60}$ and the conduction band orbital of TiO$_2$ substrate are overlapped both energetically and spatially. However, the spatial overlap of these orbitals is lifted in C$_{60}$/CuPc/TiO$_2$. Thus, the C$_{60} \rightarrow$ TiO$_2$ electron transfer should proceed via a tunneling process in C$_{60}$/CuPc/TiO$_2$, and this makes the transfer rate lower in C$_{60}$/CuPc/TiO$_2$ than CuPc/C$_{60}$/TiO$_2$.

Our observation shows that the design of the stacking structure near the electrode is another important factor along with the dimension of the composite materials to control the dynamics of photo-generated carriers in organic solar cells.

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References

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