

Suppression of Exciton Dissociation in the Fullerene/Phthalocyanine/Oxide System

Kenichi OZAWA^{1,2,*}, Susumu YAMAMOTO^{3,4}, Tetsuya MIYAZAWA⁵, Keita YANO⁶,
Koji OKUDAIRA⁶, Kazuhiko MASE^{2,5}, and Iwao MATSUDA³¹ Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan² Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK),
Tsukuba, Ibaraki 305-0801, Japan³ Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan⁴ International Center for Synchrotron Radiation Innovation Smart, Tohoku University,
Sendai, Miyagi 980-8577, Japan⁵ SOKENDAI (The Graduate University for Advanced Studies), Tsukuba, Ibaraki 305-0801, Japan⁶ Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan

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 the 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 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 ($h\nu$): they were typically 0.25 eV at $h\nu = 60$ eV at BL-3B and 0.05 eV at $h\nu = 100$ 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

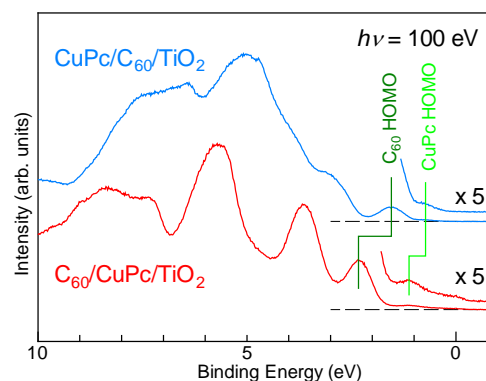


Fig. 1: Valence band spectra for CuPc/C₆₀/TiO₂ and C₆₀/CuPc/TiO₂.

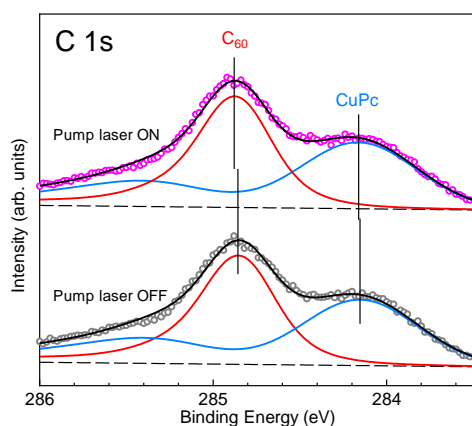


Fig. 2: C 1s spectra of the $C_{60}/CuPc/TiO_2$ system acquired with (top) and without (bottom) the pump laser. The power density of the pump laser was 0.39 mJ cm^{-2} per pulse and the spectrum was measured at the delay time of 10 ns. Energies of the pump and probe lights were 3.11 and 385 eV, respectively.

the spectrum of $C_{60}/CuPc/TiO_2$ support a partial filling of the C_{60} LUMO state. The HOMO-LUMO gap of CuPc is 1.8 eV so that the CuPc LUMO level is well above the Fermi level for both system.

Fig. 2 shows C 1s spectra of $C_{60}/CuPc/TiO_2$ with and without pump laser irradiation. The C 1s spectrum consists of CuPc and C_{60} components, and these components move temporarily towards the higher binding energy side upon laser irradiation. The magnitude of the shift tends to be increased as the power density of the laser is increased. Moreover, the peaks go back to the original positions as the spectrum is measured without the laser. These observations are indicative that the peak shift is a laser-induced and reversible phenomenon. The direction of the peak shift suggests that both C_{60} and CuPc are cationized upon laser irradiation.

An interesting finding of the photoresponse is that the magnitude of the peak shift depends on the delay time (a time difference between the pump and probe pulses). Fig.

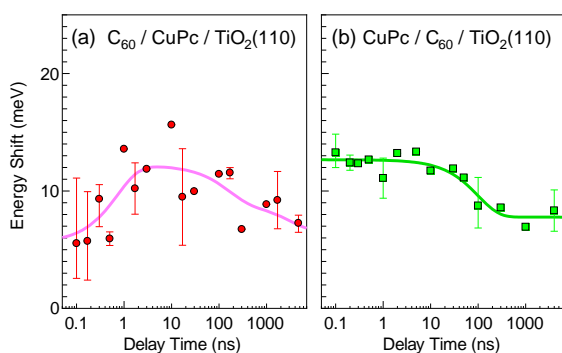


Fig. 3: Change in the laser-induced energy shift of the C_{60} C 1s XPS component as a function of the delay time for $C_{60}/CuPc/TiO_2$ (a) and $CuPc/C_{60}/TiO_2$ (b). Symbols represent the observed data and solid lines are results of least-squares fitting using the sum of exponential functions.

3a 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.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research (grant nos. 16H03867 and 16H06027) from MEXT, Japan. The XPS measurements at the Photon Factory were performed under the approval of the Photon Factory Advisory Committee (proposal nos. 2016G529, 2017G525, and 2018S2-005). The TR-XPS study at BL07LSU of SPring-8 was conducted using the facilities of the Synchrotron Radiation Research Organization, The University of Tokyo (proposal nos. 2016A7503, 2017A7533, 2017B7542, and 2018B7589).

References

- [1] F. Roth *et al.*, *Phys. Rev. B* **99**, 020303(R) (2019).
- [2] K. Ozawa *et al.*, *J. Phys. Chem. C* **123**, 4388 (2019).
- [3] K. Ozawa *et al.*, *J. Phys. Chem. C* (2021), DOI: 10.1021/acs.jpcc.1c03584.

* ozawa.k.ab@m.titech.ac.jp