Photoinduced Electron Transfer Reaction between Electron Donor and Fullerenes on the Surface of Colloidal Semiconductors

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Photoinduced electron transfer (PET) on the surface of semiconductors such as TiO_2 and SnO_2 plays a very important role for the successive photocurrent generation in the photovoltaic cells. To achieve a high efficiency conversion of photons to electrons under the solar light, Ru complexes were used as an initiator of the PET on the semiconductor.[1,2] On the other hand, fullerenes (C_{60}), which acts as a strong oxidant in its photo excited state in solution, is considered to be also good precursor for the PET in the photovoltaic cells. In this work, we observed the PET between the electron donor and C_{60} on the surface of the TiO_2 and SnO_2 colloids by the laser flash photolysis method to investigate the initial process and electron mediation processes of photon-electron conversion.

The C_{60} derivatives capable to attach the surface of colloidal semiconductors are shown Fig. 1. *p*-Anisidine (PAD) was used as an electron donor. The colloidal solutions of the semiconductors were preparated by the hydrolysis of titian (IV) tetraisopropoxide (Wako chemical) or tin (IV) *tert*-butoxide (Aldrich). In Fig. 2, UV-vis spectral changes in PAD, $C_{60}CR_2$ and SnO_2 colloid containing solution were illustrated. Absorption intensity around 400 - 500 nm was growing during the

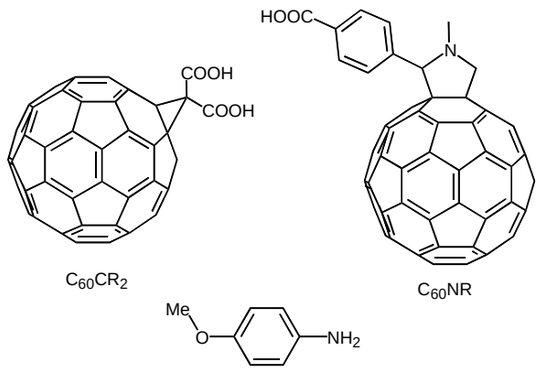

Fig. 1 C_{60} derivatives

irradiation of light longer wavelength than 560 nm. This band was assigned to the PAD radical cation ($PAD^{\bullet+}$). This observation indicates that the electron mediation from $C_{60}CR_2$ radical anion ($C_{60}NR_2^{\bullet-}$) to SnO_2 colloid occurred following the PET between PAD and $C_{60}CR_2$. Nanosecond transient absorption spectra measured by 532 nm laser irradiation, selective excitation of $C_{60}CR_2$ condition, were shown in Fig. 3. The PET from PAD to $^3C_{60}CR_2^*$ was clearly observed. The total decays of $PAD^{\bullet+}$ (460 nm) and $C_{60}NR_2^{\bullet-}$ (1000 nm) are shown in Fig. 4. The decays of the $PAD^{\bullet+}$ and $C_{60}NR_2^{\bullet-}$ were not the same because the electron mediation process from $C_{60}NR_2^{\bullet-}$ to SnO_2 colloid accelerated the decay of $C_{60}NR_2^{\bullet-}$. This difference may be one of the reason of the accumulation of $PAD^{\bullet+}$ during the light irradiation shown in Fig. 2. Now the building-up of the photovoltaic cells based on these systems is in progress.

1. Graetzel, M, *Nature* **2001**, *414*, 338
2. P. V. Kamat, M. Haria, and S. Hotchandani, *J. Phys. Chem. B*, **2004**, *108*. 5166

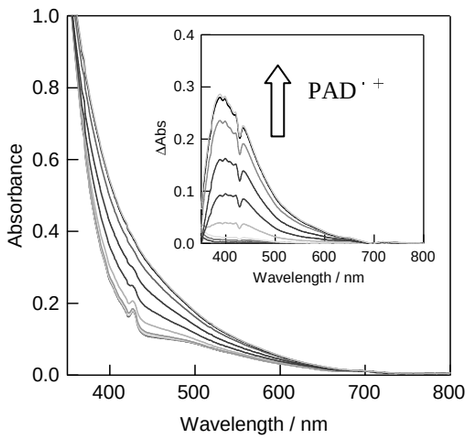

Fig. 2 Uv-vis spectral changes of SnO_2 + $C_{60}CR_2$ + PAD under the light (λ > 560 nm) irradiation.

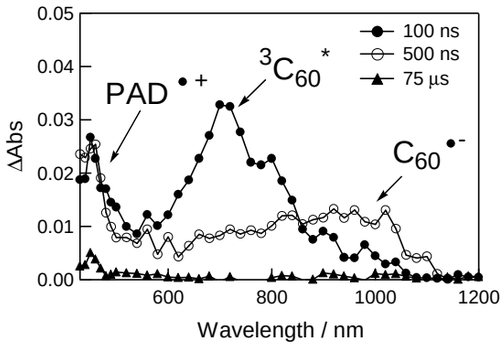

Fig. 3 Transient absorption spectra obtained by 532 nm laser irradiation of SnO_2 + $C_{60}NR_2$ + PAD in EtOH / THF (1:1) solution.

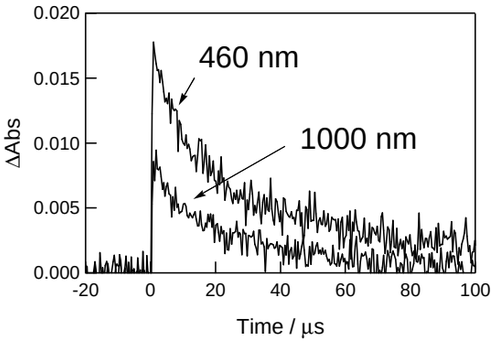

Fig. 4 Total decays of the PAD radical cation (460 nm) and C_{60} radical anion (1000 nm).