Photoinduced Electron Transfer Systems of Fullerene Carboxylic Acids Adsorbed on TiO_2 Nanoparticles

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Fullerenes show excellent electron acceptor abilities in their excited states. A quite large number of papers have reported photoinduced electron transfer processes by employing various experimental techniques including laser flash photolysis method. In order to utilize the generated radical ions in the electron transfer processes as charges of the light-energy conversion systems, several models have been demonstrated. In the present paper, we report photoinduced electron transfer systems of two types of fullerene carboxylic acids adsorbed on TiO_2 nanoparticles, which are expected to accept electrons from the fullerene radical anions generated by intermolecular electron transfer process with electron donor in the solution: The accepted electron can be regard as a carrier in the light-energy conversion systems.

The syntheses of two types of fullerene carboxylic acids, di(carbonyl acid)methano[60]fullerene ($C_{60}CR_2$) and N-methyl-2-(*p*-benzoic acid)-fulleropyorrolidine ($C_{60}NR$) (Figure 1), were carried out according to the reported procedures.[1,2] TiO_2 nanoparticles were prepared from titanium isopropoxide by hydrolysis.

Upon steady state photoirradiation of $C_{60}NR$ on TiO_2 with > 520 nm light in the presence of *p*-anisidine (PAD), triethanol amine (TEOA), and methyl viologen dibromide (MV^{2+}), absorption bands due to $MV^{\bullet+}$ appeared around 600 and 400 nm as shown in Figure 2. These absorption bands of $MV^{\bullet+}$ show continuous growth under light irradiation as shown in the inset of Figure 2. Furthermore, absorption intensity of $MV^{\bullet+}$ was not decreased substantially even after the photoirradiation, indicating persistent $MV^{\bullet+}$. Similar spectral changes were observed in the reaction systems including $C_{60}CR_2$. On the other hand, generation of $MV^{\bullet+}$ was not observed in the reaction system without TiO_2. These findings strongly indicate an electron mediation process of TiO_2 to MV^{2+} from C_{60} radical anion, which was generated from electron transfer between the triplet excited C_{60} and PAD (Scheme). Continuous growth of $MV^{\bullet+}$ can be attributed to decomposition of TEOA radical cation after donation of an electron to PAD radical cation, inhibiting back electron transfer between C_{60} radical anion and PAD radical cation.

In transient absorption spectra of $C_{60}CR_2$ on TiO_2 in the presence of PAD and MV^{2+} by 532 nm laser excitation (Figure 3), an absorption band of triplet excited $C_{60}CR_2$ appeared immediately after the laser excitation. With the decay of triplet excited $C_{60}CR_2$, radical anion of $C_{60}CR_2$ appeared, indicating electron transfer from PAD to triplet excited $C_{60}CR_2$. Generation of $MV^{\bullet+}$ was confirmed after the decay of radical anion of C_{60}. Although electron on TiO_2 was difficult to observe, contribution of TiO_2 was confirmed in the steady state photolysis experiments (Figure 2). Furthermore, the rate constant for the generation of $MV^{\bullet+}$ became low in the presence of TiO_2. This finding can be explained on the basis of electron mediating process in the generation of $MV^{\bullet+}$. In the long time scale measurements of the absorption-time profiles of $MV^{\bullet+}$, persistent $MV^{\bullet+}$ was confirmed supporting the electron transfer process of Scheme.

REFERENCES

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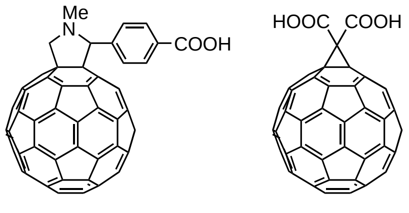


$C_{60}NR$ $C_{60}CR_2$

Figure 1. Molecular structures of $C_{60}NR$ and $C_{60}CR_2$.

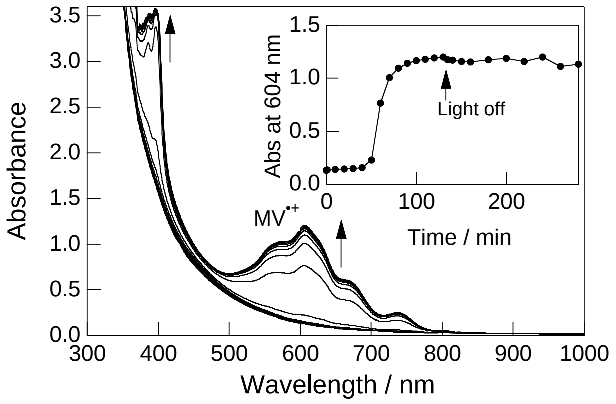
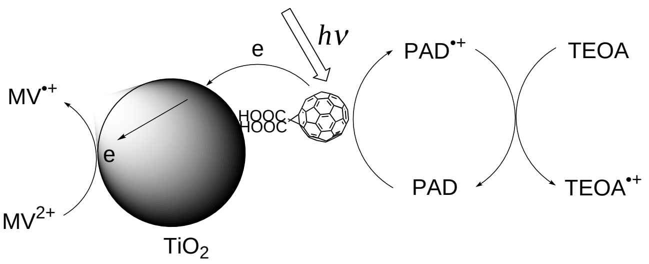
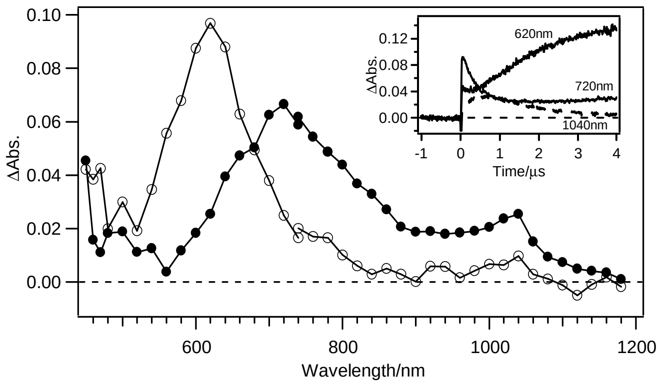


Figure 2. Steady state absorption spectra of TiO_2, $C_{60}NR$, PAD, TEOA, and MV^{2+} under steady light irradiation.





Scheme

Figure 3. Transient absorption spectra of TiO_2, $C_{60}CR_2$, PAD and MV^{2+} at 0.25 (●) and 2.5 μs (○) after 532 nm

laser irradiation. Inset: Absorption –time profiles.