Photoabsorption and Photoionization Studies of Fullerenes and Development of High-Efficiency Organic Solar Cells

Department of Photo-Molecular Science
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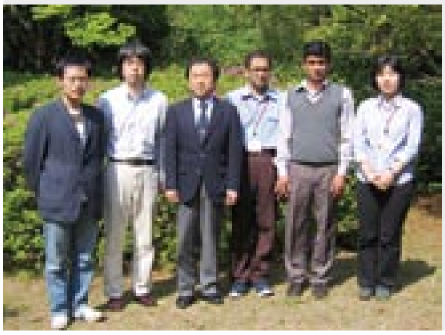

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The total photoabsorption cross section curves of C_{60} and C_{70} at $h\nu$ = 1.3 to 42 eV were determinined by using photon attenuation method in the UVSOR facility. Moreover, the yield curves of singly- and multiply-charged photoions from fullerenes were measured at $h\nu$ = 25 to 200 eV. We have thus studied the mechanisms and kinetics of sequential C_2-release reactions on the basis of (i) the yield curves for the fragments $C_{60(70)-2n}{}^{z+}$ as a function of the primary internal energy of the parent $C_{60(70)}{}^{z+}$ and (ii) the 3D velocity distributions (velocity map imaging) of the fragments.

In the second topic we have fabricated dye-sensitized solar cells (DSCs) containing Ru dye and iodide electrolyte and measured their short-circuit current density and the intensity of the transmitted light to estimate the wavelength dependence of the incidence photon-to-current conversion efficiency (IPCE) and photoabsorbance (ABS) in the range of 300 to 1000 nm. In addition, we evaluated the quantum yield (APCE) of DSCs for the electron injection from the excited orbital of Ru dye to the conduction band of TiO_2 nano particles. Our final goal is to develop DSCs with high performance and long lifetime by improving ABS and APCE mainly in the near infrared region.

1. Photoabsorption Cross Section of C_{70} Thin Films from the Visible to Vacuum Ultraviolet[1)]

Absolute photoabsorption cross sections of C_{70} thin films were determined for $h\nu$ values from 1.3 to 42 eV using photon attenuation. The spectrum showed a prominent peak of 1320 Mb at 21.4 eV with several fine structures mostly due to $\sigma \rightarrow \sigma^*$ single-electron excitation. The complex refractive index and complex dielectric function were calculated up to 42 eV with Kramers-Kronig analyses. From the present data of C_{70} thin films, the cross section curve of molecular C_{70} was calculated using the standard Clausius-Mossotti relation dealing with correction of the local electromagnetic field, with a plausible assumption that the anisotropy in molecular structure of C_{70} was smeared out by molecular rotation at room temperature.

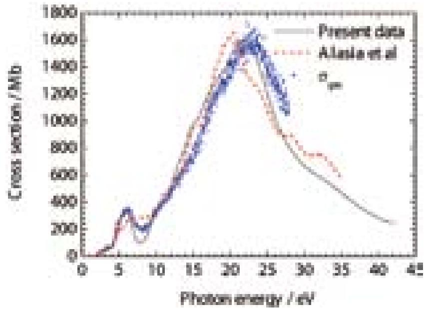

Figure 1. Absolute photoabsorption cross sections of a single C_{70} molecule.

2. Potential-Switch Mass Gate Incorporated into a TOM Spectrometer[2)]

A photoionization spectrometer for velocity map imaging (VMI) has been developed for measuring the scattering distribution of fragment ions from polyatomic molecules. The mass gate and an ion reflector in the spectrometer are capable of discriminating ions with a particular mass-to-charge ratio m/z. The basic functions and feasibility of these devices were tested experimentally. The photoions from SF_6 were extracted into a time-of-flight (TOF) mass spectrometer by pulsed electrostatic fields. Mass resolution of the fragments was very poor in Figure 2a, because the stationary reverse electric field exists at the ionization region in the absence of the extraction pulses. When the pulse-application timing on the mass gate was tuned to a specific m/z, an exclusive peak of the selected ions was present on a TOF spectrum (Figure 2b).

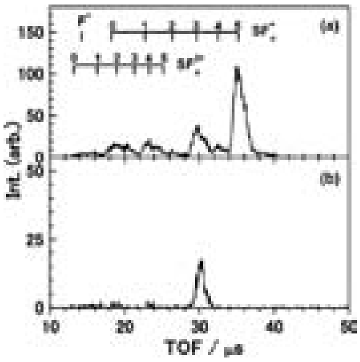

Figure 2. (a) TOF mass spectrum of photofragments from SF_6 at $h\nu$ = 100 eV. (b) Peak of SF_3^+ selected by applying a 5-V pulsed voltage to the mass gate at an appropriate timing.

3. Mass-Selected Velocity Map Imaging of Fullerenes

The performance of the mass gate in the VMI spectrometer was investigated by the computer simulations of the ion trajectories of photofragments from C_{60}. The initial three-dimensional velocity distribution of C_{58}^+ was projected onto the image plane with an energy resolution better than 10 meV. The C_{58}^+ image was free from the contamination of other ions such as C_{60}^+ and C_{56}^+. We have also tried to deconvolute the effect of the initial beam temperature with the aid of a low pass filter.[3)]

4. Measurements of IPCE and Photo-Absorbance of Dye-Sensitized Solar Cells

The IPCE curve a in Figure 3 calculated from the density of the output short-circuit current J_{SC} and the number of the incident photons on the cell I_P agrees with the curve b that was obtained using a laboratory instrument fitting a Xe lamp. An IPCE value was improved to be 0.7 when the layer of TiO_2 film is thicker than 16 µm. Two APCE curves in Figure 4 were calculated in different ways of estimation of ΔI_P, according as whether the scattered SR in the TiO_2 film is partly absorbed by dye (curve b) or not (curve a). It is clear that such multiple absorption may favorably take place in shorter wavelengths and contributes to electron injection from the dye. The quantum yield of the electron injection is expected to be more than 0.8 at shorter wavelengths, whereas it gradually decreases at longer wavelengths.

5. Transient Fluorescence Spectroscopy of DSCs

We observed fluorescence decay by time-resolved single photon counting using free electron laser (FEL) of ~580 nm. Figure 5 shows the dependence of the decay curves of the DSCs on the fluorescence wavelength. The fluorescence lifetime appears to increase with increasing wavelength. This suggests that the conversion rates to other electronic states are comparable to those of the electron injection and fluorescing emission. The decay curves were monitored at 720 nm for a complete DSC and a photovoltaic electrode of TiO_2 film covered with Ru dye. The apparent fluorescence lifetime of the complete DSC is longer than those of the photovoltaic electrode, due to either slower electron injection induced by one of the additives in the electrolyte or aggregation of the dye molecules at the surface of TiO_2.

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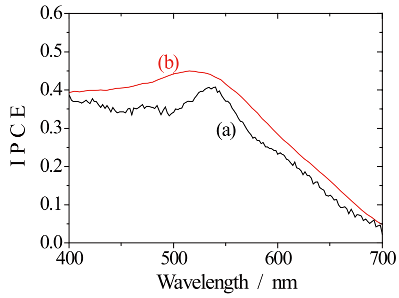

Figure 3. IPCE curves obtained using (a) the SR source and (b) an exclusive IPCE spectrometer.

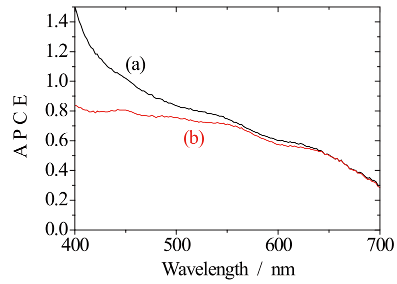

Figure 4. APCE curves calculated in different ways of estimation of ΔI_P.

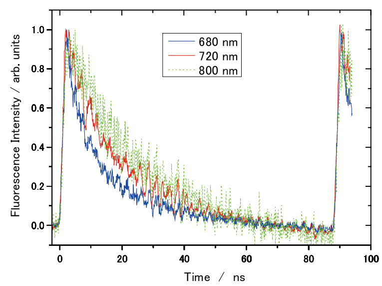

Figure 5. Fluorescence decay curves of DSSC and photovoltaic electrodes, obtained by FEL photolysis.

References

1) H. Yagi, K. Nakajima, K. R. Koswattage, K. Nakagawa, H. Katayanagi and K. Mitsuke, *J. Chem. Phys.* **130**, 234510 (2009).
2) H. Katayanagi, B. P. Kafle, C. Huang, Md. S. I. Prodhan, H. Yagi, and K. Mitsuke, *Nucl. Instrum. Methods Phys. Res., Sect. A* Submitted.
3) Md. S. I. Prodhan, H. Katayanagi, C. Huang, H. Yagi, B. P. Kafle, and K. Mitsuke, *Chem. Phys. Lett.* **469**, 19 (2009).