

## 有機太陽電池中の励起色素分子の過渡発光分光

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**抄録:** 有機色素、酸化チタン半導体と電解質液を用いて色素増感型の有機太陽電池 (DSSC) を作成し、放射光やレーザーを用いてその基本性能を試験した。エネルギー変換効率は最大で7%であった。6桁に渡る光強度の範囲で、入射光子-出力電流変換効率 (IPCE) がほぼ一定であることを初めて確認した。さらに色素と半導体界面のバルク接合における電子注入速度を推定するために、自由電子レーザー (FEL) で色素を励起し、時間分解法によって脱励起で生ずる赤外・近赤外発光を検出した。発光寿命が波長や電極種に依存することを見出し、それらの結果を色素の凝集効果や界面近傍での伝導帯の曲がり効果に基づいて解釈した。

**1. IPCE and APCE measurements** The measurements of photoabsorption cross sections and output short-circuit currents allowed us to determine the incident photon-to-current efficiency (IPCE) and the absorbed photon-to-current efficiency (APCE). The IPCE is calculated from the number of electrons  $J_{SC}S/e$  fed into an external circuit divided by that of incident photons on the cell,  $\Phi_p = I_p S = PS/h\nu$ . The APCE is derived from  $J_{SC}S/e$  divided by the number of photons absorbed by the dye  $\Delta\Phi_p$ . Here,  $J_{SC}$  is the density of the output short-circuit current;  $S$  is the area of the DSSC;  $e$  is the electron charge;  $I_p$  and  $P$  are the intensity and power density of SR, respectively.

The DSSC was prepared by applying nanocrystalline mesoporous  $\text{TiO}_2$  paste on an FTO glass and sintering the paste at  $450^\circ\text{C}$ . After soaking the glass in dye solution ("N3" or "N719"), iodide electrolyte (50 mM tri-iodide in acetonitrile, ionic liquid and 4-*tert*-butyl pyridine) was dropped on the  $\text{TiO}_2$  electrode which was combined with a counter electrode covered with Pt. The formula of N719, for instance, is written as  $\text{RuL}_2(\text{NCS})_2 \cdot 2\text{TBA}$  (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetrabutylammonium). Here, dye molecules are firmly grafted onto the surface of  $\text{TiO}_2$  through their carboxylate substituents. Our DSSC exhibits a maximum energy conversion efficiency of  $\sim 7\%$ .

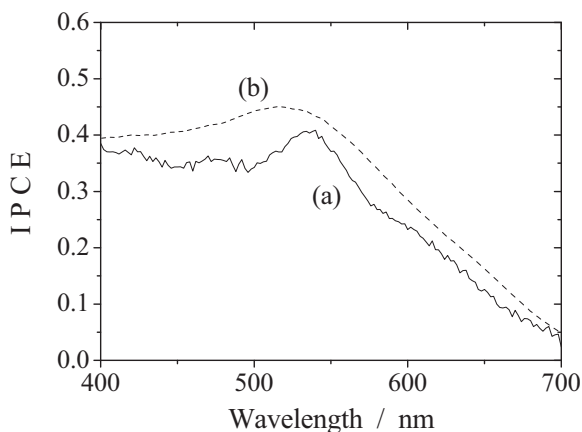


Fig. 1. IPCE curves obtained using (a) the SR source and (b) an exclusive IPCE spectrometer.

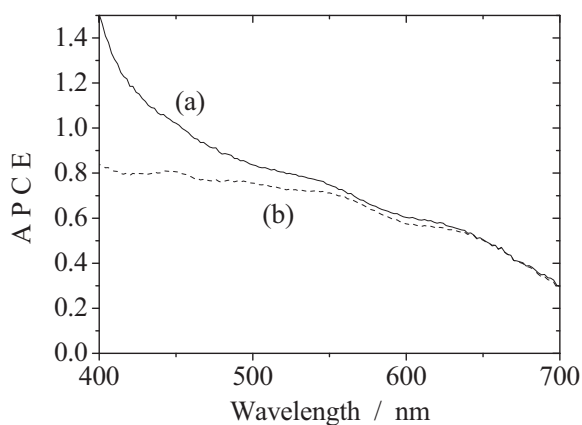


Fig. 2. APCE curves calculated in different ways of estimation of  $\Delta\Phi_p$ .

The IPCE curve a in Fig. 1 calculated from  $J_{SC}$  and  $\Phi_p$  agrees with the curve b that was obtained using an instrument fitting a Xe lamp dedicated for the IPCE measurements. An IPCE value was improved to be 0.7 when the layer of  $TiO_2$  film is thicker than 16  $\mu m$ . Figure 2 shows the two APCE curves calculated in different ways of estimation of  $\Delta\Phi_p$ , 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.

## 2. Transient fluorescence spectroscopy of DSSC

Electron injection is known to occur in a time scale of 10 ps or faster, if  $TiO_2$  film together with Ru dyes is covered in inert solvents. In contrast, the rate of injection is drastically reduced by one or two orders of magnitude in a typical redox active electrolyte. Several authors argued that the compounds in the electrolyte added for reducing undesirable electron-hole recombination have an effect of raising the conduction band edge of  $TiO_2$ . Eventually, the high-efficiency DSSCs often show lifetimes as long as 1 ns with respect to electron injection, that is, injection dynamics which is just fast enough to compete with the fluorescence decay (10 ~ 100 ns) of the excited state of the Ru dyes.

We observed fluorescence decay by time-resolved single photon counting using FEL of ~ 580 nm at a repetition rate of 11.3 MHz. The decay curves in Fig. 3A were monitored at 720 nm for (a) a photovoltaic electrode of  $TiO_2$  film prepared with N719, (b) that with Black dye, and (c) a complete DSSC fabricated using N719. The apparent fluorescence lifetime of the complete DSSC is longer than those of the two photovoltaic electrodes, 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  $TiO_2$ . Figure 3B shows the dependence of the decay curves of the DSSC on the fluorescence wavelength. The fluorescence lifetime appears to increase with increasing wavelength. This suggests that the conversion rates to other electronic states (*e.g.* that to the lowest triplet state) are comparable to those of the electron injection and fluorescing emission.

**References** [1] B. O'Regan, M. Grätzel, *Nature*, 353 (1991) 737. [2] Y. Tachibana et al., *J. Phys. Chem.*, 100 (1996) 20056. [3] A. Reynal et al., *J. Am. Chem. Soc.*, 130 (2008) 13558. [4] S.E. Koops, J.R. Durrant, *Inorg. Chim. Acta*, 361 (2008) 663.

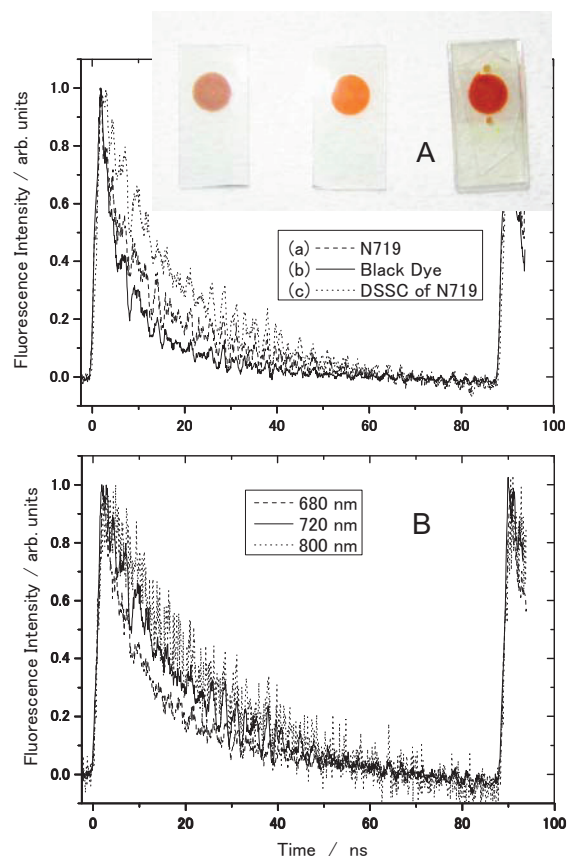


Fig. 3. Fluorescence decay curves of DSSC and photovoltaic electrodes, obtained by FEL photolysis.