

## Electron injection processes in dye-sensitized nanocrystalline rutile-TiO<sub>2</sub> films

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Dye-sensitized solar cells (DSCs) have been studied as an attractive new class of solar cells. Although DSCs have the potential for practical applications, they are unavailable as commercial products, because device performance and long-term stability have not yet been optimized. To date, solar light-to-energy conversion efficiency ( $\eta$ ) for DSCs is 11.9%. To improve device performance, detail analysis of the primary processes of DSCs is needed. In this context, we have so far studied charge generation and recombination processes in dye-sensitized TiO<sub>2</sub> nanocrystalline films by using wide-wavelength-range (400-2500 nm), highly sensitive transient absorption (TA) spectroscopy and time-resolved microwave conductivity (TRMC) technique.<sup>[1]</sup>

For DSC study, anatase-TiO<sub>2</sub> has been mainly used as electrode material, whereas there are other type TiO<sub>2</sub>, such as rutile and brookite. Primary processes in DSCs including electron injection and recombination would be affected by crystal structure. Accordingly, systematic study on crystal structure difference may give new insight for further understanding about the primary processes in DSCs. Here we studied electron injection processes in dye-sensitized rutile-TiO<sub>2</sub> nanoparticles.

We prepared a paste containing commercially available rutile-TiO<sub>2</sub> nanoparticles (STR-100N, Sakai Chemical Industry Co., LTD). Diameter of the particle was about 6 nm. The paste was printed on a glass plate. After calcination of the plates for 1 h at 800 K, transparent rutile-TiO<sub>2</sub> nanocrystalline films were obtained. Dye-sensitized nanocrystalline films were prepared by immersing the films into dye-solutions.

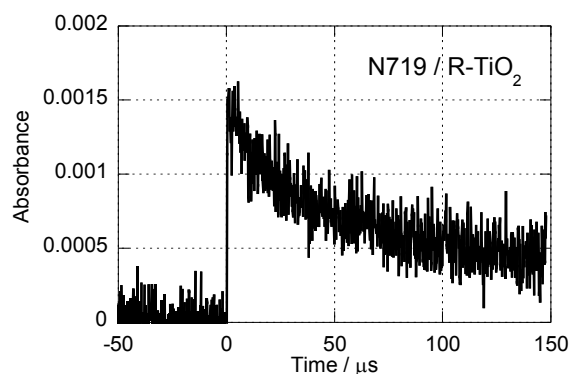


Figure 1. Transient absorption decay profile in N719 / R-TiO<sub>2</sub> observed at 830 nm ( $I_{\text{ex}} = 50 \mu\text{J cm}^{-2}$ ).

Figure 1 shows typical transient absorption signal for N719 sensitized rutile-TiO<sub>2</sub> nanocrystalline films (N719 / R-TiO<sub>2</sub>) observed at 830 nm. Excitation light intensity was  $I_{\text{ex}} = 50 \mu\text{J cm}^{-2}$ . Since oxidized form of N719 has an absorption peak at around 800 nm, the signal corresponds to generation and recombination of charge produced in R-TiO<sub>2</sub> particles. The signal decays within microsecond time region, indicating slow charge recombination, which is similar to N719 sensitized anatase-TiO<sub>2</sub> nanocrystalline films (N719 / A-TiO<sub>2</sub>).

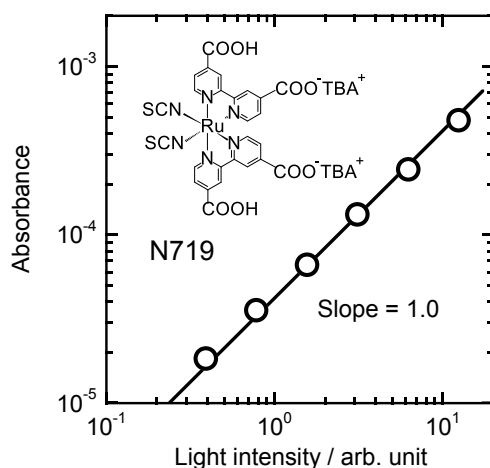


Figure 2. Transient absorption signal as a function of excitation light intensity for N719 / R-TiO<sub>2</sub>.

Figure 2 shows transient absorption signal (absorbance) as a function of excitation light intensity ( $I_{\text{ex}}$ ) for N719 / R-TiO<sub>2</sub>. Under such excitation conditions, transient absorption signals are proportional to  $I_{\text{ex}}$ . This suggests that high density excitation effect, such as ultra-fast charge recombination, can be ignored effectively. It should be noted that very small absorbance ( $< 10^{-4}$ ) have to be measured to obtain such linear relation. Since absorption coefficient of N719 in oxidized form is available,<sup>[1]</sup> electron injection efficiency ( $\Phi_{\text{inj}}$ ) can be evaluated using the value of the fraction of absorbed photons and excitation light intensity. As a result,  $\Phi_{\text{inj}}$  for N719 / R-TiO<sub>2</sub> is evaluated to be  $\Phi_{\text{inj}} = 1$ , which is similar to that for N719 / A-TiO<sub>2</sub>.<sup>[1]</sup>

Although only a few attempts have been carried out for DSC devices based on rutile-TiO<sub>2</sub>,<sup>[2]</sup> the results presented in this study clearly shows that rutile-based DSCs have a potential for high performance devices.

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#### References:

- [1] R. Katoh and A. Furube, *J. Photochem. Photobiol. C Photochemistry Reviews* **2014**, 20, 1.
- [2] N.-G. Park, J. van de Lagemaat, and A. J. Frank, *J. Phys. Chem. B* **2000**, 104, 8989.