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Femtosecond Diffuse Reflectance Transient Absorption for Dye-Sensitized Solar Cells under Operational Conditions: Effect of Electrolyte on Electron Injection

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A dye-sensitized solar cell (DSSC)[1] is one of the next generation of solar cells, and recently, their device performance has been increasing gradually, with a reported maximum efficiency of 11−12%.[2,3] Understanding the reaction mechanism of photon energy conversion into electric current and voltage as a function of numerous parameters that determine the solar cell configuration is important for achieving improvements in performance. Electron injection from the photoexcited dye to semiconductor nanoparticles (normally TiO_2), electron transport through a nanoporous network of the semiconductor, and regeneration of the oxidized dye by a redox pair (normally I^-/I_3^-) must be fast and efficient. The initial process, electron injection, must be very efficient (i.e., a 100% quantum yield is strongly desired) because the subsequent processes never compensate for any failure of the initial process.

The quantum yield of photocurrent generation is usually evaluated by the incident photon to current conversion efficiency (IPCE). Excellent DSSCs give IPCE values larger than 80% and as high as 90%. An IPCE of 100% is impossible, however, because of reflection and absorption of incident light by the transparent electrode that holds the dye-sensitized semiconductor film and relays electric current to the external circuit.

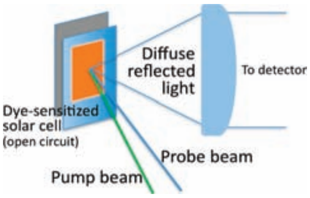

Figure 1. Schematic diagram illustrating the use of diffuse reflectance transient absorption spectroscopy to measure a completely fabricated dye-sensitized solar cell.

Transient absorption (TA) spectroscopy is widely used to directly observe the electron injection process in dye-sensitized semiconductor films, and the reaction mechanism has been understood deeply as a function of the sensitizer dye (with different LUMO levels, different distances to the semiconductor surface, and different charge transfer character), semiconductor, and environment (e.g., simply in air, in solution, and in electrolyte).[4−9] Also, additives in the electrolyte and coadsorbates are known to affect the electron injection dynamics.[8,10,11] Because of the variety of factors that influence the reaction, it is impossible to predict the reaction rate and efficiency in the actual solar cells simply from the device design. Since TA spectroscopy requires the samples to be optically transparent, the "real" reactions in a DSSC have never been observed, and in every case, only a part of the device has been tested. These difficulties have prevented us from confirming that the designed processes are actually occurring.

Diffuse reflectance transient absorption spectroscopy was realized by Wilkinson et al.[12,13] in the microsecond time region in 1981, and femtosecond resolution (i.e., a few hundred fs) was achieved by Bowman et al.[14] in 1995 and Asahi et al.[15,16] in 1996. These techniques have been successfully applied to powder samples such as organic crystals and semiconductor particles and have deepened our understanding of photochemistry in solids. Here we utilized this technique to reveal the photoinduced interfacial electron transfer dynamics under operational conditions in DSSCs whose performance had been characterized beforehand.

To highlight the usefulness of this technique, well-known (or almost standard) configurations of DSSCs were chosen. N719 sensitizer dye, a TiO_2 semiconductor nanocrystalline electrode, and the I^-/I_3^- redox pair were used. First, two electrolyte solutions were used for comparison, one based on acetonitrile (ACN) and the other on the ionic liquid (IL) 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$). Both included additives of 0.1 M LiI, 0.05 M I_2, and 0.5 M 4-*tert*-butylpyridine (TBP) as a typical manner of electrolyte preparation.[17,18] ACN is the most general solvent and has been used to give the best records of performance, while ILs have recently been used to improve the device lifetime because ILs have negligible vapor pressure and do not evaporate between two electrodes. DSSCs with ILs, however, tend to give IPCEs lower than those with ACN by 10−25%.[19] Our ACN and IL DSSCs gave peak IPCEs of 78 and 53% at peak wavelengths around 550 nm. The IPCE was recorded using low light intensities to ensure that no limitations of the electrolyte were observed.

Our diffuse reflectance transient absorption spectroscopic system was constructed by modifying a conventional (transmittance-mode) TA system based on an amplified Ti:sapphire laser combined with an optical parametric amplifier to obtain excitation light at 532 nm and white-light continuum generation optics to obtain probe light.[8] As shown in Figure 1, the two light beams were focused on the DSSC under open-circuit conditions from the transparent conductive glass side, and diffusely reflected light was collected by an achromatic lens (80 mm focal length, 50 mm diameter) to relay the probe light to an InGaAs photodetector (Thorlabs, PDA10CS) through a monochromator (Acton Research, SpectraPro-150). The pump light intensity was 0.4 μJ/pulse and the focal size on the DSSC electrode was ∼0.3 mm in diameter. The TA intensity is displayed as % absorption $= (1 - R/R_0) \times 100$, where R and R_0 are the probe pulse intensities with and without excitation, respectively. Although the TA intensity in the diffuse reflectance

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configuration depends on the scattering property of the sample,[16] comparing absorption intensities between the two DSSC samples was not a problem because ACN ($n = 1.34$) and $EMImBF_4$ ($n = 1.41$) have similar refractive indexes, resulting in the same scattering properties. Furthermore, the % absorption was kept less than 10% in order to ensure its linearity with respect to the transient species density.[16]

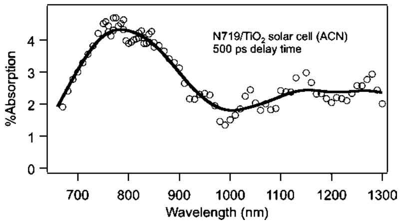

Figure 2. Transient absorption spectrum (500 ps delay time) of a DSSC with N719 dye and the acetonitrile electrolyte including 0.1 M LiI, 0.05 M I_2, and 0.5 M TBP, which produced an IPCE of 78%.

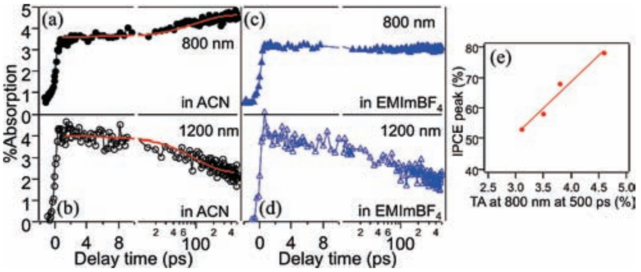

Figure 3. Transient absorption kinetics of DSSCs with the (a, b) acetonitrile and (c, d) ionic liquid electrolyte solutions at (a, c) 800 and (b, d) 1200 nm. (e) Relation between the IPCE and the transient absorption intensity at 500 ps and 800 nm for different electrolytes (see the text for details).

The TA spectrum at 500 ps after excitation of the ACN DSSC is shown in Figure 2. The absorption band at 800 nm is easily ascribed to the oxidized from of N719 ($N719^+$) on the basis of agreement with reported spectra,[8] indicating the occurrence of electron injection. The broad absorption in the near-IR region (1000−1300 nm) could be due to either the lowest triplet state (N719*), injected electrons (e^-), or both.[20]

To observe the kinetics of these three transient species, TA signals at 800 and 1200 nm were recorded as a function of the delay time for the two DSSC samples. The results are shown in Figure 3. For the ACN DSSC, the 800 nm kinetics shows two rise components with time constants of <1 ps and ~100 ps, followed by a plateau. As is already well-known, the two time constants are assigned to electron injection from the excited singlet and triplet states, respectively.[4−6,9] Corresponding to the ~100 ps rise, decay kinetics due to electron injection into TiO_2 from N719* was observed at 1200 nm. The red lines in the figure are fits using a single-exponential function with a 100 ps time constant.

On the other hand, the IL DSSC did not show any slow rise at 800 nm after the prompt subpicosecond rise, while the decay kinetics at 1200 nm was present. These kinetics indicate that N719* was quenched by some process other than electron injection. It is very significant to notice that the ratio of the $N719^+$ signal sizes for the two DSSC at 500 ps ($4.6{:}3.1 \approx 100{:}67$) agreed well with the ratio of IPCE values ($78{:}53 \approx 100{:}68$). This result clearly indicates that the low IPCE for the IL DSSC is mostly determined by the initial electron injection efficiency and that the subsequent processes (e.g., slow diffusion of redox ions) are not significantly responsible for the low IPCE. Here it would be important to mention that the IL DSSC without dye showed very small TA signals (see Figure S1 in the Supporting Information), indicating that I_3^- excitation[21] is negligible.

We also checked a 1:1 mixed solvent of ACN and $EMImBF_4$ to see which of the two solvents has a greater influence on the electron injection process. The TA kinetics at 800 and 1200 nm are shown in Figure S2. Although a small rising component on the order of 100 ps can be seen, the signal amplitude at 500 ps is as small as 3.5%, giving a good correlation with the IPCE peak value of 58%.

To further examine whether different ILs have similar effects, we measured DSSCs with a different electrolyte: 0.1 M LiI, 0.4 M I_2, and 0.5 M TBP in 1-methyl-3-propylimidazolium iodide (MPImI). The result (Figure S3) again showed flat kinetics at 800 nm with a TA intensity of 3.8% at 500 ps, giving another good agreement with the IPCE peak of 68%. The obtained linear relation between IPCE and TA intensity at 500 ps and 800 nm is plotted in Figure 3e. Therefore, the presence of imidazolium ions seems to be responsible for this low reactivity. To clarify the mechanism, further experiments are planned now, and the results will be published elsewhere.

Diffuse reflectance transient absorption spectroscopy has been demonstrated to be a very powerful technique for examining how ultrafast processes relate to the final output of solar cell devices. This technique can be applied for examining the effect of not only electrolyte solvents but also other additives in the electrolytes, device aging, and so on. These spectroscopic investigations of actual DSSCs under operational conditions will help researchers in the field accelerate device development.

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Supporting Information Available: Additional TA kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

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