



Spectroscopic investigations on Stark components observed in photoinduced absorption measurements for dye-sensitized solar cells



Katsuichi Kanemoto^{*}, Shinya Domoto

Department of Physics, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

ARTICLE INFO

Available online 18 May 2013

Keywords:

Dye-sensitized solar cell
Photo-induced absorption
Stark effect
Screening effect

ABSTRACT

Spectral features of the Stark signals that are observed in photoinduced optical spectra for dye-sensitized solar cell systems are examined using continuous-wave photoinduced absorption techniques combined with bias application. The Stark signals are found to almost disappear with increasing the bias voltage. The disappearance of Stark signal indicates that there exists a unidirectional built-in electric field acting on neutral states of dye molecules. Time-dependent measurements demonstrate that the Stark signal slowly rises, whereas the photocurrent exhibits a rapid rise and then decays slowly. This finding indicates that, although the screening effect occurs at the beginning of the cell operation, it is gradually lost during the operation. We conclude that the occurrence of the Stark effect is attributed to the electrolyte ions that gradually become deactivated or transfer away from the TiO₂ layer.

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1. Introduction

Since the first report by O'Regan and Grätzel in 1991 [1], dye-sensitized solar cells (DSCs) have attracted much interest as potential low-cost alternatives to conventional photovoltaic systems. The operation of DSC is known to consist of many partial processes caused by subset of material systems such as dye-sensitizers, a mesoporous oxide semiconductor and electrolyte ions. The underlying physics and chemistry in the cell operation are hence difficult to resolve, which has been the cause of exiguous progress in the energy-conversion efficiency. One of the most direct methods to examine such physical and chemical processes is spectroscopy, and it has indeed been employed for the research of the processes [2,3].

Recently, it has been sequentially reported that characteristic signals resulting from a Stark effect are included in optical spectra for DSC systems obtained from continuous-wave (cw-) photoinduced absorption (PIA) and transient-absorption measurements [4–8]. The previous reports suggested that occurrence of the Stark signal can directly affect essential operation processes of DSC such as charge injection into the oxidized semiconductor nanoparticles and regeneration of dye-sensitizers [4–8]. Elucidation of the origin of the signals is thus expected to present direct insight into understanding the operation processes of the DSC cells.

When applying spectroscopic techniques for a complicated system consisting of many operation processes like DSCs, a technique to enable decomposition of overlapping components is effective and

required. A cw-PIA technique combined with two-phase lock-in detection is then effective as it can decompose overlapping signals by adjusting the signal phase. The cw-PIA technique is also effective for the research of solar cells as it presents spectroscopic information under cw-photoirradiation that can mimic solar irradiation. In this article, spectroscopic features of the Stark component were investigated using the cw-PIA technique for DSCs with (Bu₄N)₂[Ru(dcbpyH)₂(NCS)₂] (dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl) (N719) as a sensitizer. We particularly employed the technique combined with bias application for complete devices operating under illumination. Such experiments also enable simultaneous measurements of the spectroscopic signals and photocurrent. It is shown that the measurements are shown to withdraw information on the Stark signals and reveal the influence of the Stark components upon the solar cell operation. The obtained findings provide direct insight into mechanisms of the DSC operation.

2. Experimental details

DSCs used were fabricated by the following procedures. Nanocrystalline TiO₂ paste (Solaronix, particle size 15–20 nm) was cast as mesoporous films on the transparent FTO glass conductive substrate. The TiO₂ films were sintered at 450 °C for 15 min and used as a working electrode. N719 (Aldrich) was employed as a dye-sensitizer. Sensitization was achieved by immersing the TiO₂ films in the N719 solution in ethanol (0.4 mg/ml) for 1 day. An alcohol based paint containing a chemical platinum precursor (Platisol T, Solaronix) was deposited on another FTO substrate and annealed at 450 °C for 10 min to obtain a transparent platinum layer. The FTO substrate with the platinum layer was used as a counter electrode. DSCs used in this study were fabricated by injecting an acetonitrile-based electrolyte

^{*} Corresponding author. Tel.: +81 6 6605 2550; fax: +81 6 6605 2522.
E-mail address: kkane@sci.osaka-cu.ac.jp (K. Kanemoto).

including both lithium iodide and imidazolium iodide as iodide salts (AN50, Solaronix) between the working and counter electrodes and by contacting the two electrodes face-to-face.

For cw-PIA measurements, a diode-pumped solid-state laser with cw 473 nm output (CNI) was used for photoexcitation. The laser output was modulated using an optical chopper with 70 Hz. The probe beam for the measurements was produced using a tungsten/halogen lamp and detected with a Si photodiode after passing a monochromator. The cw-PIA signals were measured by monitoring the probe signal using a dual-phase lock-in amplifier, which yielded in-phase and quadrature-phase signal outputs. We note that “in-phase” of the results shown later does not mean zero phase against the reference phase in our results but was set to decompose overlapping PIA signals. Time responses of the PIA signals and photocurrent were measured using a digital oscilloscope through an input resistance of 1 M Ω . All measurements were performed at room temperature.

3. Results and discussion

Cw-PIA measurements were performed for the working devices of N719-DSC. The PIA spectrum for the N719-device under the short-circuit condition is shown in Fig. 1(a). Also the steady-state absorption spectrum of the N719-DSC is shown in Fig. 1(b). The absorption spectrum has a peak around 2.3 eV, which is assigned to the absorption peak of N719 in the cell. In general, when a cw-PIA spectrum measured using a dual-phase lock-in technique results from a single

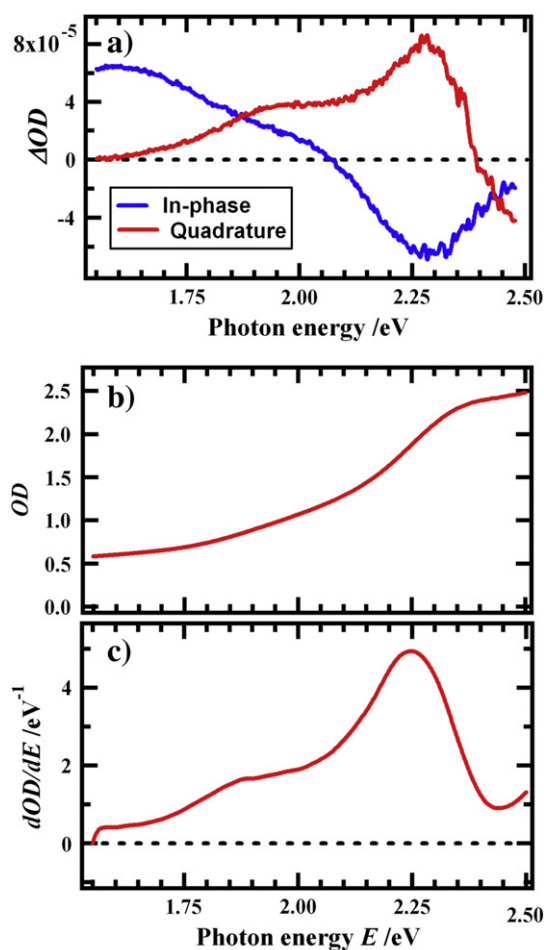


Fig. 1. (a) Cw-PIA spectra for a N719-based solar cell under the short-circuit condition. (b) Steady-state absorption spectrum for the N719-cell. (c) Differential of the spectrum in b. The horizontal broken line indicates the baseline for the spectrum.

component of photoexcitations, the amplitude of quadrature-phase signals can be made zero by adjusting the lock-in phase. The PIA spectrum for the N719-device always gave non-vanishing quadrature signals for various changes in the phase, indicating coexistence of two or more components in the spectrum. The PIA spectrum shown in Fig. 1(a) is the one obtained by purposely setting the lock-in phase to a certain value. The in-phase PIA signals have a negative peak around 2.28 eV which is close to the absorption peak in Fig. 1(b). The peak is thus assigned to the photo-bleaching signals of N719. The in-phase PIA spectrum also has a positive peak around 1.6 eV, which is assigned to the absorption signal of cations of N719 generated by injection of electrons into the TiO₂ layer. This assignment is consistent with previous reports [9–13]. On the other hand, the spectrum of quadrature phase has positive peaks around 1.93 and 2.27 eV, whose spectral features are obviously different from those of the in-phase signals. The different spectral features as well as the different lock-in phase between the in- and quadrature phase signals demonstrate the presence of two or more spectral components of different origins.

The differential steady-state absorption spectrum for the N719 cell is shown in Fig. 1(c). Its spectral lineshape is found to resemble that of the quadrature PIA-spectrum, although their peak position is somewhat different. As described in some preceding reports [4–7], spectral features similar to differential absorption spectra are regarded as evidence for a Stark effect to be observed. The spectrum of the quadrature component is thus regarded as resulting from the Stark effect. It should be noted here that, by selecting relevant lock-in phase, the Stark signal was able to be almost entirely decomposed out of the whole PIA spectrum. This is a definite advantageous feature of the cw-PIA technique over transient absorption measurements that occasionally suffer from spectral overlap of transient signals.

It has recently been reported by Ardo et al. that the Stark shift for a sensitized TiO₂ nanocrystallite system with ruthenium-polypyridyl compounds results from a strong electric field as large as 2.7 MV/cm that is accompanied by injection of electrons from the Ru-sensitizer into TiO₂ [6,7]. Also, the electric field was asserted to be not unidirectional with respect to the laboratory frame but normal to the TiO₂ surface toward the sensitizers; viz., its direction is different for each sensitizer with respect to the laboratory coordinate system [6,7]. Related to these reports, we examined a response of the quadrature-Stark signals to an external electric field. Fig. 2(a) presents the applied voltage-dependence of the intensity of the quadrature signal that was measured at 2.1 eV in the same lock-in phase as that in Fig. 1(a). It demonstrates that the intensity of quadrature signal is remarkably reduced with increasing the voltage. We also measured the cw-PIA spectra for the same device under 0.45 V applied bias to confirm the trend found in Fig. 2(a), which are shown in Fig. 2(b). The spectra demonstrate that the Stark signal in the quadrature-phase is indeed reduced almost to zero at the bias voltage. In contrast, the lineshape and intensity of the in-phase signal are almost unchanged compared to those in Fig. 1(a), except for the spectral region around 2.4 eV. The observation around 2.4 eV suggests that the bleaching component consumed for the photoexcitation may slightly change depending on the applied bias voltage.

These results provide important clues to the origin of the observed Stark signals. Spectral features that disappear depending on the applied bias have ever been shown to result from the Stark effect and well established for organic film semiconductors [14,15]. In the present case, the Stark signals are given by the total electric field consisting of that by the applied bias and a built-in electric field including a local field [6,7]. The disappearance of the Stark signals in Fig. 2(b) indicates that a unidirectional built-in electric field is present within the cell and that the applied voltage canceled the effect of the unidirectional built-in electric field. The magnitude of the disappeared built-in electric field is estimated to be ~450 V/cm, under the assumption that the inter-electrode distance of the cell was about 10 μ m.

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