



Transient states and the role of excited state self-quenching of indoline dyes in complete dye-sensitized solar cells



Jan Sobuś^{a, b}, Jerzy Karolczak^{b, c}, Dariusz Komar^b, Juan A. Anta^d, Marcin Ziółek^{b, *}

^a NanoBioMedical Centre, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland

^b Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland

^c Center for Ultrafast Laser Spectroscopy, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland

^d Departamento de Sistemas Físicos, Químicos y Naturales, Area de Química Física, Universidad Pablo de Olavide, Ctra. Utrera, Km 1, E-41013 Sevilla, Spain

ARTICLE INFO

Article history:

Received 28 August 2014

Received in revised form

6 October 2014

Accepted 9 October 2014

Available online 18 October 2014

Keywords:

Indoline dyes

Dye sensitized solar cells

Ultrafast spectroscopy

Dye aggregation

Titanium dioxide nanoparticles

Zinc oxide nanoparticles

ABSTRACT

The photo behaviour of indoline dye D149 on different metal oxide nanoparticles in functioning solar cells is investigated by time-resolved studies in the time range from 100 fs to several ns. The cells are also characterized by standard photovoltaic measurements. The electron injection is found to occur on the time scales from <200 fs to several tens of ps. Locally excited (LE) and charge transfer (CT) excited states of the dye are identified to participate in the electron injection and dye deactivation mechanisms. The dependence of the ultrafast dynamics on the coadsorbent concentration and energy density of the pump pulse indicates the important role of excited state self-quenching. A decrease in the photocurrent of the cells upon aging (very fast for ZnO and slower for TiO₂ nanoparticles) is found to be correlated with the transient absorption kinetics, with a probable explanation suggested as electrolyte-induced dye rearrangement and aggregate formation.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Indoline dye D149 [1] is a popular metal-free sensitizer used in dye-sensitized solar cells (DSSC) [2,3]. The best sunlight conversion efficiency of DSSC with this dye and iodine-based liquid electrolyte is 9% [4], which can be compared to record efficiencies of best metal-free dyes, 10.2% with iodine-based electrolyte [5], 10.65% with cobalt-based electrolyte [6], ruthenium dyes 11.7% [7], and porphyrin dyes, 13.0% [8]. Besides the high efficiency, D149 showed remarkable promising properties when used with less volatile ionic liquids, solid state electrolytes and alternative metal oxides [4,9–13]. DSSC systems with this dye were also widely studied in the context of the observed transient Stark shift [14–18]. Moreover, the new dyes containing indoline moiety have recently shown very high conversion efficiencies [6,19].

Dynamics and quantum yield of electron injection in DSSC, which can be studied by ultrafast laser spectroscopy techniques [20–28], are important parameters that might determine the sunlight conversion efficiency of the device [29,30]. This issue became even more important in recent years, when it was revealed

that in many cases the rate of electron injection from the excited state of the dye to the conduction band of metal oxide is slower in the complete cells than in the isolated systems investigated before [31–35]. Therefore, since the characteristic time scale is often longer than sub-ps, many internal deactivation processes present in the dye might efficiently compete with electron injection and lower the photovoltaic performance of DSSC. In particular, we have recently shown that lower photocurrent of D149 solar cell with ZnO nanoparticles compared to those with TiO₂ ones is directly related to the ultrafast processes occurring in the first 500 ps and that electron injection is slower for ZnO cells than for TiO₂ [36].

D149 dye has been studied in solution by femtosecond transient absorption [37] and femtosecond up-conversion techniques [38]. These studies revealed a formation of charge transfer (CT) state in polar solvent and solvent-dependent decay of CT state. Moreover, picosecond fluorescence studies with time-correlated single photon counting (TCSPC) technique indicated the occurrence of isomerization process [39] and the excited-state proton transfer process [40] as responsible for the enhanced deactivation rate. Femtosecond up-conversion of D149 on TiO₂ films showed a decay of the first singlet excited state with the averaged time constant of about 2 ps [12]. A different conclusion was drawn from femtosecond transient absorption studies of D149 (with the coadsorbent) on TiO₂ and ZnO films in the visible range [17]. In that studies the

* Corresponding author. Tel.: +48 61 829 5011.

E-mail address: marziol@amu.edu.pl (M. Ziółek).

ultrafast (<250 fs) dynamics of electron injection was observed, similar for both metal oxides. However, our recent investigation of complete solar cell of D149 without coadsorbent revealed much worse electron injection efficiency in ZnO than TiO₂ cells [36]. Next, for the reference system of D149 on ZrO₂ films fs transient absorption studies showed similar ultrafast (<250 fs) formation of a cation–electron complex (explained by the interaction of the dye with the trap states below ZrO₂ conduction band) [17]. On the contrary, TCSPC studies of D149/ZrO₂ films showed excited state deactivation on the time scale of hundreds of ps (fast component) and single ns (slow component), with increasing lifetime for higher coadsorbent (chenodeoxycholic acid, CDCA) content [39]. The mid-infrared measurements in complete D149 solar cells indicated the double exponential <300 fs to 30 ps electron injection kinetics [34]. However, for high intensity of the pulses the kinetics became significantly faster [34]. The above results, often in contradiction to each other, clearly show the need of further investigation of the dynamics of fully organic dyes, like D149, in DSSC to understand which processes play a key role in functioning devices.

Therefore, in this contribution we have significantly extended our previous study to better understand the ultrafast processes occurring in D149 molecule attached to metal oxide nanoparticles in complete solar cells. For comparison, we have also measured D149 in solution and on metal oxide films in air. The main novel features of the present studies are the following: (i) the femtosecond transient absorption measurements in the visible spectral range (450–800 nm) were performed with a higher signal-to-noise ratio and longer time window up to 3 ns; (ii) new femtosecond transient absorption studies in near-infrared (NIR, 800–1500 nm) spectral range were used; (iii) studies with different amount of coadsorbent and different pump pulse intensity were performed. All of these enabled us to better explain the differences between the dynamics in TiO₂ and ZnO solar cells, to understand the discrepancy between previous ultrafast results of D149, and to discover new processes and transient states in D149 relevant for efficient electron injection. We believe that our studies enable better understanding of the photophysics of indoline dyes interacting with inorganic nanomaterials. Moreover, the mechanisms we found should be relevant for many all-organic dyes with high extinction coefficient used in DSSC and our findings are important for improving solar cell efficiency in general.

2. Materials and methods

Indoline dye D149, chenodeoxycholic acid (CDCA) and Al₂O₃ nanoparticles (diameter <50 nm) were purchased from Sigma–Aldrich. ZnO (VP ZnO20) and TiO₂ (P25) nanoparticles were received from Evonik. The procedure of preparing the paste with oxide nanoparticles was the same for all the materials, with the exception of acetic acid content: it was 0 ml for ZnO, 0.5 ml for TiO₂ and 1 ml for Al₂O₃. Pastes were prepared as follows. First 3 g of nanoparticles powder was mixed with acetic acid, 20 ml of ethanol and left in ultrasonic bath for 3 h. Then another solution of 10 ml α -terpineol, 1.5 g of ethyl cellulose and 13.5 g of ethanol was prepared. Two solutions were mixed together and placed in ultrasonic bath for another hour. Afterwards they were stirred for 16 additional hours. Finally, the ethanol was removed with a rotary evaporator operating at 60 °C and the ready to use paste was obtained.

The films were deposited by doctor-blade technique on fluorine doped tin oxide (FTO) glass plates and heated at 450 °C (TiO₂ and Al₂O₃) or 420 °C (ZnO) for 60 min. Then, the films were immersed in a 0.2 mM solution of D149 with different concentrations of CDCA (0 mM, 0.2 mM and 2 mM) in acetonitrile (ACN): tert-butanol mixture (1:1) and kept at room temperature for about 1 h. The platinised counter electrode was obtained by spreading a Pt-based

solution (Platisol T, Solaronix SA) on FTO glass and annealing at 450 °C. The transmission of Pt layered electrode varies from 75% at 450 nm to 90% at 800 nm with respect to pure FTO glass. To make a complete solar cell (the active area of 1.1 cm² was prepared), the counter electrode was assembled with thermal adhesive film (25 μ m Surlyn, Meltronix, Solaronix SA) that acts as separator and sealing element. The cells were filled (by vacuum backfilling method) with a commercial liquid electrolyte (Iodolyte AN-50, Solaronix SA) containing the I⁻/I₃⁻ redox couple ([I₂] = 50 mM) in ACN solution.

For ultrafast transient absorption experiments a commercial femtosecond broadband transient absorption spectrometer (Helios, Ultrafast Systems) was used in a single-beam configuration, with all reflective white light continuum generator and depolarizer in the pump beam to avoid influence of rotational dynamics. The femtosecond pulses were provided by Spectra Physics setup consisting of MaiTai SP oscillator, Spitfire Ace amplifier (pumped by Empower laser) and Topas Prime wavelength convertor (optical parametric amplifier). The pump pulses were at 555 nm and the IRF (pump-probe cross correlation function) was 250–300 fs (FWHM). The typical pump pulse energy was 500 nJ, corresponding to energy density of about 1 mJ/cm². In some experiments 200 nJ and 2 μ J pulses were also used. The probe light continuum was generated in sapphire or YAG-type crystal. All the spectra analyzed were corrected for chirp of white light continuum. The transient absorption measurements were performed in the spectral ranges 450–800 nm (VIS) and 800–1500 (NIR) and in the time range of up to 3 ns.

The transient absorption spectra are the combination of positive signals originating from the absorption of transient species, negative signals due to ground state depopulation (corresponding spectrally to steady-state absorption bands), and negative signals due to stimulated emission from the excited state (occurring for the wavelength for which steady-state emission is present). To analyze the transient absorption dynamics in more detail, we used a global approach. The global analysis of the data was done using Surface Explorer program (Ultrafast Systems) which fits multi-exponential function (convoluted with IRF of our setup, FWHM between 250 and 300 fs) to the kinetic vectors of selected number of singular values and reproduces the spectra of the amplitudes associated with the time components. As a result, the characteristic time constants are revealed for the whole spectral range investigated (in our case combined VIS and NIR regions), and the wavelength-dependent amplitudes associated with these time constants are obtained (also called decay associated difference spectra). The positive value of the amplitude at certain wavelength indicates a change towards less positive (or more negative) transient absorption signals at this wavelength, while a negative value of amplitude indicates opposite. In all figures presenting transient absorption spectra the time zero (maximum of IRF) is set at 0 ps, while for all figures showing kinetic traces it is shifted to 1 ps in order to present the time axis in logarithmic scale.

Analysis at particular probe wavelength was done by fitting stretched exponential function (convoluted with IRF) to the transient absorption signals. The function is defined as:

$$A(t) = A_0 e^{-(t/\tau)^\beta} \quad (1)$$

This function contains two parameters: the characteristic time τ and the dispersion parameter β ($0 < \beta < 1$, lower β values mean more stretched decay, extending the decay time scale). The average time of the process described by function (1) was calculated as:

$$\tau_{AVG} = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (2)$$

Download English Version:

<https://daneshyari.com/en/article/6600420>

Download Persian Version:

<https://daneshyari.com/article/6600420>

[Daneshyari.com](https://daneshyari.com)