Experimental decoupling of the quantum efficiencies of light harvesting, electron injection, and steady state charge collection in the dye solar cells

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Quantitative assessment of the photocurrent limiting factors is essential for systematic development of the dye solar cell (DSC). The light harvesting efficiency η_{LH} of the cell can be estimated based on optical characterization of the cell components [1]. The electron injection efficiency (η_{INJ}) has been studied by fast transient absorption spectroscopy and by measuring the spectral incident-photon-to-collected-electron efficiency defined as

$$\eta_{IPCE}(\lambda, d) = \eta_{LH}(\lambda, d)\eta_{INJ}(\lambda)\eta_{COL}(\lambda, d) \ , \tag{1}$$

where η_{COL} is the electron collection efficiency (η_{COL}) and d the photoelectrode film thickness. A standard method for obtaining a rough estimate of η_{COL} has been dynamic measurements of the electron diffusion coefficient (D) and lifetime (τ), which determine the electron diffusion length $L = (D\tau)^{1/2}$ [2], the requirement for a high performance solar cell being $L \gg d$. However, the quantitative realization of steady state photocurrent limitations by $L < d$ has not been investigated systematically.

We have recently addressed this problem by studying experimentally the effect of d and the direction of illumination on η_{IPCE} (eq 1) [3]. A new methodology for quantitative factorization of eq 1 into its partial quantum efficiencies was presented and demonstrated with results from TiO$_2$ DSCs prepared by the compression technique on glass substrates. Two types of pressed TiO$_2$ photoelectrode films were investigated: with and without additional sintering at 450 °C.

The methodology is based on quantitative determination of the absorbed-photon-to-collected-electron efficiency $\eta_{APCE} = \eta_{IPCE}/\eta_{LH} = \eta_{INJ}\eta_{COL}$ by η_{IPCE} and optical measurements. While η_{COL} is sensitive to L and its relation to d and the light penetration depth $1/\alpha(\lambda)$, η_{INJ} is considered to be independent of d. Hence, decoupling of spectral η_{COL} and η_{INJ} can be pursued by experimental variation of d and the illumination direction. Two methods for this purpose were derived based on the standard diffusion model of electron generation and collection [4].

The first method involves extrapolation of η_{APCE} vs. d data to $d \rightarrow 0$, where we expect $\eta_{COL} \rightarrow 100$ %, and hence $\eta_{APCE} \rightarrow \eta_{INJ}$. The η_{INJ} was relatively low and strongly wavelength dependent (Fig 1a), which was attributed to a poor energetic matching between the dye excited states and the TiO$_2$ acceptor states due to the chosen electrolyte

composition. Yet, this method was not internally consistent as the $\eta_{APCE,}$ and hence, η_{COL} *increased* with d in these cells, meaning that L increased with d.

This results was confirmed by the second method which is based on quantitative comparison of η_{APCE} at the opposite illumination directions. The ratio $\eta_{APCE,CE}/\eta_{APCE,PE}$ is independent of η_{INJ} and allows determination of L as a function of d. The method was consistent with the data in the spectral region close to 535 nm where the electron generation rate was independent of d. The estimated L increased substantially with d being much lower in the cells with pressed-only TiO$_2$ films (Fig 1b). We attribute this effect qualitatively to the dependence of L on the electron concentration that increases with d at the short circuit conditions. This was also consistent with the light intensity dependence of η_{IPCE}.

An intriguing question is whether the same conclusions on η_{COL} and L as obtained here from the steady state data would be reached by dynamic photocurrent and photovoltage measurements of D and τ. Fig. 1c shows L determined by standard analysis of intensity modulated photocurrent (IMPS) and photovoltage (IMVS) spectroscopy measurements at the short circuit and open circuit conditions respectively. Consistently with the static L, the dynamic L increases linearly with d in the both type of cells being shorter in the pressed-only cells. The results differ quantitatively, but it is too early to say whether this is due to the differences in the experimental conditions, or a fundamental feature of the static vs. dynamic response of the DSC. This question will be addressed in our future work.
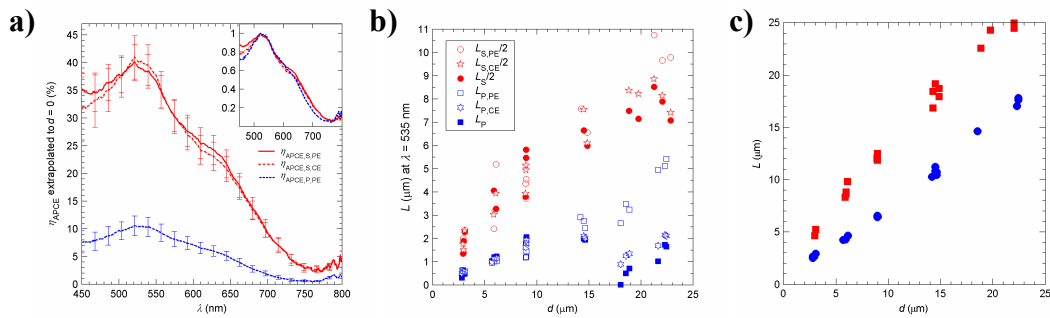

Fig. 1. Results for sintered (S, red) and pressed-only (P, blue) TiO$_2$ photoelectrode films. a) The η_{APCE} at $d \rightarrow 0$. The inset shows that the spectral shape is similar in the both type of cells. b) Steady state L at the short circuit conditions, c) L by standard IMPS and IMVS measurements and analysis.

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