*Supplementary Information*

Density of State Determination of Two Types of Intra-Gap Traps in Dye-Sensitized Solar Cell and Its Influence on Device Performance

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S1. Performance of the targeted DSSC device
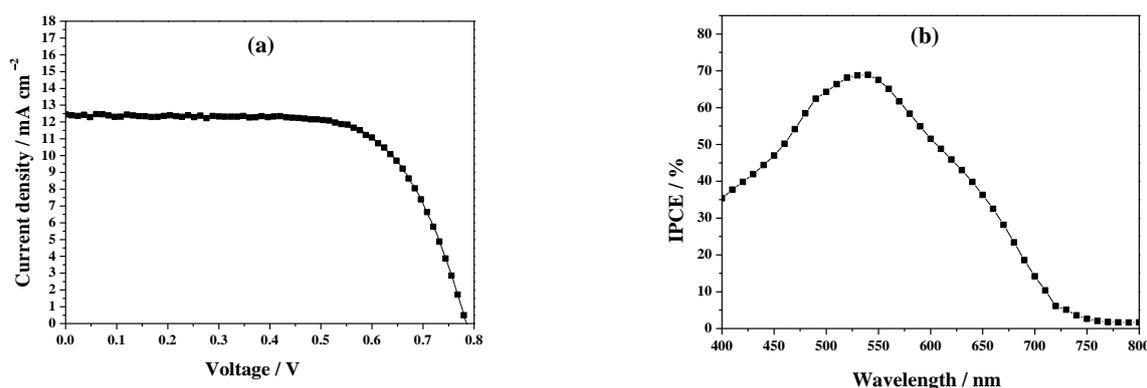
Figure 1. (a) Current density-voltage characteristics under simulated AM1.5 illumination (100 mW/cm^2) for a typical P25-based DSSC sensitized with N719. **(b)** The corresponding incident photon to current conversion efficiency (IPCE) action spectrum. J_{SC} = 12.45 mA cm^{-2}, V_{OC} = 784 mV, FF = 68.4 %, PCE = 6.68 %

S2. Photovoltage dependence of chemical capacitance and DOS

The chemical capacitance (C_μ) can be written as

$$C_\mu \equiv e^2 \frac{\partial n_t}{\partial E_{Fn}}$$

$$= e^2 \left(\frac{\partial n_S}{\partial E_{Fn}} + \frac{\partial n_D}{\partial E_{Fn}} \right), \tag{s1}$$

where e is the unit charge, n_t is the density of trapped electrons, E_{Fn} stands for the quais-Fermi level, and n_S and n_D refer to the electron densities in shallow and deep trap states respectively.

On the other hand, n_t and the electron density in conduction band (n_{cb}) can be written as

$$n_t = \int_{E_{vb}}^{E_{cb}} g_t(E) f(E, E_{Fn}) dE \quad \text{and} \quad n_{cb} = N_{cb} f(E_{cb}, E_{Fn}),$$

where E_{cb} and E_{vb} are the band edge energies of conduction band and valence band respectively, N_{cb} is the density of effective states in conduction band, and $g_t(E)$ and $f(E, E_{Fn})$, respectively, are the density of trap states as a function of energy E, and the Fermi-Dirac distribution function known as

$$g_t(E) = \frac{N_t}{k_B T_0} \exp\left(\frac{E - E_{cb}}{k_B T_0}\right) \tag{s2}$$

and
$$f(E, E_{Fn}) = \frac{1}{1 + \exp\dfrac{E - E_{Fn}}{k_B T}}. \tag{s3}$$

Following the absolute-zero approximation for trapped electrons and the Boltzmann approximation for conduction-band electrons,[s1] the electron densities n_t and n_{cb} can be expressed as the functions of E_{Fn},

$$n_t = N_t \left[\exp\left(\frac{E_{Fn} - E_{cb}}{k_B T_0}\right) - \exp\left(\frac{E_{vb} - E_{cb}}{k_B T_0}\right) \right] \tag{s4}$$

and
$$n_{cb} = N_{cb} \exp\left(\frac{E_{Fn} - E_{cb}}{k_B T}\right), \tag{s5}$$

where N_t is the density of trap states and T_0 and T represent the characteristic temperature of trap states and the room temperature, respectively.

In analogy to the above n_t expression, the two different types of trapped electron densities, n_S and n_D, can be written as

$$n_S = N_S \left[\exp\left(\frac{E_{Fn} - E_{cb}}{k_B T_S}\right) - \exp\left(\frac{E_{vb} - E_{cb}}{k_B T_S}\right) \right] \tag{s6}$$

and
$$n_D = N_D \left[\exp\left(\frac{E_{Fn} - E_{cb}}{k_B T_D}\right) - \exp\left(\frac{E_{vb} - E_{cb}}{k_B T_D}\right) \right], \tag{s7}$$

where N_S and N_D are the overall amount of *shallow* trap states and *deep* trap states respectively, and T_S and T_D are the corresponding characteristic temperatures. Substituting Eqs. (s6) and (s7) into Eq. (s1) and making use of the relation $V_{ph} = (E_{Fn} - E_{redox})/e$, where V_{ph} and E_{redox} are the photovoltage and the redox energy level of the electrolyte respectively, we obtain the biexponential expression of chemical capacitance as a function of the photovoltage

$$C_\mu = e^2 \left[B_1 \exp\left(\frac{e}{k_B T_S} V_{ph}\right) + B_2 \exp\left(\frac{e}{k_B T_D} V_{ph}\right) \right], \tag{s8}$$

where the pre-exponential factors B_1 and B_2 are defined as

$$B_1 = \frac{N_S}{k_B T_S} \exp\left(\frac{E_{F0} - E_{cb}}{k_B T_S}\right) \quad \text{and} \quad B_2 = \frac{N_D}{k_B T_D} \exp\left(\frac{E_{F0} - E_{cb}}{k_B T_D}\right). \tag{s9}$$

S3. Photovoltage dependence of trap-limited electron transport time

Because of the electric field screening effect of electrolyte and/or the negligible potential drop across the nanoscale TiO$_2$ particles, diffusion but not drift is expected for electron transport in the TiO$_2$ film. Further, because

of the electron trap-detrap equilibrium between the trap states and the conduction band, the one dimensional continuity equation can be written as

$$\frac{\partial n(x)}{\partial t} = \alpha \eta I e^{-\alpha x} + D_n \frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x) - n_0(x)}{\tau_n},$$ (s10)

where $n(x)$ is the total electron density in conduction band and trap states, α is the effective absorption coefficient of the adsorbed dyes, η is the electron injection efficiency, $I(x)$ is incident light intensity, D_n is chemical diffusion coefficient, $n_0(x)$ is the electron density in dark, and τ_n is the lifetime of electron.

The chemical diffusion coefficient D_n can be further expressed by using the electron diffusion coefficient in the conduction band (D_{cb}) as[s2]

$$D_n = \frac{\partial n_{cb}}{\partial n} D_{cb} = \frac{\partial n_{cb}}{\partial n_{cb} + \partial n_t} D_{cb}.$$ (s11)

The time constant of charge transport (τ_{tr}) and the chemical diffusion coefficient (D_n) hold the relation, $\tau_{tr} = d^2/(2.35 D_n)$,[s3] where d stands for the TiO$_2$ film thickness. This together with Eq. (s11) lead to

$$\tau_{tr} = \left(1 + \frac{\partial n_t}{\partial n_{cb}}\right) \tau_{tr}^{cb},$$ (s12)

where $\tau_{tr}^{cb} = d^2/(2.35 D_{cb})$ is the electron transport time constant in the conduction band. Eq. (s12) indicates that the transport time constant is determined by the relative electron density distribution between the trap states and the conduction band.

Eq. (s12) can be rewritten as

$$\tau_{tr} = \tau_{tr}^{cb}\left(1 + \frac{\partial n_t / \partial E_{Fn}}{\partial n_{cb} / \partial E_{Fn}}\right),$$

which together with the density functions n_t (Eq. (s4)) and n_{cb} (Eq. (s5)) lead to

$$\tau_{tr} = \tau_{tr}^{cb} + \left[\frac{N_t T}{N_{cb} T_0} \exp\left(\frac{T_0 - T}{k_B T_0 T} E_{cb}\right) \exp\left(\frac{T - T_0}{k_B T_0 T} E_{Fn}\right)\right] \tau_{tr}^{cb}.$$ (s13)

Eq. (s13) together with the relation the relation $V_{ph} = (E_{Fn} - E_{redox})/e$ lead to the expression of electron transport time constant as a function of the photovoltage,

$$t_{tr} = t_{tr}^{cb} + A \exp\left(\frac{e(T - T_0)}{k_B T_0 T} V_{ph}\right) t_{tr}^{cb},$$ (s14)

where the pre-exponential factor A is defined as

$$A = \frac{N_t T}{N_{cb} T_0} \exp\left(\frac{T_0 - T}{k_B T_0 T}(E_{cb} - E_{redox})\right).$$ (s15)

REFERENCES

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