Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information

Rate Limiting Interfacial Hole Transfer in Solid-State Solar Cells

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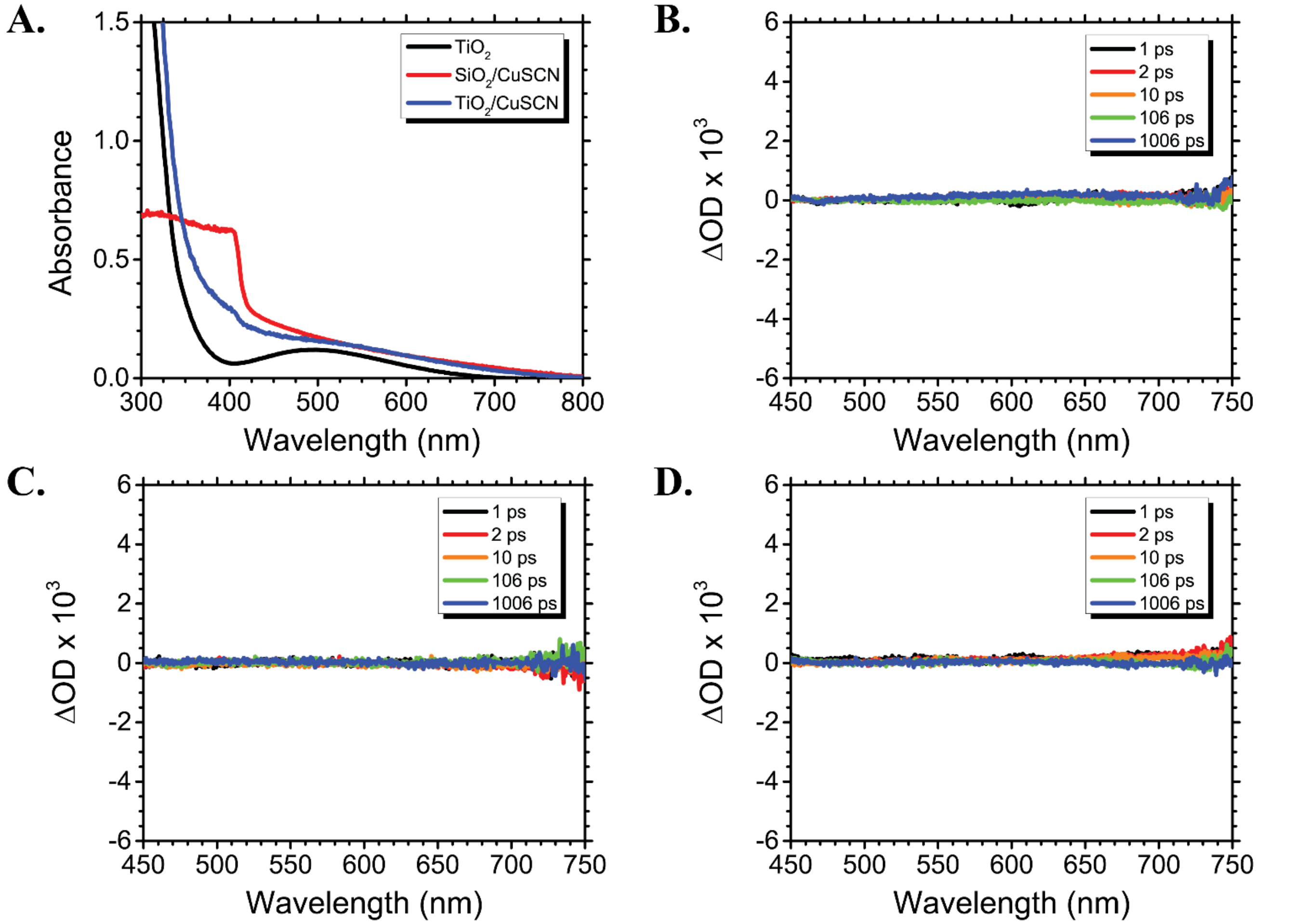

Figure SI-1. A). UV-visible absorption characteristics and time-resolved transient spectra recorded after (a) 1 ps, (b) 2 ps, (c) 10 ps, (d) 100 ps, and (e) 1000 ps following a 387 nm laser pulse excitation of films of B). TiO_2, C). SiO_2/CuSCN, and D). TiO_2/CuSCN control films which exhibit no transient absorption response under the experimental conditions used. From reference 24, reprinted with permission from the American Chemical Society.

Modeling Hole Transfer Using Fick's Law

Assumptions:

- Diffusion of holes in Sb_2S_3 follows a random walk
- There are no hole-hole interactions
- Holes have zero volume
- Holes cannot be transferred from Sb_2S_3 to TiO_2
- Holes cannot be transferred from CuSCN to Sb_2S_3
- The concentration of holes in the CuSCN is zero at all times (i.e. holes are rapidly transferred away from the Sb_2S_3 interface once in the CuSCN)
- Hole transfer coefficient across the Sb_2S_3–CuSCN interface is constant in all films studied, and for both short and long-lived holes
- Hole diffusion coefficient is constant in all films studied, and for both short and long-lived holes

Definition of Variables and Units:

h = overall concentration of holes in Sb_2S_3
h_s = concentration of short-lived holes in Sb_2S_3
h_l = concentration of long-lived holes in Sb_2S_3
s = calculated transient absorption signal for Sb_2S_3/CuSCN films
b = Sb_2S_3 film thickness (cm)
α = Sb_2S_3 absorption coefficient at 387 nm (excitation wavelength, $\alpha = 1.74\times10^5$ cm^{-1})
x = length variable (cm)
t = time variable (s)
D = diffusion coefficient of holes in Sb_2S_3 (cm^2/s)
k_i = hole transfer coefficient across Sb_2S_3–CuSCN interface (cm/s)
τ_2 = experimentally determined short exponential decay of $S^{-\bullet}$ in Sb_2S_3 films (s^{-1})
τ_3 = experimentally determined long exponential decay of $S^{-\bullet}$ in Sb_2S_3 films (s^{-1})

Model Using Fick's Second Law of Diffusion:

There are two types of holes, short-lived holes (h_s) and long-lived holes (h_l) which act independently in the Sb_2S_3 film. Therefore, the overall hole concentration (h) will be a linear combination of these two species.

$$\frac{\partial h}{\partial t} = \frac{\partial h_s}{\partial t} + \frac{\partial h_l}{\partial t}$$

We assume that h_s and h_l diffuse and transfer identically, but have differing non-radiative decay kinetics. Therefore, we can separate this into the following two problems.

$$\frac{\partial h_s}{\partial t} = D\frac{\partial^2 h_s}{\partial x^2} - {h_s}/{\tau_2}$$

$$\frac{\partial h_l}{\partial t} = D\frac{\partial^2 h_l}{\partial x^2} - {}^{h_l}/_{\tau_3}$$

These problems have almost identical solutions, therefore we will primarily look at the solution for the long-lived holes, h_l. As an initial condition we assume a distribution of holes identical to the absorption profile in the film, and we assume no hole transfer into TiO_2 and pseudo first order transfer into CuSCN as boundary conditions.

Initial Condition: $h_l|_{t=0} = (1-A)h_0e^{-\alpha x}; 0 \le x \le b$

Boundary Conditions: $\frac{\partial h_l}{\partial x}|_{x=0} = 0; t > 0$

$-D\frac{\partial h_l}{\partial x}|_{x=b} = k_i h_l|_{x=b}; t > 0$

the problem can be nondimensionalized by the following substitutions:

let, $h_l^* = \frac{h_l}{(1-A)h_0}; x^* = \frac{x}{b}; t^* = \frac{tD}{b^2}; \lambda = \frac{k_i b}{D}; \beta = \frac{b^2}{D}({}^1/_{\tau_3}); \gamma = \alpha b$

then the problem becomes,

$$\frac{\partial h_l^*}{\partial t^*} = \frac{\partial^2 h_l^*}{\partial x^{*2}} - \beta h_l^*$$

Initial Condition: $h_l^*|_{t^*=0} = e^{-\gamma x^*}; 0 \le x^* \le 1$

Boundary Conditions: $\frac{\partial h_l^*}{\partial x}|_{x^*=0} = 0; t^* > 0$

$\frac{\partial h_l^*}{\partial x^*}|_{x^*=1} + \lambda h_l^*|_{x^*=1} = 0; t^* > 0$

we postulate a separable solution where

$$h_l^*(t^*, x^*) = G(t^*)F(x^*)$$

this gives us

$$\frac{1}{F}\frac{d^2F}{dx^{*2}} = \frac{1}{G}\frac{dG}{dt^*} + \beta = -\sigma^2$$

because these two variables are independent, this gives two independent equations, where σ is an unknown to be evaluated later

we will first consider the transient component

$$\frac{1}{G}\frac{dG}{dt^*} = -(\sigma^2 + \beta)$$

the general solution of this transient part is simply

$$G(t^*) = Ae^{-\sigma^2 t^*}e^{-\beta t^*}$$

next, we will consider the spatial component

$$\frac{1}{F}\frac{d^2F}{dx^{*2}} = -\sigma^2$$

with boundary conditions

$$F'(0) = 0$$

$$F'(1) + \lambda F(1) = 0$$

This is a classic Sturm-Liouville problem analogous to the heat transfer problem of one-dimensional heat conduction from a slab of finite thickness. The solution of this problem is described in detail by Faghri et al.[1] The general solution for $F(x^*)$ is

$$F(x^*) = Asin(\sigma x^*) + Bcos(\sigma x^*)$$

using the boundary conditions

$$F'(0) = 0 \therefore A = 0$$

and,

$$F'(1) + \lambda F(1) = 0$$

we obtain the eigenfunction

$$-\sigma \sin(\sigma) + \lambda \cos(\sigma) = 0 \;\longrightarrow\; \lambda = \sigma \tan(\sigma)$$

because the equation, $\lambda = \sigma\tan(\sigma)$ has an infinite number of roots, or eigenvalues, σ_n, there must be an infinite number of solutions of the form, $B_n e^{-\sigma_n^2 t^*}\cos(\sigma_n x^*)$ and the overall solution is a linear combination of all these solutions,

$$h_l^* = \sum_{n=1}^{\infty} B_n e^{-\sigma_n^2 t^*} e^{-\beta t^*} \cos(\sigma_n x^*)$$

from the initial condition $h_l^*(0, x^*) = e^{-\gamma x^*}$, B_n can be calculated as follows[1]

$$B_n = \frac{\int_0^1 \mathrm{e}^{-\gamma x^*}\cos(\sigma_n x^*) dx^*}{\int_0^1 \cos^2(\sigma_n x^*)\, dx^*}$$

solving this, we calculate B_n to be

$$B_n = \frac{2\sigma_n[e^{-\gamma}(\sigma_n \sin(\sigma_n) - \gamma\cos(\sigma_n)) + \gamma]}{({\sigma_n}^2 + \gamma^2)[\sigma_n + \sin(\sigma_n)\cos(\sigma_n)]}$$

thus, we can describe the distribution of holes in the Sb_2S_3 film, where σ_n are eigenvalues that satisfy the relationship $\lambda = \sigma_n \tan(\sigma_n)$

because transient absorption measurements detect all holes in the Sb_2S_3 film at a given time, this expression can be simplified to describe the signal, s, arising from the trapped holes, as seen using transient absorption spectroscopy, by integrating over x^*:

$$s_l^* = \int_0^1 h^*(t^*, x^*) dx^* = \int_0^1 \sum_{n=1}^{\infty} B_n e^{-\sigma_n^2 t^*} e^{-\beta t^*} \cos(\sigma_n x^*)\, dx^*$$

$$s_l^* = \sum_{n=1}^{\infty} B_n \frac{\sin(\sigma_n)}{\sigma_n} e^{-\sigma_n^2 t^*} e^{-\beta t^*}$$

substituting back in for the dimensionless parameters yields the expression for the transient absorption signal for long-lived holes

$$s_l = (1 - A) e^{-t/\tau_3} \sum_{n=1}^{\infty} B_n \frac{\sin(\sigma_n)}{\sigma_n} e^{-\frac{\sigma_n^2 D}{b^2} t}$$

similarly, we can solve the problem for short-lived holes to give

$$s_s = Ae^{-t/\tau_2} \sum_{n=1}^{\infty} B_n \frac{\sin(\sigma_n)}{\sigma_n} e^{-\frac{\sigma_n^2 D}{b^2}t}$$

The overall hole dynamics are found by adding the contribution from s_s and s_l. If we make the assumption that the effective diffusion coefficient and interfacial hole transfer coefficient are the same for h_s and h_l, then we obtain the following solution for the modeled transient absorption response, s.

$$s = \left[Ae^{-t/\tau_2} + (1-A)e^{-t/\tau_3}\right] \sum_{n=1}^{\infty} B_n \frac{\sin(\sigma_n)}{\sigma_n} e^{-\frac{\sigma_n^2 D}{b^2}t}$$

In this model, the term in brackets describes the natural recombination dynamics of short and long-lived holes in TiO_2/Sb_2S_3 films, and the summation accounts for hole diffusion and transfer to CuSCN. The assumption that diffusion and interfacial hole transfer of short and long-lived holes is the same provides the observed factoring of the diffusion-transfer term. A priori there is no reason to assume these different hole species have similar kinetics; however, the small proportion and fast decay of the short-lived holes does not allow for any differences to be resolved. For fitting, this infinite sum can be approximated by the first five terms in the sum, n = 1 to 5 as B_n rapidly approaches zero with increasing n. This gives the final model which was applied to fit the observed transient kinetic decays following the 6 ps signal growth attributed to hole trapping.

$$s = \left[Ae^{-t/\tau_2} + (1-A)e^{-t/\tau_3}\right] \sum_{n=1}^{5} B_n \frac{\sin(\sigma_n)}{\sigma_n} e^{-\frac{\sigma_n^2 D}{b^2}t}$$

Nonlinear Regression of Diffusion-Transfer Model:

Fitting of the data to the model is a nonlinear regression analysis problem. This analysis was carried out using MATLAB computation software. This analysis fit the modeled transient absorption data to the developed model by the following method:

1. Fit all TiO_2/Sb_2S_3 data to the following triexponential equation using least square regression analysis and a logarithmic error weighting for the absorption values allowing only the magnitude of the signal, C, to vary between TiO_2/Sb_2S_3 films.

$$y = C\left[-e^{(-t/\tau_1)} + A_1 e^{(-t/\tau_2)} + (1-A_1)e^{(-t/\tau_3)}\right]$$

2. TiO_2/Sb_2S_3/CuSCN transient kinetic data at the 560 nm sulfide radical induced absorption was fit by the developed model. The sub 6 ps data was excluded to remove any complications arising from the signal growth. The transient kinetic data was then fit using least squares regression analysis with logarithmic error weighting to s by varying D and k_i and the signal magnitude.

$$s = \left[Ae^{-t/\tau_2} + (1-A)e^{-t/\tau_3}\right] \sum_{n=1}^{5} B_n \frac{\sin(\sigma_n)}{\sigma_n} e^{-\frac{\sigma_n^2 D}{b^2}t}$$

3. Undersampling of every third data point was used to obtain an estimate of the random error in this data fitting process.

4. Fitting of the diffusion only problem was achieved by letting k_i go to infinity. Therefore, σ_n becomes the nth root of cosine instead of the solution to the eigenfunction $\lambda = \sigma_n \tan(\sigma_n)$.

References

1. A. Faghri, Y. Zhang, and J. R. Howell, *Advanced Heat and Mass Transfer*, Global Digital Press, Columbia, MO, 2010.