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Triplet exciton diffusion and delayed interfacial charge separation in a Tio_2/PdTPPC bilayer: Monte Carlo simulations

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Abstract

Nanosecond photoexcitation of a bilayer of smooth anatase TiO_2 coated with palladium tetrakis(4-carboxyphenyl)porphyrin (PdTPPC) results in a delayed, after-pulse growth of the conductivity over many microseconds as monitored by time-resolved microwave conductivity. This phenomenon is attributed to the slow diffusion of PdTPPC triplet excitons followed by electron injection into the TiO_2 conduction band. The temporal form and intensity dependence of this process have been simulated by Monte Carlo (MC) calculations of exciton diffusion and exciton–exciton annihilation. Good agreement between the experimental results and MC simulations are obtained using a triplet exciton diffusion coefficient $D_E = 8 \times 10^{-11}\,m^2/s$, exciton lifetime $\tau_E \geq 10\,\mu s$, effective triplet–triplet annihilation distance $R_a = 1.5\,nm$ and interfacial electron injection efficiency $\phi_{inj} = 0.44$.

Keywords: Photovoltaics; Triplet–triplet annihilation; Exciton diffusion; Monte Carlo simulation; TiO_2

1. Introduction

Solar cells based on wide band-gap inorganic semiconductors sensitized with organic dyes have gained widespread attention as low-cost, lightweight, and

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mechanically flexible alternatives to conventional silicon-based photovoltaic devices [1]. In such dye-sensitized solar cells, visible photons are absorbed in the dye layer forming bound electron–hole pairs (excitons) which can diffuse to the semiconductor interface and undergo charge separation by injection of an electron into the conduction band of the semiconductor. These primary processes are illustrated schematically for a simple semiconductor/antenna (SC/A) bilayer configuration in Fig. 1.

For such an SC/A bilayer the overall charge separation efficiency per incident photon, which we have called the incident-photon-to-charge-separation efficiency (IPCSE) value, is given by

$$\mathrm{IPCSE} = (1-F_R)S\phi_{\mathrm{inj}}. \tag{1}$$

In (1), $(1 - F_R)$ is the fraction of incident light that actually penetrates the antenna layer (a fraction F_R being reflected), S is the combined probability that (a) photons penetrating the antenna layer are absorbed within it and (b) that the excitons formed are able to diffuse to the semiconductor interface ($z = 0$) within their natural lifetime, τ_{E}, and ϕ_{inj} is the efficiency of electron injection into the semiconductor relative to all modes of interfacial exciton deactivation.

The very low values of the IPCSE that have been found in the past for SC/A bilayers can be ascribed mainly to the fact that the characteristic distance over which excitons can diffuse within their lifetime (the "exciton diffusion length", Λ_{E}) is usually much smaller than the "photon penetration depth", Λ_{hv}, in organic materials [2–4]. The magnitude of Λ_{E} is related to the exciton lifetime and diffusion coefficient, D_{E}, by

$$\Lambda_{\mathrm{E}} = \sqrt{D_{\mathrm{E}}\tau_{\mathrm{E}}}. \tag{2}$$

For singlet excitons Λ_{E} values of only a few tens of nanometers at most have been determined even in conjugated-polymer antenna layers [2,5–7]. In contrast, the value of Λ_{hv}, which defines the exponential decrease in light intensity in an optically

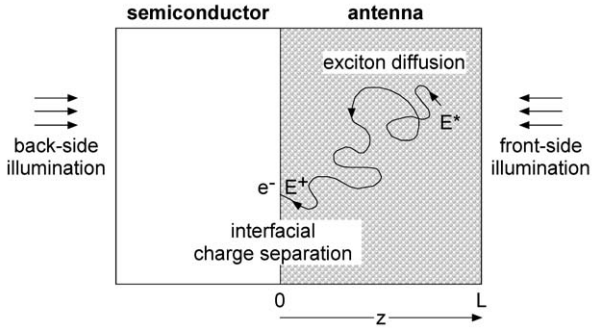

Fig. 1. A schematic representation of exciton diffusion and interfacial charge separation in a semiconductor/antenna bilayer.