Contactless Determination of the Trap Density, Photoconductivity Action Spectrum and Charge Separation Efficiency of Porphyrin-Sensitized Nanoporous TiO_2

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Key factors governing the efficiency of a photovoltaic device are the wavelength dependence of the interfacial charge separation efficiency (the 'action spectrum'), the intensity dependence of the photoconductivity and the exciton diffusion length. The determination of these parameters from photovoltaic measurements may be complicated by factors such as exciton deactivation at the cathode, non-ohmic electrode contacts, filter effects, and pinhole defects in the photoactive layers. These complications can be surmounted by using the flash-photolysis time-resolved microwave conductivity (FP-TRMC) technique to probe the change in conductivity on photoexcitation of inorganic-semiconductor/organic-antenna heterojunctions. In this method, no electrical contacts are necessary: the change in conductivity within the sample is directly related to the amount of mobile electrons present in the conduction band of the semiconductor.

We have studied photo-induced charge separation in a bare 3 μm thick layer of nanoporous ("*np*") anatase TiO_2 and *np*-TiO_2 layers coated with free-base 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (H_2TPPC) using the FP-TRMC technique. Photoconductivity transients resulting from the formation of mobile, conduction band electrons in the semiconductor were measured on pulsed excitation with UV (300 nm) and visible (420-700 nm) light. At 300 nm electrons are formed by bandgap excitation of the semiconductor. In the visible, electron formation results from interfacial electron injection from photoexcitations created in the porphyrin antenna layer. All data are expressed as the product of the yield η of electrons per incident photon and the sum of the charge carrier mobilities, Σμ.

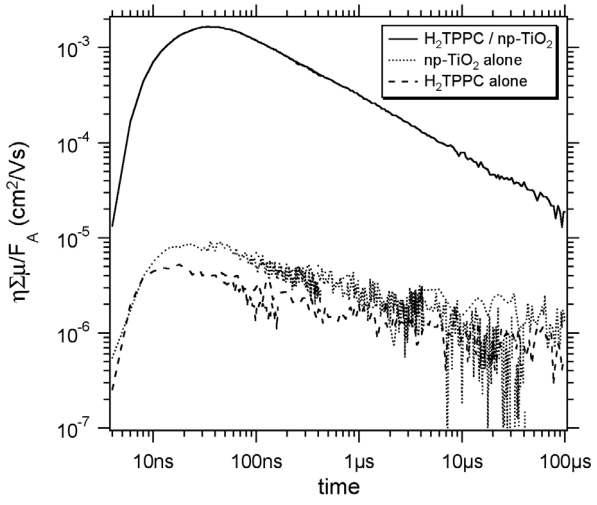

Figure 1 TRMC transients observed on excitation at 520 nm for an H_2TPPC film alone (dashed line), a *np*-TiO_2 film alone (dotted line) and an H_2TPPC-coated *np*-TiO_2 film (solid line), all on quartz substrates.

1. Photoconductivity transients on visible excitation

Figure 1 shows the TRMC transients obtained on pulsed illumination at 520 nm (where H_2TPPC is selectively excited) of a *np*-TiO_2/H_2TPPC bilayer, a *np*-TiO_2 layer alone and a H_2TPPC layer alone. For the latter two layers, hardly any measurable

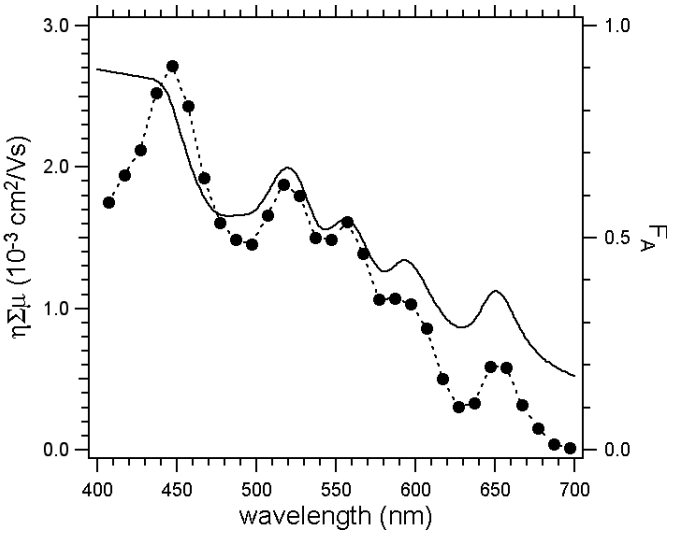

Figure 2 Wavelength dependence ("action spectrum") of the product $\eta\Sigma\mu$ of the yield of charge carrier formation and the mobility of an H_2TPPC/*np*-TiO_2 film (solid circles), obtained with ca. 10^{15} photons/cm^2 incident. The solid line represents the fraction F_A of photons absorbed by the film.

conductivity change was observed. Oppositely, readily measurable photoconductivity transients resulting from electron injection from the excited-state sensitizer were however found for the H_2TPPC-coated *np*-TiO_2 layer. Photoconductivity transients similar in magnitude and temporal shape were observed for other excitation wavelengths in the visible region.

2. Wavelength dependence of $\eta\Sigma\mu$

The wavelength dependence ("action spectrum") of the product $\eta\Sigma\mu$ of the yield of charge carrier formation and the mobility of an H_2TPPC-coated *np*-TiO_2 film is shown in Figure 2. This photoconductivity action spectrum is seen to match the spectral dependence of the fraction F_A of absorbed photons in this film, indicating that electron injection occurs from the porphyrin first singlet excited state.

3. Intensity dependence of $\eta\Sigma\mu_{max}$

The intensity dependence of the product $\eta\Sigma\mu_{max}$ of the yield for charge carrier generation, η, and the sum of the positive and negative charge carrier mobilities, $\Sigma\mu$, for various excitation wavelengths, taken at the maximum of the transients, is plotted in Figure 3. On 300 nm excitation, the curves display a gradual increase in $\eta\Sigma\mu$ upon increasing light intensity up to 10^{13} incident photons per cm^2, where a plateau value is reached. This initial superlinear behavior is considered to result from equilibrium localization of electrons in surface trapping sites. With increasing light intensity, deep traps are filled progressively, eventually leaving shallow traps left for electron transport. This saturation of deep traps then leads to the observed plateau region observed for the excitation wavelengths shown.

For higher excitation energies, a sublinear intensity dependence of $\eta\Sigma\mu$ is observed, most likely due to increased charge carrier recombination lowering η and/or a decrease in the effective value of μ due to electron-electron interactions within the semiconductor particles.

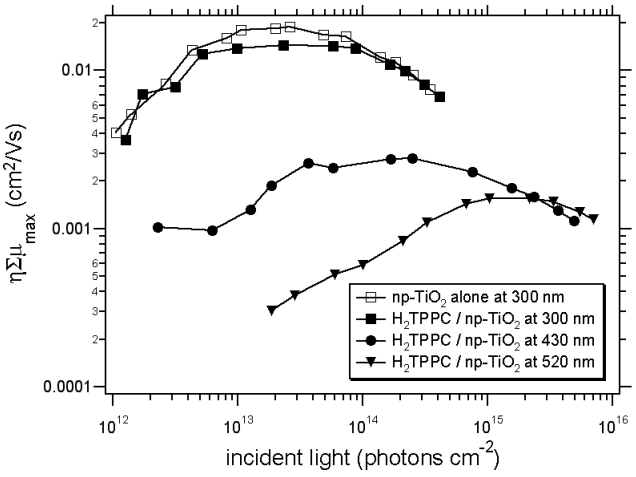

Figure 3 Intensity dependence of $\eta\Sigma\mu_{max}$ for a *np*-TiO_2 film (open circles) and an H_2TPPC-coated (closed symbols) *np*-TiO_2 film on excitation with 300 nm (squares), 430 nm (circles) and 530 nm (triangles) light.