

Femtosecond Electron-Transfer Dynamics at a Sensitizing Dye–Semiconductor (TiO₂) Interface

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The charge injection dynamics of dye sensitization from a surface-bound dye (coumarin 343 (C343)) to the conduction band (CB) of the TiO₂ is reported here for the first time. Ultrafast fluorescence dynamics demonstrate that the charge injection from the C343 dye to the CB of the TiO₂ occurs on a time scale of ca. 200 fs. The charge injection efficiency is attributed to strong electronic coupling between the dye and TiO₂ energy levels. The results yield a rate of injection of $5 \times 10^{12} \text{ s}^{-1}$.

Photoinduced electron transfer between dyes and colloidal semiconductors plays a vital role in silver halide photography, electrophotography, and more recently in solar energy cells. Sensitizing semiconducting oxides such as TiO₂,^{1,2} SnO₂,³ and ZnO₂⁴ has proven an effective way to achieve electron injection for solar cells.⁵ The photostability of TiO₂, combined with its ability to effectively and quickly separate charge, makes it a potentially attractive material for solar energy cells. However, since the bandgap lies in the ultraviolet, to make TiO₂ colloids sensitive to visible (sun)light, sensitizing dyes must be added to the surface. The efficiency of sensitization depends critically on the ratio of charge injection rate to the charge recombination rate. Previous studies have demonstrated slow recombination for dyes bound to high-surface-area TiO₂.⁶ However, the very rapid charge injection could not be resolved in this earlier work.⁶ The dynamics on charge injection from coumarin 343 (C343) dye to the conduction band (CB) of the TiO₂, which control the overall efficiency of sensitization, is studied here using ultrafast fluorescence upconversion technique.

TiO₂ was prepared according to the procedure of Grätzel and co-workers.⁷ The fluorescence upconversion experimental setup is given elsewhere.⁸ A fluorescence up-conversion signal ($\lambda_{\text{ex}} = 400 \text{ nm}$, $\lambda_{\text{em}} = 480 \text{ nm}$) is shown in Figure 1. The figure contains a cross-correlation trace, a sample trace, and a fit. There are two components to the lifetime. The dominant fast component ($180 \pm 50 \text{ fs}$, amplitude = 95%) is attributed to the electron transfer from the C343 dye to the CB of the TiO₂. The slow component ($> 10 \text{ ps}$, amplitude = 5%) corresponds to free dye recombination.⁹

In these experiments, it is important to distinguish between energy transfer, surface energy transfer, a dynamic fluorescence

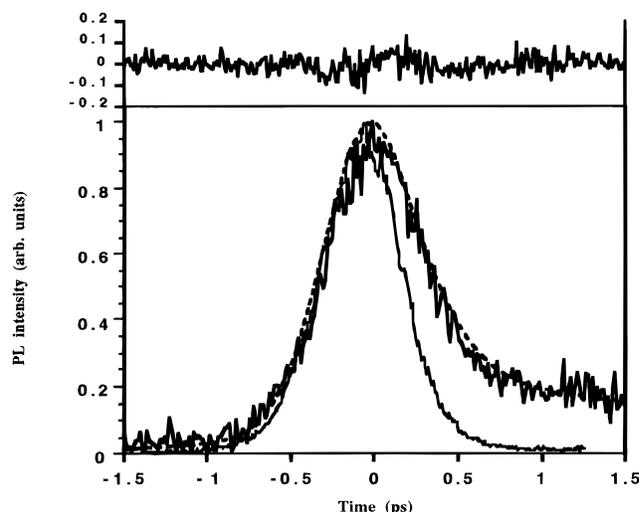


Figure 1. Fitted ultrafast fluorescence up-conversion signal of a sensitized colloidal TiO₂ solution. The sample is $1 \times 10^{-4} \text{ M}$ C343, 1 g/L TiO₂ in 95:5 H₂O:acetone monitored at 480 nm. The excitation wavelength was 400 nm. The two-component fit, $\sim 180 \text{ fs}$ (95%) and $> 5 \text{ ps}$ (5%), is shown as well.

Stoke's shift, and electron transfer. Since the TiO₂ colloidal suspension does not absorb at wavelengths below 400 nm and has no absorption longer than 400 nm, direct energy transfer between the dye and TiO₂ is precluded.⁸ A competition between dye to dye and electron transfer was considered. Since there are only ~ 16 dye molecules/TiO₂ particle and only 50% of the Ti ions are coordinated by dye, the distance between the dye molecules is too large for "hopping" energy transfer to occur.^{10,11} The wavelength-independent nature of the fluorescence up-conversion data provides evidence that the transfer mechanism

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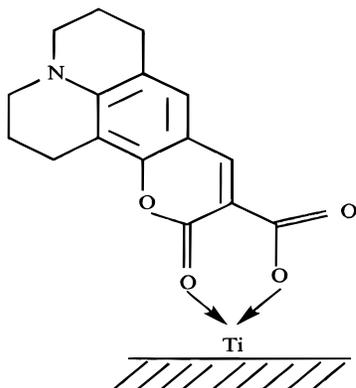


Figure 2. TiO₂ and C343 complex.

is not due to a dynamic fluorescence Stokes shift.⁸ Finally, we conducted direct pulse probe measurements of the cation radical formation. The rise time of 250 fs agrees within experimental error with the more precise up-conversion data. We therefore conclude that the observed rapid process is a surface electron-transfer event which occurs with $\Delta G = 0.7$ V. The overall quantum efficiency for net injection is ca. 0.9.⁹

The heterogeneous electron transfer just described is among the fastest electron-transfer events ever studied. How can we account for this fast process? To achieve ultrafast electron transfer, there must be ultrafast charge separation *and* a slow back reaction. The slow recombination process has been discussed elsewhere.⁹ In a situation where the photoexcited dye is strongly coupled to the surface, the level matching (in Marcus' theory) that ensures energy conservation during electron transfer involves not simply molecular energy levels as in solution reactions, but rather a continuum of electronic energy levels that exist in the semiconductor. In such a case, when the system is coupled to an electronic continuum and nuclear degrees of freedom are neglected, the rate constant for transfer is given by the golden rule expressions,¹² $k_{CT} = (2\pi/h)|V|^2\rho$, where V is the electronic coupling (per state) and ρ is the density of final electronic states. (When ρ is large, V becomes independent of the total number of electronic states.¹²) The subsequent dephasing which traps the electron can occur on an ultrafast time scale if the electronic states is high (i.e., above the band edge) and the electronic coupling of the dye and semiconductor is large.^{12,13} Thus, the injection efficiency is primarily attributed to strong electronic coupling between the dye energy level and the TiO₂ continuum, presumably associated with surface chelation of the Ti by the dye (see Figure 2). The electronic transition involved in the excitation of the dye should produce the transfer of an electron from a nitrogen atom to the salicylate group. This salicylate is directly bound to empty d orbitals of Ti^{IV} (a strong Lewis acid) and can therefore mediate very efficient charge transfer to the Ti^{IV} orbital manifold forming the conduction band of the oxide. Surface Ti^{IV} states, which act as electron traps, aid in charge separation by slowing charge recombination, as discussed elsewhere.^{9,13} Combining the ultrafast injection with slow recombination results in the highly efficient quantum yield of ca. 0.9.¹³ An energy scheme for the charge-separation process is given in Figure 3.

In summary, fluorescence up-conversion experiments together with pulse probe measurements suggest an ultrafast electron injection ($\tau = 200$ fs) from surface-bound coumarin 343 to TiO₂. This rapid process is consistent with a model^{12,14} involving strong coupling of the dye and semiconductor and direct

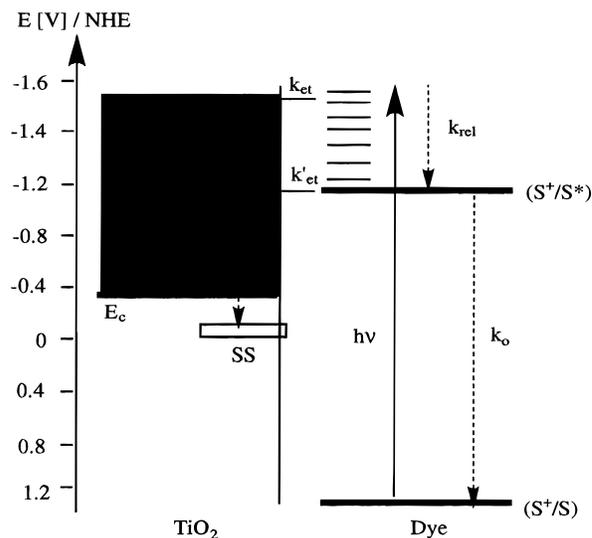


Figure 3. Energy scheme of the charge-separation process in the sensitized colloidal TiO₂ sample. Here S*/S* is the excited sensitized dye/cation radical couple, E_c the conduction band edge, SS a surface state, k_0 the relaxation rate constant to the ground state, and k_{th} the thermalization rate constant for the photoinjected electron.

injection into the conduction band, wherein the electronic energy levels replace the vibronic level matching in a conventional Marcus' theory analysis.¹² It is anticipated that such ultrafast injection can be a general process (see, e.g., ref 14) under strong coupling conditions.

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Supporting Information Available: Experimental procedure (8 pages). Ordering information is given on any current masthead page.

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SUPPLEMENTARY MATERIAL

Supplementary Data for:

Electron Injection Dynamics in a Sensitized Titanium Dioxide ColloidJulie M. Rehm,¹ George L. McLendon²Yutaka Nagasawa,³ Keitaro Yoshihara⁴Jacques Moser,⁵ Michael Grätzel⁵¹Department of Chemistry, University of Rochester, Rochester, NY 14627²Department of Chemistry, Princeton University, Princeton, NJ 08544³The Graduate University for Advanced Studies, Myodaiji, Okazaki 444, Japan⁴Institute for Molecular Science, Myodaiji, Okazaki 444, Japan⁵Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland**Experimental****TiO₂ Preparation**

TiO₂ was prepared following the procedure in reference 1. Under a stream of dry nitrogen, 25 ml of titanium isopropoxide Ti(OCH(CH₃)₂)₄ was added to a 50 ml dropping funnel which contained 4 ml of 2-propanol. The nitrogen gas was removed and the solution was added, over 10 min., to 150 ml of vigorously stirred Millipore water. Within 10 min. 1 ml of 70% nitric acid was added. The mixture was stirred at 80 °C for 1.5 hr. to evaporate the 2-propanol. The crystals were dried over night using a lyophilizer. According to the literature (ref. 1), this preparation yielded crystals of ca. 80 Å.

Fluorescence UpConversion Experimental Set-Up

Traditionally, fluorescence lifetime measurements have been limited to 10 ps which is the instrument response of a photon counting apparatus. The development of the fluorescence upconversion technique has lowered this limit to the width of the laser pulse, less than 50 fs with modern ultrafast systems.

The mode-locked Titanium sapphire laser, which produced 450 mW, 100 fs pulses at 800 nm with a repetition rate of 82 MHz, was pumped with a CW Spectra Physics Ar:Ion laser (all lines ~9 W). Second-harmonic light (400 nm) was generated in a 1 mm BBO crystal, with an average power of ~45 mW, and was used to excite the sample. The remaining fundamental was used to up-convert fluorescence from the sample in a 0.3 mm BBO crystal. The cross correlation measured between SHG and fundamental had a full-width-half-maximum of 330 fs. This was reduced to 150 fs when quartz lenses were replaced with reflective mirrors. The up-converted signal was measured at the magic angle with a photon counting system after a monochromator. The samples, in a 1 mm thick cell, were circulated using a micro-pump. See Figure 5.2 for the experimental set-up.

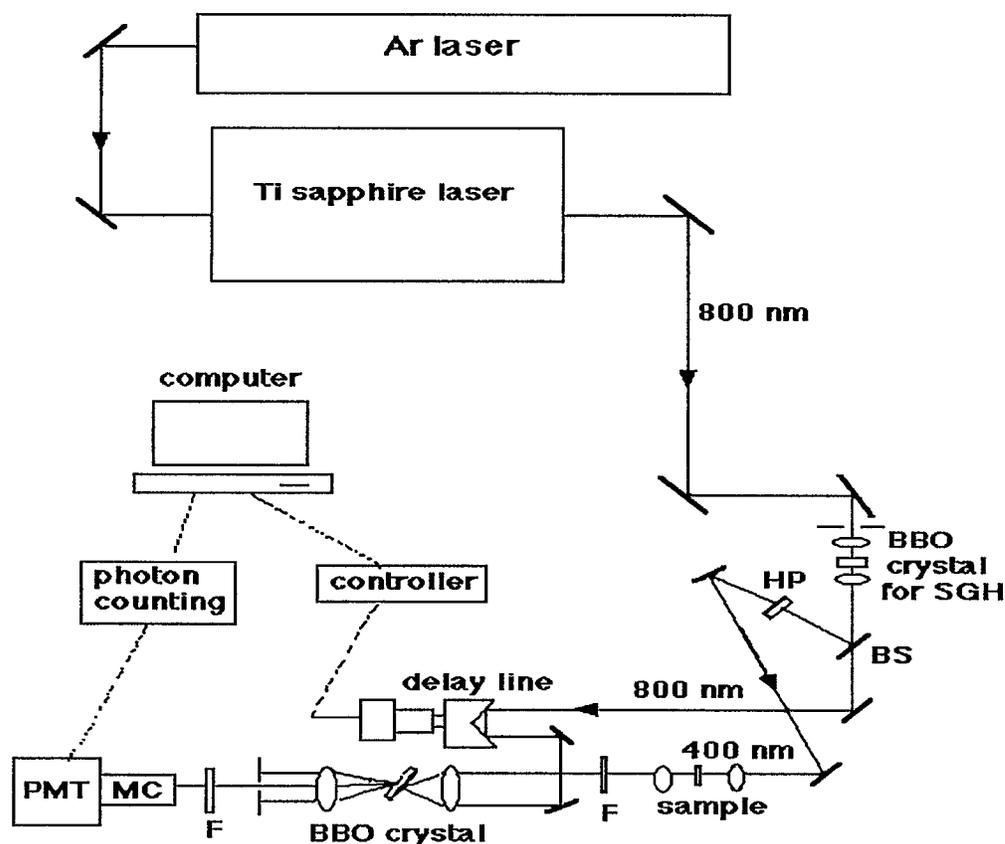


Figure 1 Ultrafast fluorescence upconversion set-up. SHG = second harmonic generation, BS = beam splitter, HP = half-wave plate, F = filter, MC = monochromator, PMT = photomultiplier tube.

Results

Steady-state absorption spectra, obtained from a Perkin-Elmer UV/Vis absorption spectrometer, of dye only (5×10^{-5} M in EtOH), and sample (TiO_2 at 5 g/L with 1×10^{-4} M C343 dye in 90:10 $\text{H}_2\text{O}:\text{EtOH}$), are given in Figures 2 and 3 respectively. A 1 cm cuvette was used for the measurements.

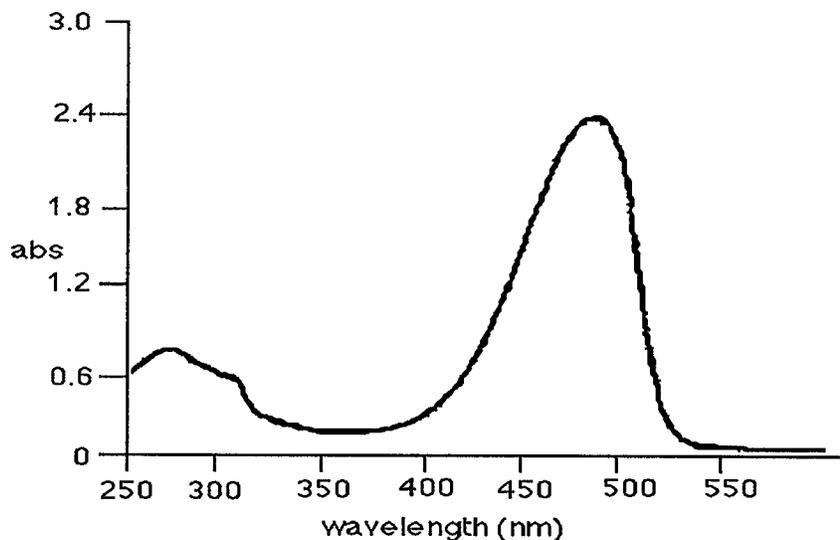


Figure 2 Steady-state absorption spectrum of a Coumarin 343 dye solution. The sample is 5×10^{-5} M in EtOH.

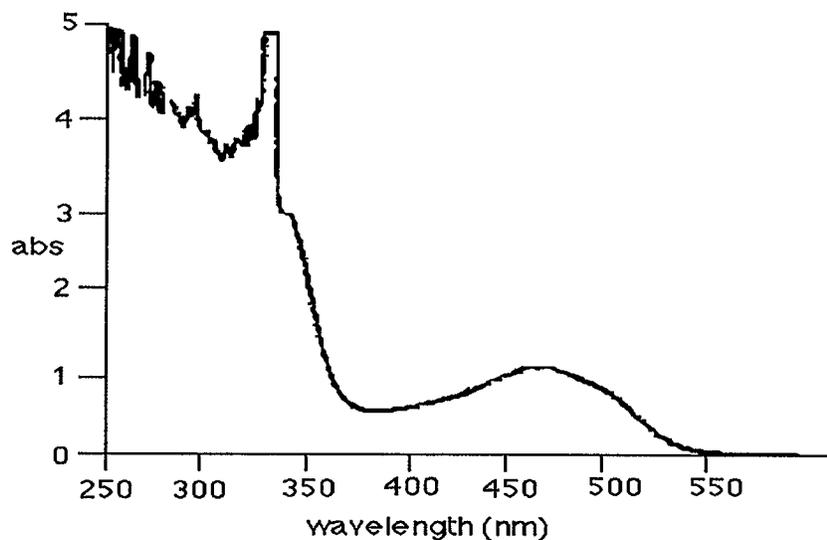


Figure 3 Steady-state absorption spectrum of a sensitized colloidal TiO_2 solution. The sample is 1×10^{-4} M C343 and 5 g/L TiO_2 in 90:10 $\text{H}_2\text{O}:\text{EtOH}$.

Ultrafast fluorescence upconversion spectra are shown in Figures 4-9. Each spectrum contains a cross-correlation trace and a sample trace. The excitation wavelength for all spectra was 400 nm. Dye only (1×10^{-4} M C343 in MeOH) and solvent only (95:5 H₂O:acetone) are represented in Figures 4 and 5 respectively. Both spectra were monitored at 480 nm. The lifetime of the C343 dye alone is very long (~10 ns) while the solvent has the same time response as the cross-correlation.

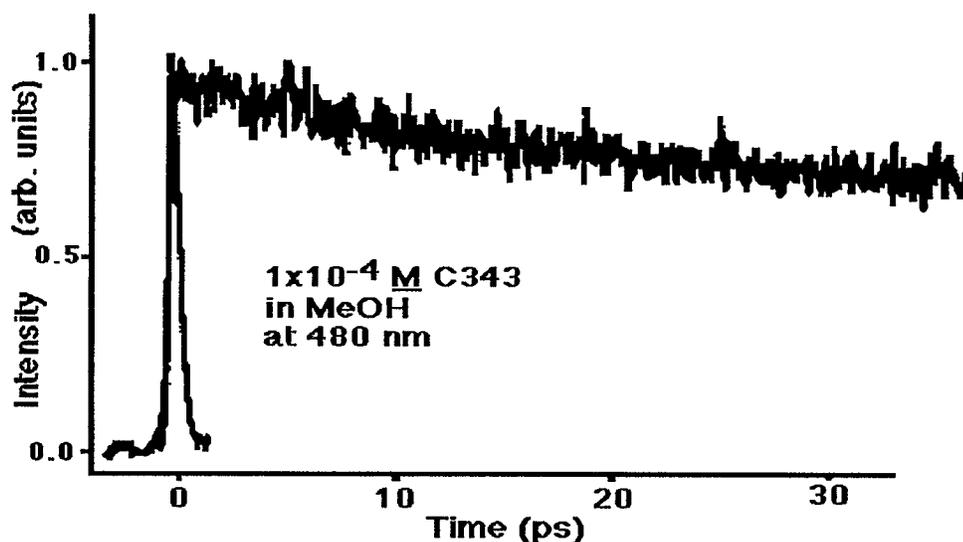


Figure 4 Ultrafast fluorescence upconversion spectrum of a Courmarin 343 dye solution. The sample is 1×10^{-4} M C343 in MeOH monitored at 480 nm.

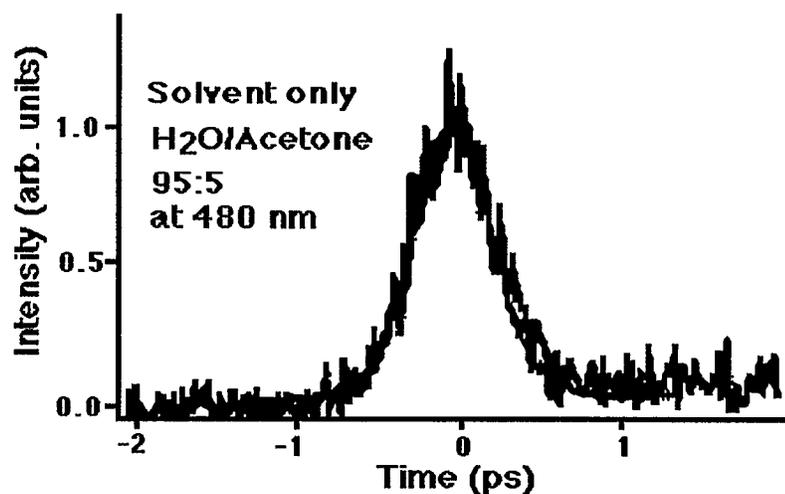


Figure 5 Ultrafast fluorescence upconversion spectrum of solvent only. The sample is 95:5 H₂O/acetone monitored at 480 nm.

Ultrafast upconversion spectra of the sample monitored at 480 nm and 530 nm are given in Figures 6 and 7 respectively. The time profile is independent of monitoring wavelength which provides compelling evidence that the signal is not due to a dynamic fluorescence Stoke's shift.

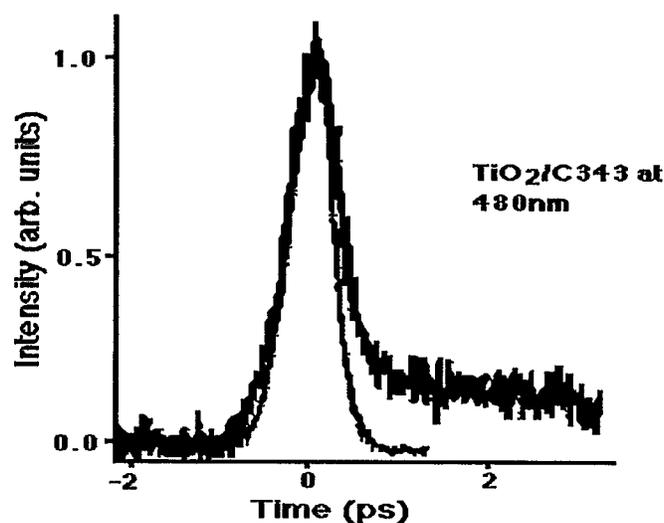


Figure 6 Ultrafast fluorescence upconversion spectrum of a sensitized colloidal TiO_2 solution at 480 nm. The sample is 1×10^{-4} M C343, 1 g/L TiO_2 in 95:5 H_2O :acetone.

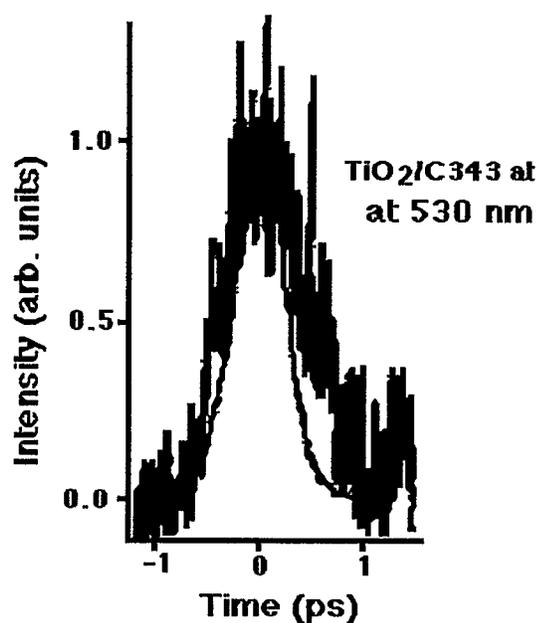


Figure 7 Ultrafast fluorescence upconversion spectrum of a sensitized colloidal TiO_2 solution at 530 nm. The sample is 1×10^{-4} M C343, 1 g/L TiO_2 in 95:5 H_2O :acetone.

A fitted ultrafast fluorescence upconversion spectrum of the solvent is given in Figure 8. The solvent signal overlaps with the cross correlation signal and the fit yields a lifetime of $100 \text{ fs} \pm 50 \text{ fs}$.

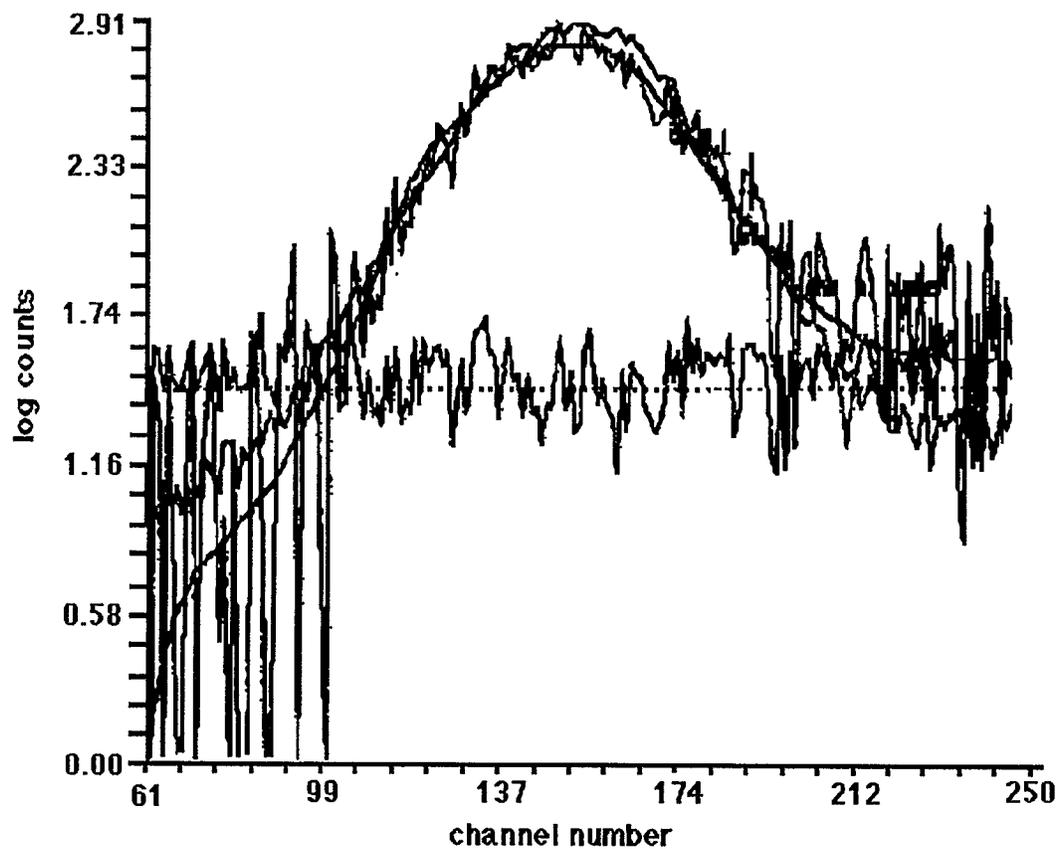


Figure 8 Fitted ultrafast fluorescence upconversion spectrum of solvent alone. The sample is 95:5 H_2O /acetone monitored at 480 nm.

Steady-state fluorescence spectra, measured on a Jasco FP-777 fluorimeter, of dye only (1×10^{-5} M C343 dye in 90:10 H₂O:acetone), and sample (TiO₂ at 1 g/L with 1×10^{-4} M C343 dye in 90:10 H₂O:EtOH) are given in Figures 10 and 11 respectively. The sample is 5 g/L TiO₂ in MeOH. The PL peak for the dye is 491 nm and for the dye with TiO₂ is 517 nm. The excitation wavelength was 400 nm. The steady-state absorption spectrum of a colloidal TiO₂ solution is given in Figure 12.

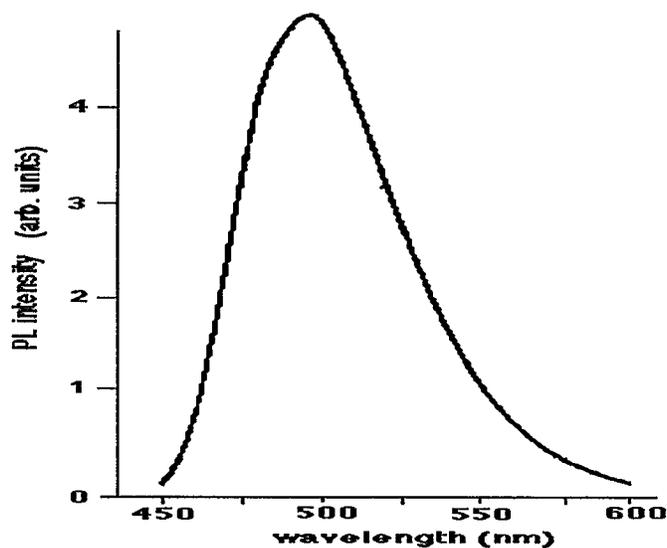


Figure 10 Steady-state PL spectrum of a Coumarin 343 dye solution. The sample is 1×10^{-5} M C343 in 90:10 H₂O:acetone. PL peak wavelength is 491 nm.

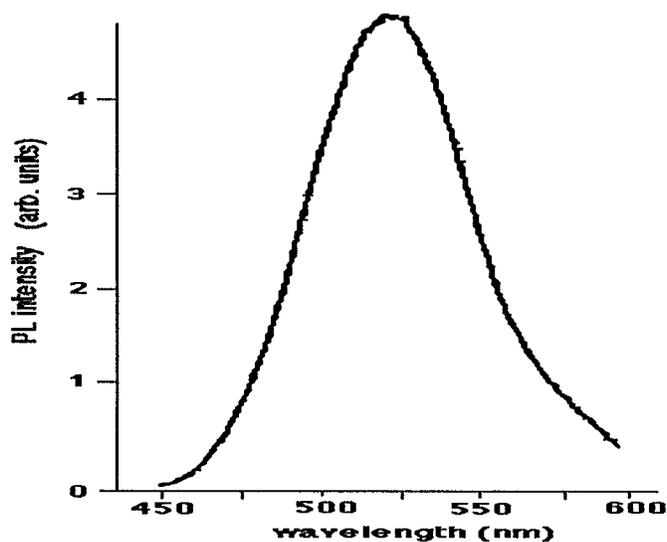


Figure 11 Steady-state PL spectrum of a sensitized colloidal TiO₂ solution. The sample is 1x10⁻⁴ MC343, 1 g/L TiO₂ in 90:10 H₂O:EtOH. PL peak wavelength is 517 nm.

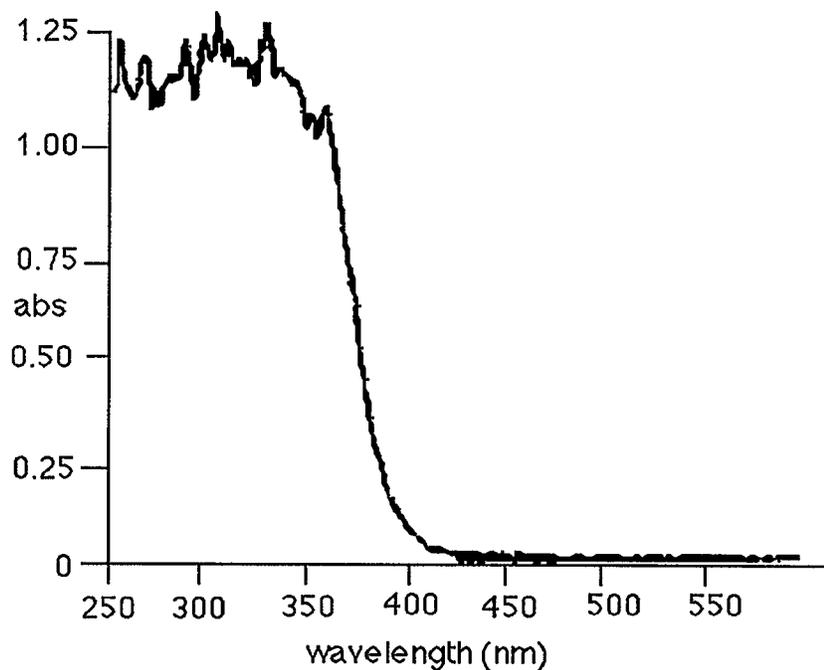


Figure 12 Steady-state absorption spectrum of a colloidal TiO₂ solution. The sample is 5 g/L TiO₂ in MeOH.

¹ O'Regan, B.; Moser, J.; Anderson, M.; Grätzel, M. *J. Phys. Chem.* **1990**, *94*, 8720.