

J. Electroanal. Chem., 259 (1989) 59–65
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Achievement of incident photon to electric current conversion yields exceeding 80% in the spectral sensitization of titanium dioxide by coumarin

Octav Enea ^{*}, Jacques Moser and Michael Grätzel

Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne (Switzerland)

(Received 22 July 1988; in revised form 19 September 1988)

ABSTRACT

We have discovered that the laser dye coumarin 343 sensitizes the visible light induced injection of electrons in the conduction band of TiO₂ films with a very high yield. The incident photon to current conversion efficiency (IPCE) exceeds 70% in the entire wavelength domain between 400 and 500 nm. It is as high as 83.5% around the absorption maximum of the dye, i.e. 440 nm. These unprecedentedly high current yields arise from efficient light collection by the dye attached to the surface of the TiO₂ film and practically unit quantum yield for charge injection. Factors contributing to the unusually high visible light harvesting efficiency of the dye-coated TiO₂ films, which is related to their specific surface texture, are scrutinized.

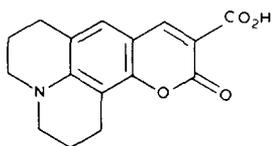
INTRODUCTION

The worldwide quest to develop clean and renewable energy sources has encouraged a large research activity in the field of regenerative photo-electrochemical cells [1]. One configuration of particular interest makes use of dye-sensitized, large band-gap semiconductor films as a light harvesting unit [2]. In such a device, the sensitizer absorbs visible light and after excitation, injects an electron in the conduction band, producing an electric current. The difficulties in obtaining reasonable conversion efficiencies with such systems are notorious. Apart from poor injection quantum yields, the light absorption by a monolayer of sensitizer adsorbed on a flat surface is at best a few percent. Multilayer deposition has proved to be an unsuccessful approach to solve this problem due to the lack of photoactivity and the

^{*} On leave of absence from Université de Poitiers, Faculté des Sciences, Laboratoire de Chimie IV, France.

filtering action of dye molecules which are not in direct contact with the semiconductor.

A recent unexpected and very encouraging development in this field is that oxide semiconductor films, such as TiO_2 , with a specific fractal-type surface topology can be sensitized with surprisingly large yields [3–8]. The highest incident photon to current conversion efficiency (IPCE) has so far been obtained with RuL_3 ($\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylate) as a sensitizer, for which the IPCE is 73% at 480 nm with iodide as the electron donor [8]. Encouraged by this result, we are screening systematically a number of other chromophores suitable for sensitization of these semiconducting films. Here, we report the results obtained with the laser dye coumarin 343,



which shows very promising properties in this regard. Apart from the charge injection process, we examine the specific texture of our films leading to the practically quantitative light harvesting effect observed with this system.

EXPERIMENTAL

Coumarin 343 was obtained from Kodak. Other chemicals were reagent grade and were used as supplied by the vendor. Tris(2,2'-bipyridyl-4,4'-dicarboxylate), RuL_3 , was synthesized by Dr. M. Nazeeruddin in our laboratory. Deionized "Millipore" quality water was used.

The preparation of the high surface area TiO_2 (anatase) films has been described previously [3–8]. Films were deposited onto glass slides, titanium rods (6 mm diameter) or Ti sheets (ASTM grade 2, size 2×2 cm, thickness 0.05 cm). Unless otherwise stated, their thickness was ca. 5–10 μm . The roughness factor was measured by adsorption of RuL_3 (immersion of the film for 1 h in an aqueous solution of 2×10^{-4} M RuL_3 in 10^{-3} M HClO_4) and subsequent desorption of the dye in 10 ml of 0.01 M NaOH. An extinction coefficient of 2.1×10^4 M^{-1} at 470 nm was employed and the experimentally determined value [9] of 1.00 nm^2 was used for the TiO_2 surface area requirement per adsorbed RuL_3 molecule. In order to characterize the quality of the films produced, the incident photon to current conversion efficiency (IPCE) at 480 nm was measured for RuL_3 -coated electrodes in 0.1 M KI, pH 3. IPCE values of 73% have been obtained previously with this system [8].

The coating of the anatase film with coumarin 343 was carried out by dipping the electrode for 15 min in a methanolic solution of 10^{-3} M of the dye and 10^{-4} M HClO_4 and subsequent rinsing with water. The TiO_2 film assumed an intense yellow colour. In acidic aqueous solution, the adsorption is irreversible, no leaching being

observed at the moderately high electrolyte concentrations (0.1 M KI , 10^{-3} M HClO_4) used in further experiments. In order to determine the quantity of adsorbed dye, the coumarin was desorbed in methanol and the concentration determined by UV/visible spectroscopy. The extinction coefficient at the absorption maximum (466 nm) is $4.37 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$. Reflection and transmission spectra were recorded on a Perkin-Elmer/Hitachi 340 spectrometer equipped with an integrating sphere. MgO was used as the standard for the reflection measurements.

In the photoelectrochemical experiments, a three-compartment cell equipped with a quartz window, the auxiliary (a platinum flag) and reference (saturated calomel) electrodes being separated from the working electrode by glass frits, was used. Potentials were adjusted with a Pine Instruments potentiostat. The regenerative cell consisted of a dye-loaded $2 \times 2\text{ cm}$ Ti sheet immersed in KI solution and a Pt flag as the counter-electrode.

Monochromatic illuminations were performed with a PTI system equipped with a 150 W Xe lamp. A 450 W high pressure Xe lamp used in conjunction with a water jacket and suitable cut-off filters was employed for polychromatic experiments. The photon flux impinging on the cell was determined by a YSI Kettering model 65 A radiometer. In addition, chemical actinometry with ferrioxalate was performed. The results obtained by the two methods agreed within 10%.

RESULTS AND DISCUSSION

Figure 1 shows the photocurrent action spectrum for the coumarin-coated TiO_2 film in 0.001 M HClO_4 in the presence of 0.1 M KI as electron donor. The lower curve gives the results obtained in the absence of the dye. The incident photon to

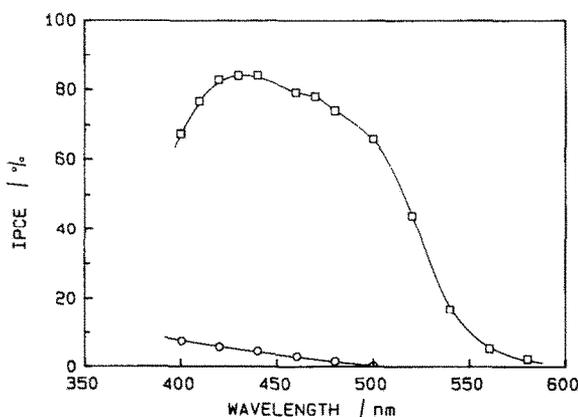


Fig. 1. Photocurrent action spectrum for polycrystalline TiO_2 (anatase) films in aqueous HClO_4 (10^{-3} M) containing 0.1 M NaI as electron donor. (□) Coumarin 343-coated electrode; (○) bare TiO_2 film.

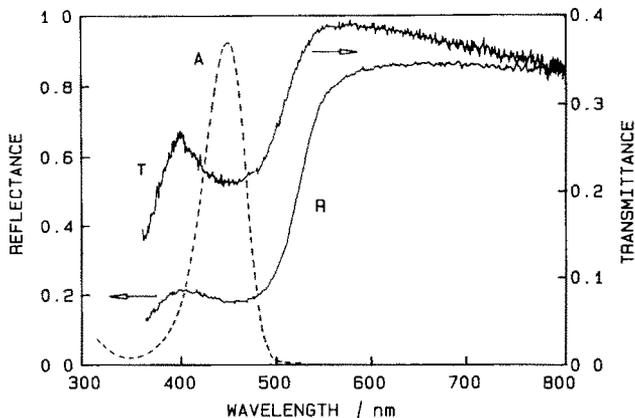


Fig. 2. Spectra of coumarin 343-loaded TiO_2 films deposited on Pyrex glass slides. (T) Diffuse transmission spectrum; (R) diffuse reflectance spectrum; (A) absorption spectrum of a solution of coumarin 343 in methanol (arbitrary scale).

current conversion yield is plotted as a function of the excitation wavelength. This was calculated from the photocurrent by the equation

$$\text{IPCE}(\%) = \frac{[(1.24 \times 10^3) \times (\text{photocurrent density}/\mu\text{A cm}^{-2})]}{[(\text{wavelength}/\text{nm}) \times (\text{photon flux}/\text{W m}^{-2})]} \quad (1)$$

The striking feature of Fig. 1 is that the IPCE values reach 80% in the visible region in the vicinity of the adsorption maximum of the dye. This is the highest efficiency achieved so far in the sensitization of semiconductors. It implies that practically all the incident photons in this wavelength domain are converted into electrical current.

The IPCE can be formulated as the product of the light harvesting efficiency and the quantum yield for charge injection:

$$\text{IPCE} = (1 - I/I_0) \phi_{inj} \quad (2)$$

where $(1 - I/I_0)$ is the fraction of the incident light flux which is absorbed in the dye-loaded semiconductor film. To obtain quantitative information on the light harvesting efficiency, 13 layers of TiO_2 were deposited on a Pyrex microscope slide. After coating with coumarin, the diffuse reflectance and transmittance of dry films were recorded; the results are shown in Fig. 2. Curve A corresponds to the absorption spectrum of coumarin 343 in methanol and is used as a reference, while T and R refer to the diffuse transmittance and reflectance of the dye-loaded film, respectively, deposited on the glass slide. Around 450 nm, where the coumarin has its absorption maximum, both the transmittance and the reflectance have a minimum corresponding to a light absorption $(1 - R - T)$ of ca. 60%.

In Fig. 3 we plot the fraction of absorbed light at 480 and 440 nm for coumarin 343 and at 480 nm for RuL_3 as a function of the product of the extinction coefficient and surface concentration of the dyes. The values at 440 nm are

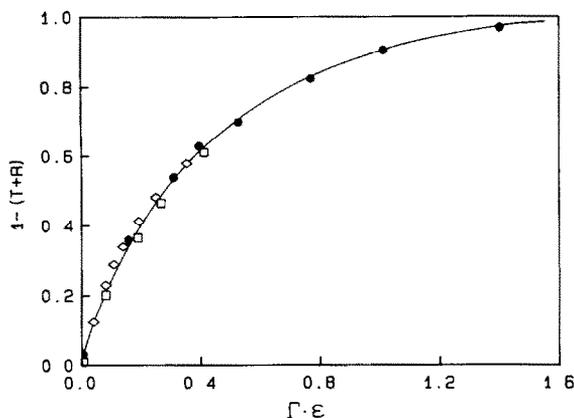


Fig. 3. Light absorption by dye-coated anatase films as a function of the absorbance parameter $\Gamma\epsilon$, where Γ is the surface concentration of the dye (in mol/cm^2) and ϵ is the decadic extinction coefficient of the dye (in cm^2/mol). (●) Coumarin 343, $\lambda = 440$ nm (corrected for specular reflection); (◇) coumarin 343, $\lambda = 480$ nm, (□) RuL_3 , $\lambda = 480$ nm. The surface concentration of the dyes was varied by partial desorption of the dye from a saturated film using methanol and 0.01 M NaOH as the solvent for coumarin 343 and RuL_3 , respectively. The solid line represents the exponential function $1 - T - R = 1 - 10^{-\epsilon\Gamma}$; ϵ values for methanolic solution (coumarin 343) or water (RuL_3) were employed.

corrected for the specular reflectance of dry TiO_2 , which is 0.21 at this wavelength but close to zero in water and at 480 nm ($(1 - T - R)_{\text{corr}} = (1 - I/I_0) = (1 - T - R)/(1 - R_{\text{spec}})$). The data can be fitted approximately to an exponential function, i.e. $(1 - I/I_0) = 1 - 10^{-\epsilon\Gamma}$, where ϵ is the decadic extinction coefficient (in cm^2/mol) and Γ is the surface concentration (in mol/cm^2). This is indicated by the solid line. A more precise analysis of the absorption behaviour of these dye-covered layers is under way and involves integration of the Kubelka-Munk differential equations for homogeneous and inhomogeneous distribution of the chromophore within the TiO_2 layer. From Fig. 3, the highest surface concentration of coumarin 343 is derived as 3.5×10^{-8} mol/cm^2 , and at this concentration the incident 440 nm light is practically absorbed quantitatively by the dye-covered film. For RuL_3 , the maximum coverage achieved with this film was 2×10^{-8} mol/cm^2 , corresponding to a high harvesting efficiency of ca. 60%. Using this surface concentration, one derives a roughness factor of the TiO_2 layer deposited onto the Pyrex slide of 120. A TiO_2 film prepared by a similar method on a titanium substrate gave a roughness factor of 180 [8]. From Fig. 3, the light harvesting efficiency at 480 nm of such a film is expected to be 75%. Since the IPCE value obtained with this system at the same wavelength was 73% [8], the charge injection from the excited state of RuL_3 in the conduction band of the fractal anatase layer must occur with an efficiency of practically unity.

Returning to Fig. 1, the IPCE value close to the absorption maximum of the coumarin is 83%. The surface coverage of the anatase film in this experiment was

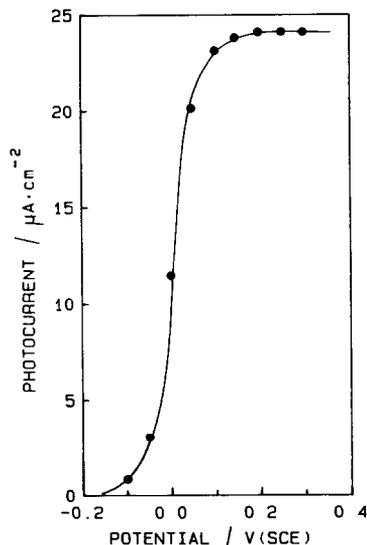


Fig. 4. Photocurrent–potential curve recorded during 460 nm irradiation of a coumarin 343-coated TiO_2 film in aqueous $10^{-3} M \text{ HClO}_4$ containing $0.1 M \text{ NaI}$ as electron donor.

$3.5 \times 10^{-8} \text{ mol/cm}^2$, which, according to Fig. 3, corresponds to a light harvesting efficiency of 96%. Hence, $\phi_{\text{inj}} = 0.87$.

Figure 4 shows a photocurrent–potential plot obtained with the coumarin 343-loaded anatase film in the presence of $0.1 M$ iodide as electron donor. The photocurrent onset is at -0.2 V , which is close to the flatband potential of the TiO_2 electrode (-0.4 V at pH 3 in the absence of iodide). The photocurrent rises steeply, reaching a plateau at 0.1 V . The implication of this result is that a band bending of ca. 0.5 V in the depletion layer is sufficient to obtain practically complete charge separation. This value is ca. 300 mV higher than the band bending required for charge separation in the case of RuL_3 in the presence of iodide as a donor. Further time-resolved experiments with colloidal TiO_2 and diffuse reflectance laser flash photolysis are under way to explore the kinetics of the heterogeneous electron-transfer reactions involved in the sensitization process.

CONCLUSIONS

Coumarin 343, a laser dye, displays an extraordinarily high efficiency in the spectral sensitization of fractal-type anatase films. The incident photon to current conversion efficiency exceeds 80% in the wavelength domain close to the absorption maximum of the dye. This is the highest efficiency achieved so far in the sensitization of semiconductors. The present investigation shows that both light harvesting and charge injection from the excited dye in the conduction band of the semiconductor occur with a yield close to unity. The findings presented here confirm the

very promising properties of the high surface area fractal-type films employed in conjunction with suitable sensitizers for visible light energy conversion.

ACKNOWLEDGEMENTS

This work was supported by the Gas Research Institute, Chichago, IL, USA (subcontract with the Solar Energy Research Institute, Golden, CO) and the Nationaler Energie-Forschungs-Fonds (NEFF) and the Office Fédéral de l'Energie (OFEN), Switzerland.

REFERENCES

- 1 H. Gerscher in M. Schiavello (Ed.), Photoelectrochemistry, Photocatalysis and Photoreactors, NATO ASI Series C, Vol. 146, Reidel, Dordrecht, 1985, p. 39.
- 2 T. Watanabe, A. Fujishima and K. Honda in M. Grätzel (Ed.), Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983, Ch. 11, p. 359.
- 3 J. Desilvestro, M. Grätzel, L. Kavan, J. Moser and J. Augustynski, *J. Am. Chem. Soc.*, 107 (1985) 2988.
- 4 K. Kalyanasundaram, N. Vlachopoulos, V. Krishnan, A. Monnier and M. Grätzel, *J. Phys. Chem.*, 91 (1987) 2342.
- 5 E. Vrachnou, N. Vlachopoulos and M. Grätzel, *J. Chem. Soc., Chem. Commun.*, (1987) 868.
- 6 N. Vlachopoulos, P. Liska, A.J. McEvoy and M. Grätzel, *Surf. Sci.*, 189 (1987) 823.
- 7 P. Liska, N. Vlachopoulos, M.K. Nazeeruddin, P. Comte and M. Grätzel, *J. Am. Chem. Soc.*, 110 (1988) 3686.
- 8 N. Vlachopoulos, P. Liska, J. Augustynski and M. Grätzel, *J. Am. Chem. Soc.*, 110 (1988) 1216.
- 9 D.N. Furlong, D. Wells and W.H.F. Sasse, *J. Phys. Chem.*, 90 (1986) 1107.