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# PHOTOCHEMICAL SOLAR CELLS BASED ON DYE-SENSITIZATION OF NANOCRYSTALLINE $\text{TiO}_2$

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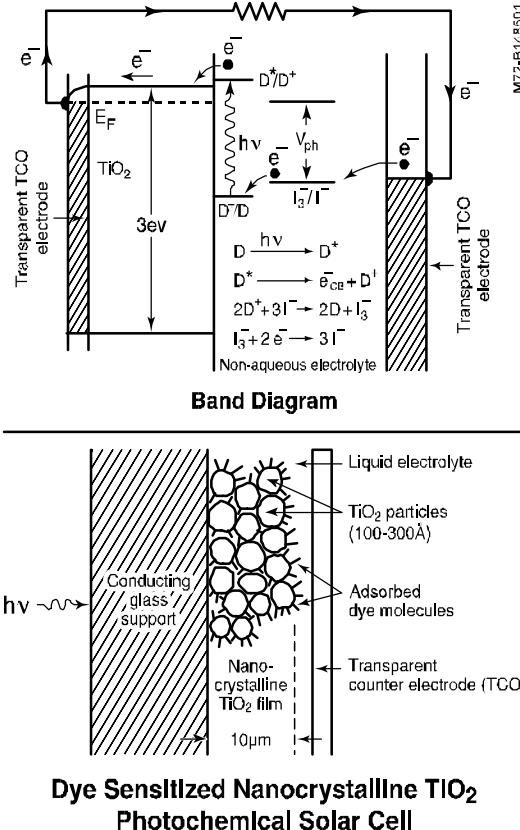
**ABSTRACT:** A photoelectrochemical solar cell that is based on the dye-sensitization of thin nanocrystalline films of  $\text{TiO}_2$  (anatase) nanoparticles in contact with a non-aqueous liquid electrolyte is described. The cell, fabricated at NREL, shows a conversion efficiency of ~9.2% at AM1.5, which approaches the best reported value of 10%-11% by Grätzel at EPFL in Lausanne, Switzerland. The femtosecond (fs) pump-probe spectroscopy has been used to time resolve the injection of electrons into the conduction band of nanocrystalline  $\text{TiO}_2$  films under ambient conditions following photoexcitation of the adsorbed Ru(11)-complex dye. The measurement indicates an instrument-limited ~50 fs upper limit on the electron injection time. We also report the sensitization of nanocrystalline  $\text{TiO}_2$  by a novel iron-based dye, CIS-[Fe<sup>II</sup>(2,2'-bipyridine-4,4'-dicarboxylic acid)<sub>2</sub>(CN)<sub>2</sub>], a chromophore with an extremely short-lived, nonemissive excited state. The dye also exhibits a unique "band selective" sensitization through one of its two absorption bands. The operational principle of the device has been studied through the measurement of electric field distribution within the device structure and studies on the pH dependence of dye-redox potential. The incorporation of  $\text{WO}_3$ -based electrochromic layer into this device has led to a novel photoelectrochromic device structure for "smart window" application.

Keywords: Dye-sensitized photoelectrochemical solar cel -1: Photoelectrochromic window-2

## 1. INTRODUCTION

The idea of dye-sensitization of inorganic materials goes back several decades, and a vast body of literature exists on the dye-sensitization of  $\text{AgBr}$  for photographic applications. The first use of dye-sensitized  $\text{TiO}_2$  for solar energy conversion was reported in a U.S. patent issued in 1978, in which a photoelectrochemical cell based on dye-sensitization of  $\text{TiO}_2$  particles, particularly in anatase form, was reported [1]. The dye used was N-methylphenazinium ion which extended the spectral response of  $\text{TiO}_2$  to the 500-nm region. However, the conversion efficiency of such a device was relatively low and the stability of dye was an issue. A breakthrough occurred in recent years when M. Grätzel and B. O'Regan reported a photochemical solar cell using nanoparticle  $\text{TiO}_2$  sensitized by a more efficient and stable Ru(11)-complex dye [2]. The standard dye used in present cells [3] is Ru(11)(4,4'-dicarboxy-2,2'-bipyridine)<sub>2</sub>(NCS)<sub>2</sub> (absorption peak at 550 nm); this system shows conversion efficiencies of 7%-10% under standard solar conditions. A recent new "black" dye (4,9,14-tricarboxy 2,2'-6,6'-terpyridyl ruthenium(11)trithiocyanate) has recently been reported by Grätzel that produces an efficiency of nearly 11% [4].

The photoelectrode of a dye-sensitized PV cell consists of a 10-20- $\mu\text{m}$  film of nanocrystalline  $\text{TiO}_2$  particles (10-30 nm in diameter) that contain a monolayer of adsorbed dye molecules; the dye-coated particles are supported on a transparent conducting glass substrate (e.g., tin oxide) (see Fig. 1). The pores of the nanocrystalline  $\text{TiO}_2$  film are filled with a liquid electrolyte containing the iodide/triiodide redox couple in a non-aqueous electrolyte, such as acetonitrile. A transparent counter electrode is placed over the nanocrystalline  $\text{TiO}_2$ , and the edges of the cell are sealed. Upon photoexcitation of the cell, the excited dye molecules inject electrons efficiently into the  $\text{TiO}_2$  conduction band, effecting charge separation. The injected electrons traverse the nanocrystalline film with little loss and are collected at the conducting glass substrate. After passing through the external circuit and delivering power to a load, the electrons re-enter the cell at the counter electrode and reduce triiodide to iodide, which then diffuses into the pores of the  $\text{TiO}_2$  film to reduce the photo-oxidized dye back to its original state.



**Dye Sensitized Nanocrystalline  $\text{TiO}_2$  Photochemical Solar Cell**

Figure 1: Band diagram and structure of photochemical solar cell

In this paper we report the fabrication of an ~9.2% - efficient cell using an essentially similar technology. Dynamics of electron injection into nanocrystalline  $\text{TiO}_2$  films sensitized with Ru-based dye has been studied by transient infrared absorption spectroscopy. We also report the sensitization of  $\text{TiO}_2$  by an iron bipyridyl complex, a chromophore with an extremely short-lived, nonemissive excited state.

## 2. THE NREL PHOTOCHEMICAL SOLAR CELL PROJECT

The Photoelectrochemical Solar Cell project at NREL is an integrated program of basic and applied research that is jointly planned and funded by the U.S. Department of Energy's Office of Energy Research and Office of Energy Efficiency and Renewable Energy. In this section we discuss our research on the development of dye-sensitized photovoltaic cells and elucidate the operating principle of these devices.

### 2.1 NREL Cell Preparation and Efficiency

We have fabricated a dye-sensitized  $\text{TiO}_2$  solar cell (with no antireflection coating) with a conversion efficiency of 9.2%. This value approaches the best achieved, to date, by the group of Grätzel at EPFL (10%-11%) and is substantially higher than efficiencies reported by other laboratories. The ~9.2% cell displayed a short-circuit photocurrent  $J_{sc}$  of 17.899 mA/cm<sup>2</sup>, an open-circuit photovoltage  $V_{oc}$  of 756 mV, and a fill factor of 68%.

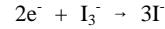
The preparation of  $\text{TiO}_2$  film was adapted from the literature [5-6]. A conducting glass plate (Asahi Glass; F-doped  $\text{SnO}_2$  overlayer, 80 % transmittance in the visible, 14% haze, 7 $\Omega/\text{sq}$ ) was used as the substrate for depositing  $\text{TiO}_2$  films. To control the thickness of the  $\text{TiO}_2$  film and to mask electrical contact strips, 0.5-cm width of the conducting glass plate was covered along the length of each edge with adhesive tape. A mixture of  $\text{TiO}_2$  colloids and  $\text{TiO}_2$  powder were deposited on the surface of the conducting glass. After removing the adhesive tapes, the assemblage was heated in air for 30 min at 450°C and then allowed to cool. The  $\text{TiO}_2$ -covered plate was cut into a 1.25 x 1.2 cm electrode. The film was then immersed in an aqueous 0.3 M  $\text{TiCl}_4$  solution for 2 days in a closed chamber, washed with distilled water, and annealed again at 450 °C for 30 min. The thickness of the resulting film was about 12  $\mu\text{m}$ .

The  $\text{TiO}_2$  electrodes were coated with  $[\text{RuLL}'(\text{NCS})_2]$  ( $\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid,  $\text{L}' = 2,2'$ -bipyridyl-4,4'-ditetrabutylammoniumcarboxylate). The dye-coated nanocrystalline  $\text{TiO}_2$  electrode was soaked in 4-*tert*-butylpyridine for 15 min and then dried under a  $\text{N}_2$  stream. Pt counter electrodes with a mirror finish were prepared by electron beam, depositing a 60 nm layer of Pt on top of a 40 nm layer of Ti on a glass plate. The Pt electrode and the dye-coated  $\text{TiO}_2$  electrode were sealed together with 25- $\mu\text{m}$  thick strip of Surlyn (Dupont), sandwiched along the length of each edge. Sealing was accomplished by pressing the two electrodes together at a pressure of 900 psi and a temperature of 120 °C. A small quantity of a redox electrolyte, consisting of an alkyl methylimidazolium iodide and  $\text{I}_2$  in acetonitrile, was introduced into the porous structure of the dye-covered  $\text{TiO}_2$  film by capillary action. The dye-coated  $\text{TiO}_2$  film was illuminated through the transparent conducting glass support.

### 2.2 Improving the Photovoltage Through Surface Modification

A major factor limiting the conversion efficiency of present dye-sensitized  $\text{TiO}_2$  solar cells is the low photovoltage [7], which is substantially below the theoretical maximum [8-10]. Charge recombination at the nanocrystallite/redox electrolyte interface is expected to play a significant role in limiting the photovoltage. There are two likely recombination pathways occurring at the interface. The injected conduction-band electrons may recombine with oxidized dye molecules or react with redox species in the electrolyte. Owing to the rapid rate of reduction of the

oxidized dye molecules by  $\text{I}^-$  ions, which are present at high concentration, the contribution of this latter energy-loss channel to the recombination current can usually be ignored [11]. The net recombination process, controlling the photovoltage, is represented by the reaction [6]:



Some suppression of back electron transfer in  $\text{TiO}_2$ , as manifested by a higher open-circuit photovoltage  $V_{oc}$ , has been reported [12,13] as a result of chemically treating the surface with 4-*tert*-butylpyridine.

In this paper, we report on the effect of various surface modifying reagents on  $V_{oc}$  and the underlying mechanism [14,15] for their action. An unexpected result is the discovery that the reaction rate for recombination is second order in triiodide ion concentration. The mass-transport theory is also applied to determine whether the nanoporous  $\text{TiO}_2$  film impedes the diffusion of triiodide ions in the cell.

The fill factor is also not significantly changed by surface treatment. The major effect of surface treatment is to increase  $V_{oc}$  and consequently the cell efficiency. The improved  $V_{oc}$  with respect to the untreated surface ( $V_{oc} = 0.57$  V) ranges from 0.64 V for vinylpyridine-treated electrodes to 0.73 V for polyvinylpyridine-treated electrodes, corresponding to respective increases of 70 and 160 mV. The largest improvement was for an  $\text{NH}_3$ -treated electrode, which yielded a  $V_{oc}$  of 0.81 V, corresponding to an increase of 240 mV, and a conversion efficiency of 7.8 %.

To determine whether the nanoporous  $\text{TiO}_2$  film impedes the diffusion of  $\text{I}_3^-$  ions in the liquid phase, the dependence of  $V_{oc}$  on the radiant power at low  $\text{I}_3^-$  concentration was studied, and mass transport theory was applied to the experimental data to obtain the diffusion coefficient of  $\text{I}_3^-$ . The calculated curve coincides closely with the experimental data for an optimized diffusion coefficient of  $7.55 \cdot 10^{-6} \text{ cm}^2/\text{s}$  for  $\text{I}_3^-$  ions in  $\text{CH}_3\text{CN}/\text{NMO}$  (50:50 wt%)/ $\text{TiO}_2$ . After correcting for the  $\text{TiO}_2$  porosity (0.3) [16], the diffusion coefficient of  $\text{I}_3^-$  ions in the solution phase was determined to be  $2.5 \cdot 10^{-5} \text{ cm}^2/\text{s}$ , which is in good agreement with values obtained for  $\text{I}_3^-$  ions in  $\text{CH}_3\text{CN}$  [(8.5-30)  $\cdot 10^{-6} \text{ cm}^2/\text{s}$ ] and  $\text{NMO}$  ( $2.8 \cdot 10^{-6} \text{ cm}^2/\text{s}$ ) [17-19]. The similarity of our measured value of the diffusion coefficient with those reported in the literature implies that, in the  $\text{I}_3^-$  concentration range investigated, most of the  $\text{I}_3^-$  remains in solution and is not adsorbed to the  $\text{TiO}_2$  surface. In other words, the porous structure of the  $\text{TiO}_2$  films does not significantly retard the diffusion of  $\text{I}_3^-$  ions in the solution phase.

### 2.3 Mechanisms

#### 2.3.1 Time-Resolved Infrared Spectroscopic Studies of Electron Injection in Dye-Sensitized $\text{TiO}_2$

We have used femtosecond pump-probe spectroscopy [20] to time resolve the injection of electrons into nanocrystalline  $\text{TiO}_2$  film electrodes under ambient conditions following photoexcitation of the adsorbed dye  $[\text{Ru}(4,4'-\text{dicarboxy}-2,2'-\text{bipyridine})_2(\text{NCS})_2]$  (N3). Pumping at one of the metal-to-ligand charge transfer absorption peaks and probing the absorption by injected electrons in the  $\text{TiO}_2$  at 1.52  $\mu\text{m}$  and in the range of 4.1 to 7.0  $\mu\text{m}$ , we have directly observed the arrival of electrons injected into the  $\text{TiO}_2$  film. Our measurements indicate an instrument-limited ~50-fs upper limit on the electron injection time. We have compared the infrared transient absorption for noninjecting systems consisting of N3 in ethanol and N3 adsorbed to films of nanocrystalline  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ , and found no indication of electron injection at probe wavelengths in the mid-IR (4.1 to 7.0  $\mu\text{m}$ ).

Several groups studying the transient absorption of the excited and oxidized states of the dye in the visible and near-IR have reported evidence for ultrafast (<1 ps) charge separation and electron injection. Tachibana *et al.* [21] reported transient absorption measurements at 750 nm which were ascribed to the formation of oxidized N<sub>3</sub> (pumped at 605 nm); analysis of the rise time of the 750-nm absorption indicated biphasic electron injection with injection times of 150 fs (instrument limited) and 1.2 ps. Hannappel *et al.* [22] measured the rise of the near-infrared absorption of injected electrons at 1100 nm following photoexcitation of N3 at the lower-energy metal-to-ligand charge transfer (MLCT) absorption peak (550 nm). However, to obtain unambiguous results, it was necessary for these experiments to be conducted under ultrahigh vacuum (UHV) conditions. Based on time-resolved infrared (TRIR) absorption measurements, our measurements provide further evidence of ultrafast electron injection times (50 fs) for the N3-TiO<sub>2</sub> electrode under ambient conditions. By measuring the time-resolved absorption in the mid-IR, we are able to obtain unambiguous conclusions without the need for UHV. Probing in the mid-IR allows us to bypass the issue of the correct absorption spectrum for oxidized N3 and eliminate the possibility of any signal contributions from the cationic or excited states of the dye.

### 2.3.2 Induced pH-Sensitivity in Sensitizing Dyes

It was recently reported [23] that the rate of recombination between the electron in the TiO<sub>2</sub> and the oxidized dye was dependent on pH. Because the conduction-band potential of the TiO<sub>2</sub> is known to have a Nernstian dependence on pH, whereas the potentials of the usual family of ruthenium-based sensitizing dyes show little or no pH dependence in solution, it was assumed that varying the pH would vary the driving force for the recombination reaction. Surprisingly, the rate of the electron transfer reaction was independent of pH over a range where it was expected to change by many orders of magnitude.

Here we report measurements on a similar dye and show that, although its oxidation potential is independent of pH when the dye is dissolved in solution, its potential becomes pH-dependent when it is adsorbed on the TiO<sub>2</sub>. The pH dependence is close to the 59-mV/unit pH expected theoretically for the flatband potential of an oxide semiconductor. Therefore, in this system, there is little or no change in the difference between the TiO<sub>2</sub> flatband potential and the Ru(II)/Ru(III) potential of the adsorbed dye over the range from pH 2.5 to pH 8. This may explain the lack of pH dependence of the recombination rate observed in reference 23. Therefore, it is not necessary to invoke unusual models of electron transfer to explain the behavior of the dye-sensitized cells. Such a change in pH-dependent behavior of a sensitizing dye upon adsorption has not been previously reported.

We have extended our experiments to include several types of dyes on both semiconducting and insulating surfaces and see similar behavior in all cases. We believe the effect is caused by the dye being inside the Helmholtz plane of the semiconductor; thus, it experiences a substantial fraction of the potential experienced by the semiconductor upon adsorption or desorption of ions such as H<sup>+</sup> and OH<sup>-</sup>. The induced pH-dependence of the oxidation potential has implications for the design and optimization of dye-sensitized solar cells. Specifically, it is not possible to independently adjust the potentials of the semiconductor and the dye by the use of potential-determining ions. Although our experiments were in aqueous systems, the same effect should occur in the non-aqueous solvents used in the

standard PV cell configuration that contains the potential-determining Li<sup>+</sup> ions.

### 2.3.3 Potential Distribution in Dye-Sensitized Cells

One important factor that has never been clearly understood about the dye-sensitized cells is the distribution of electrical potential through the cell under working conditions. The individual TiO<sub>2</sub> particles are too small to support a space-charge layer, but they are sintered together to form an electrically conducting, porous film. Is there then a space-charge layer across the film at short-circuit and/or at open-circuit? We have investigated this problem by impedance spectroscopy measurements and electrochemical-dye desorption measurements. The results are unambiguous: because of the porous nature of the TiO<sub>2</sub> film, ions can migrate through the film to neutralize any applied fields over very short distances. Therefore, under normal operating conditions, there are essentially no electric fields of range longer than about 10 nm in the cell. It is clear from these considerations that charge motion through the TiO<sub>2</sub> films occurs entirely by diffusion, rather than by drift.

This understanding has important consequences for the design of solid-state analogues of the dye-sensitized cells. Because there are essentially no electric fields present in the dark, an electric field is created by the photojunction process upon illumination, and this electric field must oppose charge separation. In the standard, solvent-containing configuration, this induced electric field is quickly neutralized by the motion of electrolyte ions, and thus, the electrons can be separated from the holes (oxidized ions). However, in the solid-state analogues proposed and studied so far, there have been no mobile electrolyte ions. The conversion efficiency in such systems has been uniformly low. We now believe this was caused by the induced, uncompensated electric field in such cells that opposed charge separation. It should be possible, however, to design a solid-state version of these cells that contains mobile electrolyte ions that will eliminate this problem.

## 3. PHOTOSENSITIZATION OF TiO<sub>2</sub> BY IRON-BASED DYE

Herein we report the sensitization of nanocrystalline TiO<sub>2</sub> by CIS-[Fe<sup>II</sup>(2,2'-bipyridine-4,4'-dicarboxylic acid)<sub>2</sub>(CN)<sub>2</sub>], a chromophore with an extremely short-lived, nonemissive excited state. The complex was prepared via a modified procedure of Schilt [24]. Its absorbance spectrum exhibits one bipyridyl based  $\pi$ - $\pi^*$  transition (318 nm) and two MLCT bands (430 nm, 635 nm, with a shoulder at ~550 nm). The complex adsorbs out of a 10<sup>-3</sup> M methanolic solution containing 20 mM chenodeoxycholic acid [25] onto nanocrystalline films of TiO<sub>2</sub> [26], rendering the films a dark blue. Under white-light illumination of approximately "one sun" (75 mW/cm<sup>2</sup>,  $\lambda > 400$  nm) in a regenerative cell configuration, a short-circuit photocurrent of 290  $\mu$ A/cm<sup>2</sup> and an open-circuit photovoltage of -360 mV are obtained. No attempt was made to optimize the cell performance.

This is the first report of a substantial photosensitization effect by an iron(II) bipyridyl complex. Like those of bipyridyl complexes of ruthenium(II), their intense visible absorptions are due to excitation into initially singlet MLCT states via  $t_{2g} \rightarrow \pi^*$  electronic transitions.

The photocurrent action spectrum for [Fe<sup>II</sup>(2,2'-bipyridine-4,4'-dicarboxylic acid)<sub>2</sub>(CN)<sub>2</sub>] on TiO<sub>2</sub> is superimposed upon the absorption spectrum of the adsorbed dye. It can be seen that while injection is relatively efficient (10%-11%) from the higher energy MLCT (~420 nm), injection is much less efficient (~2%) from the lower energy MLCT transition

(~600 nm). For all dyes heretofore reported in the photocurrent action spectra qualitatively trace the dyes' absorbance features. To our knowledge, this is the first observation of a "band selective" sensitization phenomenon.

A precise explanation for why injection is more efficient from one of two absorption transitions is not yet possible without detailed knowledge of the excited-state configuration of  $[Fe^{11}(2,2\text{-bipyridine-4,4'\text{-dicarboxylic acid}}_2)(CN)_2]$ [27].

#### 4. PHOTOELECTROCHROMIC CELLS

A dye-sensitized solar cell electrode was recently combined with an electrochromic film to produce what we called a "photoelectrochromic" window [28]. Because of the complementary nature of the two technologies, we were able to combine just one half of a typical dye-sensitized solar cell with one half of a typical electrochromic cell. The electrochromic film was deposited on the counterelectrode of a dye-sensitized solar cell and lithium ions were added to the electrolyte solution. The  $I_2$  required in the electrolyte for high-power solar cells was eliminated in order to maximize the photovoltage, and a low concentration of a more transparent dye was employed as the sensitizer. In this configuration, the photovoltage produced by the dye-sensitized electrode drives electrons and compensating  $Li^+$  cations into the  $WO_3$  film, resulting in a colored electrochromic film. When illumination ceases, the potential of the charged  $WO_3$  film causes the coloration process to reverse, expelling  $Li^+$  from the  $WO_3$  film and transferring electrons, via the external circuit, back to the oxidized iodine species in solution.

#### 5. ACKNOWLEDGMENTS

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