Photochemical Solar Cells Based on Dye-Sensitization of Nanocrystalline TiO$_2$

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NREL

PHOTOCHEMICAL SOLAR CELLS BASED ON DYE-SENSITIZATION OF NANOCRYSTALLINE TIO$_2$

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ABSTRACT: A photoelectrochemical solar cell that is based on the dye-sensitization of thin nanocrystalline films of 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 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 TiO$_2$ by a novel iron-based dye, CIS-[Fe^{11}(2,2'-bipyridine-4,4'-dicarboxylic acid)$_2$(CN)$_2$], 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 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 AgBr for photographic applications. The first use of dye-sensitized 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 TiO$_2$ particles, particularly in anatase form, was reported [1]. The dye used was N-methylphenazinium ion which extended the spectral response of 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 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)$_2$(NCS)$_2$ (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-μm film of nanocrystalline 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 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 TiO$_2$, and the edges of the cell are sealed. Upon photoexcitation of the cell, the excited dye molecules inject electrons efficiently into the 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 TiO$_2$ film to reduce the photo-oxidized dye back to its original state.

Band Diagram

Dye Sensitized Nanocrystalline TiO$_2$ Photochemical Solar Cell
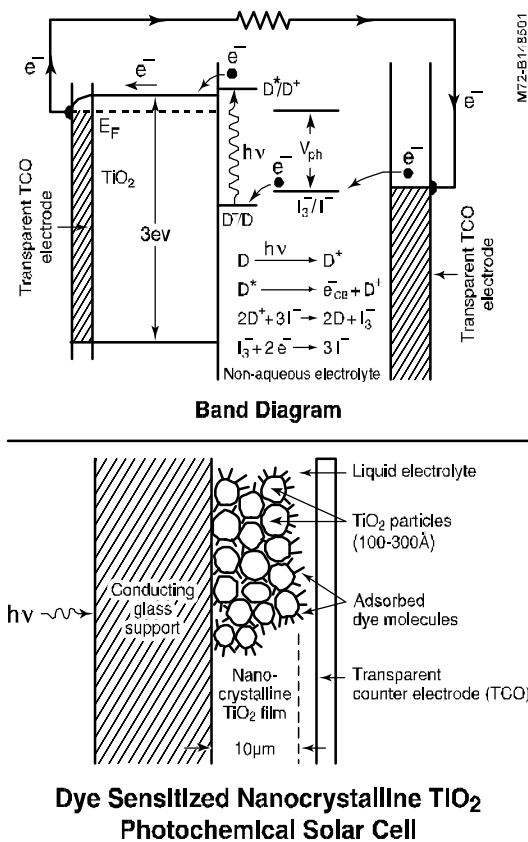
Figure 1: Band diagram and structure of photochemical solar cell

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

2. THE NREL PHOTOELECTROCHEMICAL 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 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^2, an open-circuit photovoltage V_{oc} of 756 mV, and a fill factor of 68%.

The preparation of TiO_2 film was adapted from the literature [5-6]. A conducting glass plate (Asahi Glass; F-doped SnO_2 overlayer, 80 % transmittance in the visible, 14% haze, 7Ω/sq) was used as the substrate for depositing TiO_2 films. To control the thickness of the 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 TiO_2 colloids and 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 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 $TiCl_4$ 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 ìm.**

The TiO_2 electrodes were coated with [RuLL'(NCS)$_2$] (L = 2,2'-bypyridyl-4,4'-dicarboxylic acid, L' = 2,2'-bipyridyl-4,4-ditetrabutylammoniumcarboxylate). The dye-coated nanocrystalline TiO_2 electrode was soaked in 4-*tert*-butylpyridine for 15 min and then dried under a 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 TiO_2 electrode were sealed together with 25-μm 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 I_2 in acetonitrile, was introduced into the porous structure of the dye-covered TiO_2 film by capillary action. The dye-coated 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 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 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]:

$$2e^- + I_3^- \rightarrow 3I^-$$
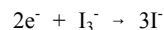
Some suppression of back electron transfer in TiO_2, as manifested by a higher open-circuit photovoltage V_{oc}, has been reported [12,13] as a result of chemically treating the surface with 4-tert-butylpyridine.

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 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 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 TiO_2 film impedes the diffusion of I_3^- ions in the liquid phase, the dependence of V_{oc} on the radiant power at low I_3^- concentration was studied, and mass transport theory was applied to the experimental data to obtain the diffusion coefficient of I_3^-. The calculated curve coincides closely with the experimental data for an optimized diffusion coefficient of 7.55 10^{-6} cm^2/s for I_3^- ions in CH$_3$CN/NMO (50:50 wt%)/TiO_2. After correcting for the TiO_2 porosity (0.3) [16], the diffusion coefficient of I_3^- ions in the solution phase was determined to be 2.5 10^{-5} cm^2/s, which is in good agreement with values obtained for I_3^- ions in CH$_3$CN [(8.5-30) 10^{-6} cm^2/s] and NMO (2.8 10^{-6} cm^2/s) [17-19]. The similarity of our measured value of the diffusion coefficient with those reported in the literature implies that, in the I_3^- concentration range investigated, most of the I_3^- remains in solution and is not adsorbed to the TiO_2 surface. In other words, the porous structure of the TiO_2 films does not significantly retard the diffusion of I_3^- ions in the solution phase.

2.3 Mechanisms
2.3.1 Time-Resolved Infrared Spectroscopic Studies of Electron Injection in Dye-Sensitized TiO_2

We have used femtosecond pump-probe spectroscopy [20] to time resolve the injection of electrons into nanocrystalline TiO_2 film electrodes under ambient conditions following photoexcitation of the adsorbed dye [Ru(4,4=-dicarboxy-2,2=-bipyridine)$_2$(NCS)$_2$] (N3). Pumping at one of the metal-to-ligand charge transfer absorption peaks and probing the absorption by injected electrons in the TiO_2 at 1.52 μm and in the range of 4.1 to 7.0 μm, we have directly observed the arrival of electrons injected into the 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 Al_2O_3 and ZrO_2, and found no indication of electron injection at **probe wavelengths in the mid-IR (4.1 to 7.0 ìm).**

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_3 (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_2 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_2 and the oxidized dye was dependent on pH. Because the conduction-band potential of the TiO_2 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_2. 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_2 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^+ and OH^-. 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^+ 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_2 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_2 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_2 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 photoinjection 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_2 BY IRON-BASED DYE

Herein we report the sensitization of nanocrystalline TiO_2 by CIS-[Fe^{II}(2,2'-bipyridine-4,4'dicarboxylic acid)$_2$(CN)$_2$], 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 π-π^* transition (318 nm) and two MLCT bands (430 nm, 635 nm, with a shoulder at ~550 nm). The complex adsorbs out of a 10^{-3} M methanolic solution containing 20 mM chenodeoxycholic acid [25] onto nanocrystalline films of TiO_2 [26], rendering the films a dark blue. Under white-light illumination of approximately "one sun" (75 mW/cm^2, $\lambda > 400$ nm) in a regenerative cell configuration, a short-circuit photocurrent of 290 μA/cm^2 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^{II}(2,2'-bipyridine-4,4'-dicarboxylic acid)$_2$(CN)$_2$] on TiO_2 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 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 $[Fe^{11}(2,2\text{-bipyridine-4,4'-dicarboxylic acid})_2(CN)_2]$[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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