

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

S.K. Deb, S. Ferrere, A.J. Frank, B.A. Gregg, S.Y. Huang, A.J. Nozik, G. Schlichthörl, and A. Zaban  
National Renewable Energy Laboratory (NREL), Golden, Colorado 80401

## ABSTRACT

A new type of photovoltaic cell is described. It is a photoelectrochemical device that is based on the dye-sensitization of thin (10-20  $\mu\text{m}$ ) nanocrystalline films of  $\text{TiO}_2$  nanoparticles in contact with a non-aqueous liquid electrolyte. The cell is very simple to fabricate and, in principle, its color can be tuned through the visible spectrum, ranging from being completely transparent to black opaque by changing the absorption characteristics of the dye. The highest present efficiency of the dye-sensitized photochemical solar cell is about 11%. The cell has the potential to be a low-cost photovoltaic option. Unique applications include photovoltaic power windows and photoelectrochromic windows.

## INTRODUCTION

The application of dye-sensitized semiconductor electrodes to a new type of photovoltaic (PV) cell has generated much interest recently. The photoelectrode of these PV cells 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, 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. These cells are termed either photochemical solar cells, dye-sensitized solar cells, or Grätzel cells, the latter because of the breakthrough report [1] by M. Grätzel and B. O'Regan on dye-sensitization of  $\text{TiO}_2$ . The standard dye used in present cells [2] is  $\text{Ru}(\text{II})(4,4'\text{-dicarboxy-2,2'\text{-bipyridine})_2(\text{NCS})_2$  (absorption

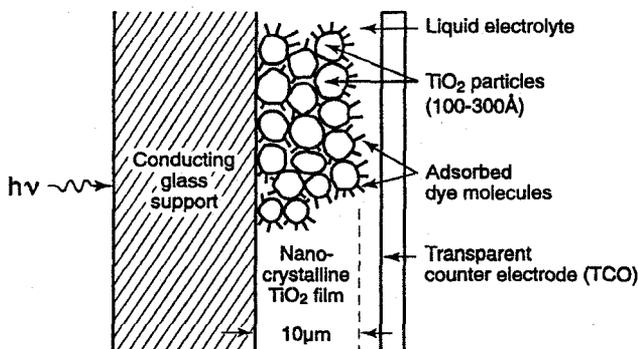
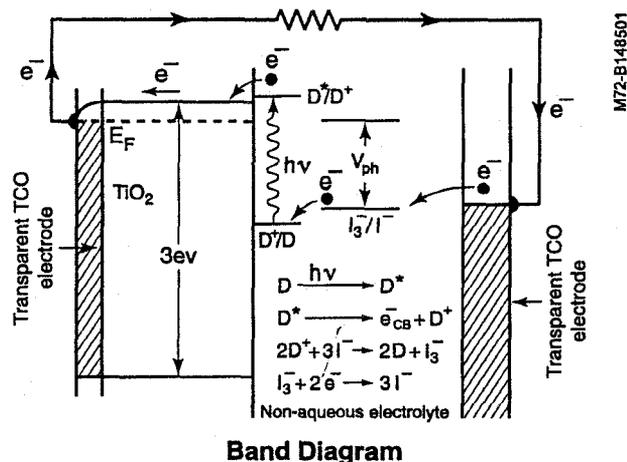


Fig. 1. Band diagram and structure of photochemical solar cell

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(II) trithiocyanate) has recently been discovered that produces an efficiency of nearly 11%.

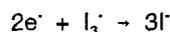
## THE NREL PHOTOCHEMICAL SOLAR CELL PROJECT

The Photochemical 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. It has three components: (1) applied research and development of dye-sensitized PV cells; (2) basic studies of the dynamics of electron injection from dye molecules into the conduction band of TiO<sub>2</sub>; and (3) research and development of dye-sensitized solar cells that split water into hydrogen and oxygen rather than produce electricity. In this report we only cover work on the applied research and development of dye-sensitized photovoltaic cells; the report is presented in three parts.

### A. Improving the Photovoltage Through Surface Modification

A major factor limiting the conversion efficiency of present dye-sensitized TiO<sub>2</sub> solar cells is the low photovoltage [3], which is substantially below the theoretical maximum [4-6]. 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<sup>-</sup> ions, which are present at high concentration, the contribution of this latter energy-loss channel to the recombination current can usually be ignored [7]. The net recombination process, controlling the photovoltage, is represented by the reaction [3]:



Some suppression of back electron transfer in TiO<sub>2</sub>, as manifested by a higher open-circuit photovoltage V<sub>oc</sub>, has been reported [8,9] 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<sub>oc</sub> and the underlying mechanism [10,11] 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<sub>2</sub> film impedes the diffusion of triiodide ions in the cell.

The methodology for preparing the dye-sensitized nanocrystalline solar cells is detailed elsewhere [10]. Table 1 summarizes the PV characteristics of cis-di(thiocyanato)-N,N-bis(2,2'-bipyridyl)-4,4'-dicarboxylic acid)-ruthenium(II) (RuL<sub>2</sub> (NCS)<sub>2</sub>)-coated nanocrystalline TiO<sub>2</sub> electrodes exposed to 4-tert-butylpyridine (TBP), 2-vinylpyridine (VP), poly(2-vinylpyridine) (PVP), or ammonia. The electrodes were immersed in CH<sub>3</sub>CN/3-methyl-2-oxazolidinone (NMO) (50:50 wt %) containing 0.3 M LiI and 30 mM I<sub>2</sub>. A comparison of the untreated and treated electrodes shows that the surface treatment does not significantly alter the short-circuit photocurrent density J<sub>sc</sub> and does not therefore

affect electron injection into the conduction band by excited dye molecules. The fill factor is also not significantly changed by surface treatment. The major effect of surface treatment is to increase V<sub>oc</sub> and consequently the cell efficiency. The improved V<sub>oc</sub> with respect to the untreated surface (V<sub>oc</sub> = 0.57 V) ranges from 0.64 V, for the VP-treated sample, to 0.73 V, for the PVP-treated sample, corresponding to respective increases of 70 and 160 mV. The largest improvement was for an NH<sub>3</sub>-treated electrode, which yielded a V<sub>oc</sub> of 0.81 V, corresponding to an increase of 240 mV, and a conversion efficiency of 7.8%. The latter efficiency represents a 34% improvement over that of the untreated electrode.

**Table 1.** Photocurrent-Voltage Characteristics of Untreated and Pyridine-Derivative-Treated, [RuL<sub>2</sub> (NCS)<sub>2</sub>]-Coated, Nanocrystalline TiO<sub>2</sub> Solar Cells.<sup>a,b</sup>

Electrode Treatment	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (mV)	FF	η (%)
Untreated	14.9	570	0.68	5.8
VP <sup>c</sup>	14.8	640	0.70	6.6
TBP <sup>c</sup>	14.7	710	0.72	7.5
PVP <sup>c</sup>	14.5	730	0.71	7.5
NH <sub>3</sub>	15	810	0.64	7.8

<sup>a</sup>Radiant power: 100 mW/cm<sup>2</sup> (AM 1.5). <sup>b</sup>Redox electrolyte: CH<sub>3</sub>CN/NMO (50:50 wt %), LiI (0.3 M), and I<sub>2</sub> (30 mM). <sup>c</sup>VP (2-vinylpyridine); TBP (4-tert-butylpyridine); PVP (poly(2-vinylpyridine)).

To determine whether the nanoporous TiO<sub>2</sub> film impedes the diffusion of I<sub>3</sub><sup>-</sup> ions in the liquid phase, the dependence of V<sub>oc</sub> on the radiant power at low I<sub>3</sub><sup>-</sup> concentration was studied, and mass transport theory was applied to the experimental data to obtain the diffusion coefficient of I<sub>3</sub><sup>-</sup>. The calculated curve coincides closely with the experimental data for an optimized diffusion coefficient of 7.55 10<sup>-6</sup> cm<sup>2</sup>/s for I<sub>3</sub><sup>-</sup> ions in CH<sub>3</sub>CN/NMO (50:50 wt%)/TiO<sub>2</sub>. After correcting for the TiO<sub>2</sub> porosity (0.3) [12], the diffusion coefficient of I<sub>3</sub><sup>-</sup> ions in the solution phase was determined to be 2.5 10<sup>-5</sup> cm<sup>2</sup>/s, which is in good agreement with values obtained for I<sub>3</sub><sup>-</sup> ions in CH<sub>3</sub>CN [(8.5-30) 10<sup>-6</sup> cm<sup>2</sup>/s] and NMO (2.8 10<sup>-6</sup> cm<sup>2</sup>/s) [13-15]. The similarity of our measured value of the diffusion coefficient with those reported in the literature implies that in the I<sub>3</sub><sup>-</sup> concentration range investigated, most of the I<sub>3</sub><sup>-</sup> remains in solution and is not adsorbed to the TiO<sub>2</sub> surface. In other words, the porous structure of the TiO<sub>2</sub> films does not significantly retard the diffusion of I<sub>3</sub><sup>-</sup> ions in the solution phase.

### B. Mechanisms

#### 1. Induced pH-Sensitivity in Sensitizing Dyes

The photosensitization of high-bandgap semiconductor electrodes by adsorbed sensitizing dyes has been studied

for a number of years. Despite the high level of activity, a comprehensive fundamental understanding is lacking, and unexpected results are still being encountered. One such result was recently reported [16], where the rate of recombination between the electron in the  $\text{TiO}_2$  and the oxidized dye was measured as a function of pH. Because the conduction-band potential of the  $\text{TiO}_2$  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.

We report here 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  $\text{TiO}_2$ . 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  $\text{TiO}_2$  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 16. 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  $\text{H}^+$  and  $\text{OH}^-$ . 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  $\text{Li}^+$  ions.

## 2. 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  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  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. Such experiments are in progress.

## ACKNOWLEDGMENTS

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