

# Visible Light Sensitization by *cis*-Bis(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) of a Transparent Nanocrystalline ZnO Film Prepared by Sol-Gel Techniques

Gareth Redmond and Donald Fitzmaurice\*

Department of Chemistry, University College Dublin, Dublin 4, Ireland

Michael Graetzel

Institute de Chimie Physique, Ecole Polytechnique Federale de Lausanne, CH-1015, Lausanne, Switzerland

Received December 20, 1993. Revised Manuscript Received March 2, 1994\*

Transparent nanocrystalline ZnO films have been prepared on a conducting glass substrate by sol-gel techniques. Their sensitization by adsorption of a ruthenium-based complex and subsequent incorporation as the light harvesting unit in a regenerative photoelectrochemical cell are described. The resulting device has a monochromatic incident photon-to-current conversion efficiency of 13% at 520 nm.

## Introduction

Highly efficient regenerative photoelectrochemical cells based on visible light sensitized transparent nanocrystalline films of TiO<sub>2</sub> have recently been described.<sup>1</sup> The most efficient cell of this type, based on a TiO<sub>2</sub> film sensitized by an adsorbed monolayer of *cis*-bis(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) molecules, possesses a solar-to-electric energy conversion efficiency of 10%.<sup>2</sup> To date, reported work has concentrated on optimization of the sensitizer molecules and electrolyte solutions used in such cells. Relatively little attention has been given to the use of alternate transparent nanocrystalline semiconductor films.

We have described preparation of transparent nanocrystalline ZnO films.<sup>3</sup> Preparation of these films was facilitated by a recently reported method for preparation of ZnO sols described by Spanhel and Anderson.<sup>4</sup> Using these films and adsorbed *cis*-bis(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) as a sensitizer, it has been possible to construct a regenerative photoelectrochemical whose efficiency compares favourably with previously reported values for this semiconductor.<sup>5</sup>

## Experimental Section

### Preparation of Transparent Nanocrystalline ZnO Films.

Ethanollic dispersions of ZnO were prepared at 40 °C following the procedure of Spanhel and Anderson.<sup>4</sup> Reagents used were the following: Zinc acetate dihydrate (Fluka, puriss), lithium hydroxide (Merck), and absolute ethanol (Fluka, puriss over molecular sieve). The resulting dispersion was allowed age for

**Table 1. Monochromatic Conversion Efficiencies for Regenerative Photoelectrochemical Cells Based on *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub>-Sensitized ZnO Films Having Thicknesses between 0.5 and 1.5 μm and Fired for 1 h at Temperatures between 300 and 400 °C**

firing temp (°C)	A <sub>λ<sub>max</sub></sub> (Abs. Units)	thickness (μm)	IPCE(520 nm) (%)
One Layer			
300	0.38	0.6	7
350	0.29	0.5	6
400	0.28	0.6	7
Two Layers			
350	0.31	0.8	13
350	0.61	1.0	13
Five Layers			
350	0.42	1.5	1

3 days at room temperature and centrifuged to remove the largest (bulk) ZnO particles. These particles cause streaking in subsequently formed films. Using a quasi-elastic light-scattering technique (Brookhaven BI 2030), the average particle diameter of the above dispersion was determined to be 10 (±1) nm. The above dispersion was reduced on a rotary evaporator to yield a sol of 150 g dm<sup>-3</sup> ZnO. Triton X-100 (1% by volume) was added to facilitate film formation. Preparation of ZnO films on a conducting indium tin oxide (ITO) glass substrate (Flach Glas 0.3 μm coating) has been described in detail elsewhere.<sup>3</sup> Briefly, the conducting glass substrate was fixed to a clean surface using adhesive tape. This tape formed a guide between which the ZnO sol was spread using a glass rod. Films, formed as a result of the application of between one and five layers of ZnO, were fired at temperatures between 300 and 400 °C for 1 h in air. The resulting films were between 0.5 and 1.5 μm thick; see Table 1. Film thickness was determined using a Tencor Instruments alpha-step 200 apparatus with an accuracy of ±0.1 μm. Immediately following firing, a UV-visible spectrum was recorded for each film using an HP 8452A diode-array spectrophotometer. A piece of ITO glass, fired with the film, was used as a reference. Note that all films were prepared immediately prior to use. Surface morphology of these films was studied by high-resolution scanning electron microscopy (SEM) performed at 10 kV on a Hitachi S-900 "in-lens" field-emission SEM.

**Sensitization of Transparent Nanocrystalline ZnO Films.** Prior to sensitization freshly prepared films were heated at their firing temperature for 20 min to activate the film surface by removing adsorbed water. The still warm electrode (about 80

\* To whom correspondence should be addressed.

• Abstract published in *Advance ACS Abstracts*, April 1, 1994.

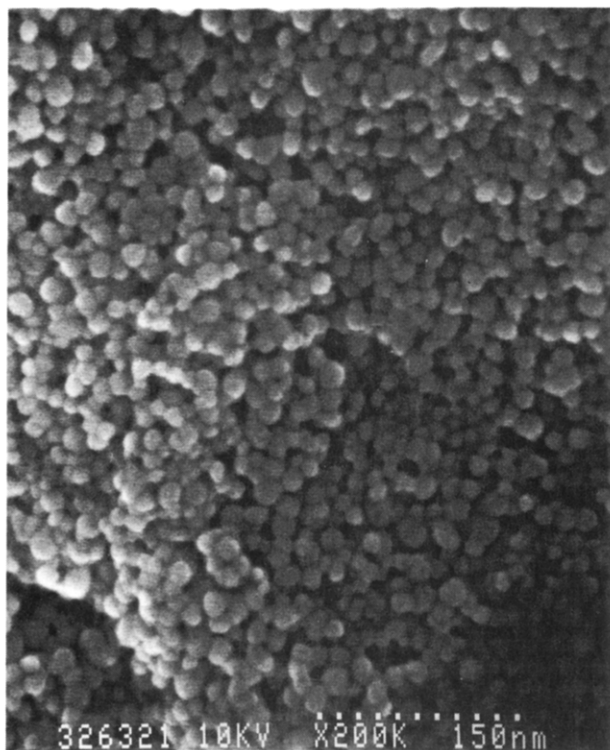
(1) O'Regan, B.; Graetzel, M. *Nature* 1991, 353, 737.

(2) Nazeerudin, M.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. *J. Am. Chem. Soc.* 1993, 115, 6382.

(3) Redmond, G.; O'Keefe, A.; Burgess, C.; MacHale, C.; Fitzmaurice, D. *J. Phys. Chem.* 1993, 97, 11081.

(4) Spanhel, L.; Anderson, M. *J. Am. Chem. Soc.* 1991, 113, 2826.

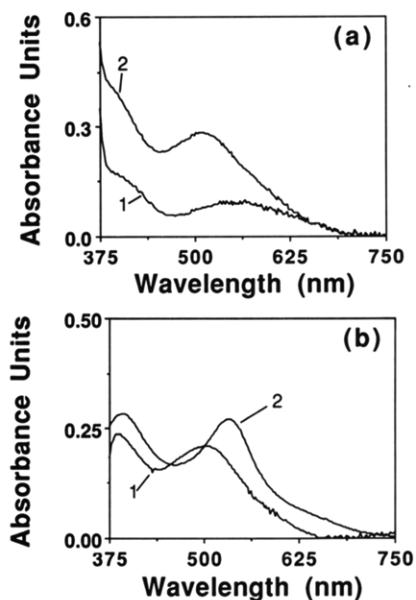
(5) (a) Matsumura, M.; Matsudaira, S.; Tsubomura, H.; Takata, M.; Yanaginda, H. *Ind. Eng. Chem. Prod. Res. Dev.* 1980, 19, 415. (b) Alonso, N.; Beley, V. M.; Chartier, P.; Ern, U. *Rev. Phys. Appl.* 1981, 16, 5.



**Figure 1.** High-resolution scanning electron micrograph of a nanocrystalline ZnO film (0.5- $\mu\text{m}$  thickness) deposited on conducting glass following sintering for 1 h at 350  $^{\circ}\text{C}$ .

$^{\circ}\text{C}$ ) was immersed in a  $10^{-3}$  mol  $\text{dm}^{-3}$  ethanolic solution of *cis*-bis(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II), hereafter denoted by *cis*-(NCS) $_2$ Ru $^{\text{II}}$ L $_2$  and referred to as the sensitizer. The film remained in the above solution for up to 7 days. The sensitized film was stored in ethanol until required for use.

**Photoelectrochemical Characterization of Sensitized Films.** Monochromatic incident photon-to-current conversion efficiencies IPCE( $\lambda$ ) were determined using a thin-layer regenerative photoelectrochemical cell configuration; see eq 1 below. The working electrode (typically about 0.5  $\text{cm}^2$ ) was formed by the *cis*-(NCS) $_2$ Ru $^{\text{II}}$ L $_2$ -sensitized transparent ZnO films whose preparation is described above. The counter electrode consisted of a thin platinum layer electrodeposited on ITO glass. An inert spacer (45  $\mu\text{m}$ ) was used to define the active area of the working electrode and to prevent the cell shorting upon clamping the working and counter electrodes together. The electrolyte solution consisted of 0.5 mol  $\text{dm}^{-3}$  KI (Fluka, anhydrous) and 0.03 mol  $\text{dm}^{-3}$  I $_2$  (Fluka, anhydrous) in an ethylene carbonate (EC) and acetonitrile (MeCN) mixed solvent system (60:40% by volume). The dry electrolyte solution was attracted into the interelectrode cavity by capillary forces. The working electrode was illuminated from the ITO glass side by a 450-W xenon lamp followed by polycarbonate and Schott Tempax 113 (3 mm) filters. This configuration was used to simulate AM 1.5 type solar radiation and to determine the percentage solar-to-electric energy conversion efficiency  $\eta^2$ . The intensity of the illuminating source was determined using a YSI Kettering Model 65A radiometer. Insertion of an Oriel Corp. Model 77250 monochromator (500-nm blaze, 120- $\mu\text{m}$  slit width, and 2-nm bandpass) provides an illumination source for determination of the monochromatic conversion efficiency, IPCE( $\lambda$ ). The potential applied to the cell was controlled using a PAR Model 362 scanning potentiostat. Typically a potential of 0.1 V (SCE) is applied to the working electrode. To measure the potential current curves, a Graph-Tec WX 2400 xy recorder was combined with the above scanning potentiostat. Finally, to study the potential dependence of the IPCE( $\lambda$ ) a three-electrode single-compartment cell was used. The sensitized film formed the working electrode, the counter electrode was Pt, and the reference, connected via an appropriate salt bridge, was a saturated calomel electrode (SCE). For all of the above cell characterization techniques, the resulting data are



**Figure 2.** (a) Absorption spectrum in ethanol of a nanocrystalline ZnO film (0.5- $\mu\text{m}$  thickness) sintered on conducting glass for 1 h at 350  $^{\circ}\text{C}$  (1) before and (2) after immersion in a  $3 \times 10^{-4}$  mol  $\text{dm}^{-3}$  ethanolic solution of *cis*-(NCS) $_2$ Ru $^{\text{II}}$ L $_2$  for 7 days. (b) Difference (1) of spectra in (a) compared with (2) spectrum of  $2 \times 10^{-5}$  mol  $\text{dm}^{-3}$  *cis*-(NCS) $_2$ Ru $^{\text{II}}$ L $_2$  in ethanol.

uncorrected for intensity losses due to light absorption and reflection by the glass supports.

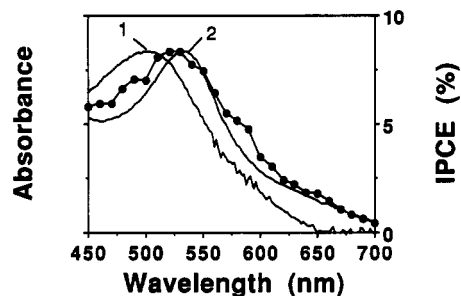
## Results

**Preparation and Characterization of Transparent Nanocrystalline ZnO Films.** Some studies were performed in an attempt to optimize aspects of film preparation. Parameters varied were film thickness and firing temperature. On the basis of the results of these preliminary studies, summarized in Table 1, subsequent experiments were performed using films formed by application of one and two layers of ZnO, having thicknesses between 0.4 and 0.8  $\mu\text{m}$ , fired in air at 350  $^{\circ}\text{C}$  for 1 h, and containing 1% by volume Triton X-100. These films were sensitized by adsorption of *cis*-(NCS) $_2$ Ru $^{\text{II}}$ L $_2$  from a  $10^{-3}$  mol  $\text{dm}^{-3}$  ethanolic solution for 7 days. Shown in Figure 1 is the SEM of a ZnO film (0.5- $\mu\text{m}$  thickness) fired at 350  $^{\circ}\text{C}$  for 1 h prior to sensitization. The porous nature of this film is apparent. Shown in Figure 2a are the UV-visible spectra of a similar film in ethanol prior to and following sensitization by adsorbed *cis*-(NCS) $_2$ Ru $^{\text{II}}$ L $_2$ . We note the absorption maximum of the adsorbed sensitizer (500 nm) is blue shifted with respect to that of the free complex (534 nm); see Figure 2b.

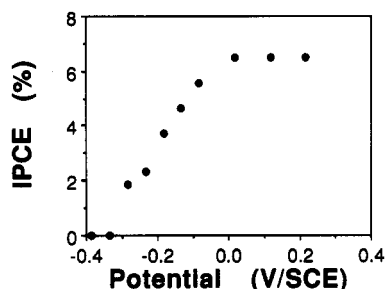
**Photoelectrochemical Characterization of Cell.** The IPCE( $\lambda$ ) was determined for a thin-layer cell, into which had been incorporated the sensitized film whose spectrum is shown in Figure 2 (active area 0.38  $\text{cm}^2$ ), at 10-nm intervals between 400 and 750 nm. IPCE( $\lambda$ ) was calculated using eq 1. The resulting photocurrent action

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

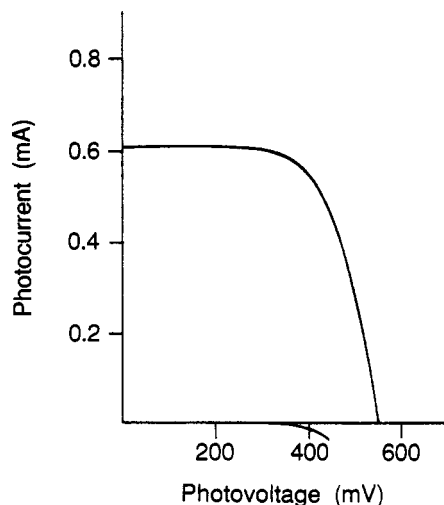
spectrum is plotted in Figure 3. Also shown are the normalized spectra of the free and adsorbed sensitizer in



**Figure 3.** Photocurrent action spectrum (filled circles) for sensitized nanocrystalline ZnO film in Figure 2 (active area 0.38 cm<sup>2</sup>). The spectrum was obtained using a thin-layer cell containing 0.5 mol dm<sup>-3</sup> KI and 0.03 mol dm<sup>-3</sup> I<sub>2</sub> in an ethylene carbonate acetonitrile mixture (60:40 by volume) solvent mixture and operating in the short-circuit mode. Also shown are normalized absorption spectra (1) for *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub> adsorbed at ZnO and (2) free in ethanolic solution.

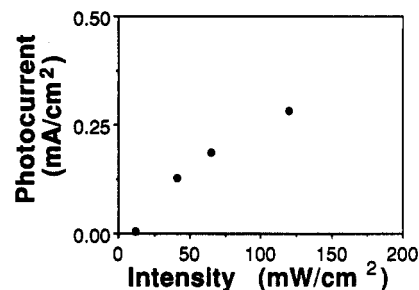


**Figure 4.** Photocurrent-potential curve for 520 nm (51.3 mW cm<sup>-2</sup>) irradiation of a nanocrystalline ZnO film (0.4-μm thickness, active area 1.0 cm<sup>2</sup>) sensitized by adsorbed *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub> (*A*<sub>520</sub> 0.42). The ZnO film formed the working electrode of a three-electrode single-compartment photoelectrochemical cell; the counter electrode was Pt-coated conducting glass. The saturated calomel reference electrode was connected by an appropriate salt bridge. The electrolyte solution was 0.5 mol dm<sup>-3</sup> KI and 0.03 mol dm<sup>-3</sup> I<sub>2</sub> in an ethylene carbonate acetonitrile (60:40 by volume) solvent mixture.



**Figure 5.** Photocurrent-voltage characteristics of a thin-layer cell based on a *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub> sensitized ZnO film (0.8-μm thickness, *A*<sub>520</sub> 0.31, IPCE<sub>520</sub> 13%) containing 0.5 mol dm<sup>-3</sup> KI, 0.03 mol dm<sup>-3</sup> I<sub>2</sub> in ethylene carbonate-acetonitrile (60:40 by volume). The counter electrode was Pt-coated conducting glass. Conditions: AM 1.5 spectral irradiance (119 mW cm<sup>-2</sup>), room temperature, active area 0.51 cm<sup>2</sup>. The onset of the dark current is also shown.

ethanolic solution. We note that the photocurrent action spectrum matches most closely that of the free sensitizer.



**Figure 6.** Effect of light intensity on the short-circuit photocurrent of a thin-layer cell based on a *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub>-sensitized ZnO film (0.6-μm thickness, *A*<sub>520</sub> 0.26, IPCE<sub>520</sub> 6%) containing 0.5 mol dm<sup>-3</sup> KI, 0.03 mol dm<sup>-3</sup> I<sub>2</sub> in ethylene carbonate-acetonitrile (60:40 by volume). The counter electrode was Pt-coated conducting glass. Conditions: AM 1.5 spectral irradiance, room temperature, active area 0.31 cm<sup>2</sup>.

Shown in Figure 4 is a plot of IPCE(λ) at 520 nm (51.3 mW cm<sup>-2</sup>) measured as a function of the applied potential (SCE) in a single-compartment three-electrode cell. The working electrode consisting of a nanocrystalline ZnO film (0.4-μm thickness, active area 1.0 cm<sup>2</sup>) sensitized by adsorbed *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub> (absorbance at 520 nm equal to 0.42).

A current-voltage curve measured for a *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub>-sensitized ZnO film (0.8-μm thickness, absorbance at 520 nm equal to 0.31, IPCE(520 nm) 13%, active area 0.51 cm<sup>2</sup>), using simulated AM 1.5 type solar radiation, is shown in Figure 5. From this curve we calculate a fill factor using eq 2. *V*<sub>opt</sub> (415 mV) and *I*<sub>opt</sub> (1.06 mA cm<sup>-2</sup>)

$$\text{fill factor} = \frac{V_{\text{opt}} (\text{mV}) \times I_{\text{opt}} (\text{mA/cm}^2)}{V_{\text{oc}} (\text{mV}) \times I_{\text{sc}} (\text{mA/cm}^2)} \quad (2)$$

are the cell voltage and current at maximum power output. *V*<sub>oc</sub> (550 mV) is the cell open-circuit photovoltage and *I*<sub>sc</sub> (1.22 mA cm<sup>-2</sup>) is the cell short-circuit photocurrent. For the cell whose current-voltage curve is shown in Figure 5, we determine the fill factor to be 0.66. The solar conversion

$$\eta (\%) = \frac{100 \times \text{fill factor} \times V_{\text{oc}} (\text{V}) \times I_{\text{sc}} (\text{A/m}^2)}{\text{light intensity} (\text{W/m}^2)} \quad (3)$$

efficiency is calculated using eq 3. We determine η to be 0.4%.

Shown in Figure 6 is a plot of the short-circuit photocurrent against the intensity of the incident simulated solar radiation (Type AM1.5). The response is approximately linear over the range studied (0.1–1.0 sun) for a *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub>-sensitized ZnO film (0.6-μm thickness, *A*<sub>520</sub> 0.26, IPCE<sub>520</sub> 6%, active area 0.31 cm<sup>2</sup>).

## Discussion

The monochromatic incident photon-to-current conversion efficiency of the regenerative photoelectrochemical cell described above is 13% at 520 nm. Analogous devices based on nanocrystalline TiO<sub>2</sub> possess IPCE(λ)'s of between 85% and 95% at the same wavelength.<sup>2</sup> An understanding of the reasons for the significantly smaller IPCE(λ) of the ZnO-based device would assist in identifying strategies for optimization of a cell based on this semiconductor. The IPCE(λ) at a wavelength λ is given by eq 4. LHE(λ) is the monochromatic light harvesting efficiency, φ<sub>inj</sub> is the quantum yield for charge carrier

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda)\phi_{\text{inj}}\eta_c \quad (4)$$

injection, and  $\eta_c$  is the fraction of injected charge carriers which reach the external circuit. Each of these terms will be considered.

**Light-Harvesting Efficiency.** Absorbance by adsorbed sensitizer molecules at 520 nm is 0.22; see Figure 2. Using the molar extinction coefficient of *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub> in ethanol ( $1.42 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$  at 534 nm), we estimate an adsorbate concentration of  $2 \times 10^{-8} \text{ mol cm}^{-2}$  or  $1 \times 10^{16} \text{ molecules cm}^{-2}$ .<sup>2</sup> Applying eq 5, where

$$\text{LHE}(\lambda) = 1 - 10^{-\Gamma\sigma(\lambda)} \quad (5)$$

$\Gamma$  is the number of moles of sensitizer per square centimeter and  $\sigma$  is the absorption cross section in units of  $\text{cm}^2/\text{mol}$  ( $1.42 \times 10^7 \text{ cm}^2 \text{ mol}^{-1}$ ), we calculate a LHE( $\lambda$ ) of 0.48 at 520 nm. The above value is half that measured at the same wavelength for a nanocrystalline TiO<sub>2</sub> film sensitized by the same molecule.<sup>2</sup> The reduced LHE( $\lambda$ ) is a consequence of an adsorbed sensitizer concentration that is one-seventh that present in the case of TiO<sub>2</sub>. The reduced sensitizer uptake is attributed to smaller roughness factor due to the reduced thickness of the film (0.5  $\mu\text{m}$  for ZnO, compared to  $>5 \mu\text{m}$  for TiO<sub>2</sub>).

**Injection Efficiency.** A value of 0.48 at 520 nm for the LHE( $\lambda$ ) of the sensitized nanocrystalline ZnO film in Figure 2 only partly accounts for the IPCE( $\lambda$ ) of 8%, measured at the same wavelength following incorporation of this film into the cell for which results are given in Figure 3. Therefore we must consider whether  $\phi_{\text{inj}}$  is significantly less than the value of close to unity reported for TiO<sub>2</sub> based cells.<sup>2</sup>  $\phi_{\text{inj}}$  is given by eq 6, where  $k_{\text{inj}}$  is the

$$\phi_{\text{inj}} = \frac{k_{\text{inj}}}{\tau^{-1} + k_{\text{inj}}} \quad (6)$$

rate constant for electron injection by the electronically excited sensitizer and  $\tau$  is the excited-state lifetime in the absence of charge injection.<sup>7</sup> A value of  $k_{\text{inj}}$  for *cis*-(NCS)<sub>2</sub>-Ru<sup>II</sup>L<sub>2</sub> adsorbed at ZnO is not available. However,  $k_{\text{inj}}$  would have to be 4 orders of magnitude smaller than the corresponding value for TiO<sub>2</sub> ( $>1.4 \times 10^{11} \text{ s}^{-1}$ ),<sup>6</sup> assuming an unchanged excited-state lifetime for the adsorbed sensitizer (50 ns),<sup>2</sup> before  $\phi_{\text{inj}}$  would be reduced significantly. Concerning the excited-state lifetime of the adsorbed sensitizer, the fact that the photocurrent action spectrum closely resembles that of the free complex suggests that the lifetime of those molecules for which charge injection is facile may be close to that of the free complex.<sup>8</sup> To account for the IPCE( $\lambda$ ) of 8% at 520 nm for the cell in Figure 3 a value for  $\eta_c\eta_{\text{het}}$  of 0.17 is necessary. If we assume that  $\eta_c$  is unity, then  $\phi_{\text{inj}}$  is 0.17 and only one in six excited sensitizer molecules photoinject an electron into the conduction band of the ZnO substrate following absorption of a suitably energetic photon.

To understand why  $\phi_{\text{inj}}$  might be significantly less than unity, we consider the photocurrent action spectrum shown in Figure 3. The close agreement between the photocurrent action spectrum and the absorbance spectrum of the free

complex suggests that the metal-to-ligand transition in molecules which photoinject an electron is not energetically perturbed upon adsorption.<sup>2,9</sup> This differs from the reported behavior of this sensitizer on a TiO<sub>2</sub> substrate, there being a significant red shift of the photocurrent action spectrum with respect to the spectrum of the free complex.<sup>2</sup> This red shift is accounted for by delocalization of the  $\pi^*$  state of the sensitizer ligand into the TiO<sub>2</sub> conduction band following complexation via the carboxylate groups of the bipyridyl ligands. Failure to observe such behavior in the case of a ZnO-based cell would suggest that those molecules which photoinject are interacting with the semiconductor substrate either very weakly or in a qualitatively different manner. In the former case we would continue to envisage chelation of the sensitizer through the carboxylate groups of the bipyridyl ligands to surface Zn<sup>2+</sup> atoms, but the degree of delocalization of the  $\pi^*$  state into the conduction band of the semiconductor substrate is limited. The very much slower uptake of sensitizer by ZnO (7 days), compared to TiO<sub>2</sub> (1 h), is consistent with there being a weak interaction between sensitizer and substrate. The reduced interaction diminishes the rate of electron injection,  $k_{\text{inj}}$ . In the latter case the sensitizer may interact with the ZnO substrate through the NCS<sup>-</sup> ligands. It is also possible that the sensitizer is chelated through one NCS<sup>-</sup> ligand and one carboxylated bipyridyl ligand. Consistent with this view, Danzmann and Hauffe have shown that selected azo dyes exhibit sensitizing ability if two OH groups or one OH and a nitrogen atom are present with the required relative geometry.<sup>10</sup> It was concluded from measured photocurrent action spectra that it is the zinc chelate that is the sensitizing chemical entity and not a dye molecule adsorbed at the surface. However, these workers also note that while chelation is necessary for sensitization, it is not sufficient.

The other aspect of this question, i.e., those adsorbed sensitizer molecules which do not photoinject following electronic excitation, is addressed by comparing the spectrum of the adsorbed sensitizer molecules with that of the free complex and the photocurrent action spectrum; see Figure 3. Generally, the observed blue shift in the spectrum of the adsorbed complex may be assigned to one of the following: a change in the dielectric constant at the semiconductor electrode-electrolyte solution interface; dye molecules adsorbed as aggregates or oligomers; dye molecules chemisorbed site specifically.<sup>11</sup> At present it is not possible to distinguish between these possibilities. However, it is possible to conclude that a significant fraction of these molecules are adsorbed in a manner such that they do not inject an electron into the semiconductor substrate following photoexcitation. There is precedent to support this assertion. Memming and co-workers have shown that for a cyanine dye adsorbed at a SnO<sub>2</sub> electrode the photocurrent action spectrum does not agree with the spectrum of the sensitized electrode.<sup>12</sup> This was accounted for by the fact that for such molecules charge injection by the monomer was more efficient than injection by dimers or higher aggregates. In a similar study Spitler has shown that sensitization of ZnO single-crystal electrodes by rhodamine B results in two classes of adsorbed molecules.<sup>13</sup>

(6) O'Regan, B.; Moser, J.; Anderson, Graetzel, M. *J. Phys. Chem.* **1990**, *94*, 8720.

(7) Eichberger, R.; Willig, F. *Chem. Phys.* **1990**, *141*, 159.

(8) Kajiwara, T.; Hasimoto, K.; Kawai, T.; Sakata, T. *J. Phys. Chem.* **1982**, *86*, 4516.

(9) Gulino, D.; Drickamer, H. *J. Phys. Chem.* **1984**, *88*, 1173.

(10) Danzmann, H.; Hauffe, K. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 438.

(11) Gerischer, H.; Willig, F. *Top. Curr. Chem.* **1976**, *61*, 31.

(12) Memming, R. *Faraday Discuss.* **1974**, *58*, 261.

(13) Spitler, M. *J. Phys. Chem.* **1986**, *90*, 2156.

First, those which photoinject an electron following photoexcitation and for which the rate of back electron transfer is slow; second, those which photoinject an electron following photoexcitation and for which the rate of back electron transfer is fast. The former account for the measured photocurrent action spectrum; the latter do not. Similar behavior was reported for Rose Bengal by Danzmann and Hauße and has been described above.<sup>10</sup>

In summary, we suggest that sensitizer molecules adsorbed at the semiconductor-electrolyte solution interface do not undergo photoinduced separation with unit efficiency as in the case of TiO<sub>2</sub>. Assuming  $\eta_c$  is unity we obtain a lower limit of 0.17 for  $\phi_{inj}$ .

**Charge Collection Efficiency.** If  $\phi_{inj}$  is greater than 0.17,  $\eta_c$  will be less than the value of unity assumed above. Studies which might be used to estimate  $\eta_c$  in nanocrystalline ZnO electrodes are not available. However, such studies are ongoing for nanocrystalline TiO<sub>2</sub> electrodes and are considered below.

Time-resolved laser photolysis studies have shown that electrons injected by electronically excited dye molecules can percolate without significant loss through the network of interconnected particles present in nanocrystalline TiO<sub>2</sub> electrodes.<sup>7</sup> The efficiency of this process is in part due to a sufficiently rapid reaction of the relay (iodide) with the oxidized sensitizer and in part due to reverse biasing of the photoelectrode. In the absence of a reverse bias, photoinjected electrons mainly react with the oxidized relay and/or sensitizer as is the case for unsensitized and sensitized colloidal particles of TiO<sub>2</sub>.<sup>14,15</sup> The data presented in Figure 4 is consistent with this general view. At applied potentials more negative than about -0.3 V (SCE), the measured IPCE( $\lambda$ ) at 520 nm is less than 1%. As a more positive potential is applied, the measured IPCE( $\lambda$ ) increases to a constant value of about 7%. The above data suggest a value of about -0.3 V (SCE) for the flatband potential of the sensitized nanocrystalline ZnO electrode based on a comparison with similar data for a TiO<sub>2</sub> nanocrystalline electrode for which the flatband potential is known.<sup>7</sup> In short, a potential gradient within the sensitized ZnO nanocrystallites constituting the cell electrodes is necessary for efficient charge separation.

Recent studies have also considered charge separation and collection yields following bandgap excitation of a nanocrystalline TiO<sub>2</sub> electrode in a conventional three-electrode cell.<sup>16</sup> Time-resolved photoconductivity experiments have been performed by Schwarzberg and Willig<sup>17</sup> and Konenkamp *et al.*<sup>18</sup> There appears to be agreement, consistent with the reduced mobility of photoinjected electrons,<sup>7</sup> that transport is by a hopping mechanism between trap states.<sup>18-19</sup> These traps may be either defects within the constituent particles of the nanocrystalline film or defects at the grain boundaries.<sup>16,18</sup> For very small nanocrystallites such a distinction may not be important. It is also accepted that under illumination equilibrium trap occupancy is greater and that average distances related to transport properties are probably longer than the average diameter of the constituent

particles.<sup>18</sup> Related to the former is the effect of trap-filling on the Fermi level and therefore the potential field at points within the nanocrystalline film.<sup>17</sup> Further, it has been shown that chelation of sensitizer molecules to the TiO<sub>2</sub> surface promotes surface states assigned to Ti<sup>4+</sup> atoms into the conduction band and increases the rate of charge accumulation.<sup>19</sup>

No equivalent studies are available for nanocrystalline ZnO films. Possible mechanisms of charge conduction within and between the sintered crystallites of ZnO films similar to those used in these studies have been discussed by other workers.<sup>20,21</sup> Generally, however, it is accepted that the defects present in ZnO thin films, and consequently the mechanism of charge carrier transport, are strongly dependent on the method of preparation.<sup>22</sup> Work directed toward characterizing the defect and transport properties of the ZnO films used in these studies is in progress. At this time it is not possible to accurately estimate  $\eta_c$  for nanocrystalline ZnO films.

**Optimization of Cell.** It is clear from the above discussion that improvement of the IPCE( $\lambda$ ) of the ZnO-based cell described above will require an increased uptake of the sensitizer and a higher electron injection yield.

Some initial experiments were performed which provide insight into possible practical methods for improving the total solar-to-electric conversion efficiency of a ZnO-based cell. Specifically, films prepared from a single layer of deposited ZnO nanocrystallites were fired for 1 h at 300, 350, and 400 °C. Firing at these temperatures results in sintering of the constituent crystallites. Sintering is performed in air to prevent loss of oxygen from the crystallite surfaces and formation of a metallic zinc layer.<sup>23</sup> There is no apparent decrease in porosity at the higher firing temperatures. This assertion is supported by examination of SEMs of the film surfaces, by the fact that the film thickness remains constant between 0.5 and 0.6  $\mu\text{m}$  and by the fact that the amount of *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub> adsorbed from solution does not differ significantly. The corresponding IPCE<sub>520</sub> of about 7%, as expected, also shows no significant variation. These results are summarized in Table 1. Films prepared from two layers of deposited ZnO nanocrystallites were on average thicker, specifically, ranging from 0.8 to 1.0  $\mu\text{m}$ . No reproducible increase in dye uptake was observed as a consequence of increased film thickness. However, there does appear to be a significant increase in IPCE(%) at 520 nm to a maximum reproducible value of 13%; see in Table 1. Films prepared from five layers of ZnO while showing a similar degree of dye uptake have a very significantly reduced IPCE( $\lambda$ ) at 520 nm of about 1%. Further work in this area is in progress.

## Conclusions

Transparent nanocrystalline ZnO films have been prepared on an ITO glass substrate by sol-gel techniques. Their sensitization by adsorption of *cis*-(NCS)<sub>2</sub>Ru<sup>II</sup>L<sub>2</sub> and subsequent incorporation as the light-harvesting unit in a regenerative photoelectrochemical cell has been de-

(14) Fitzmaurice, D.; Frei, H. *Langmuir* 1991, 7, 1129.

(15) Fitzmaurice, D.; Eschle, M.; Frei, H.; Moser, J. *J. Phys. Chem.* 1993, 97, 3806.

(16) Hagfeldt, A.; Bjorksten, U.; Lindquist, S.-E. *Sol. Energy Mater. Sol. Cells* 1992, 27, 293.

(17) Schwarzberg, K.; Willig, F. *Appl. Phys. Lett.* 1991, 58, 2520.

(18) Konenkamp, R.; Henninger, R.; Hoyer, P. *J. Phys. Chem.* 1993, 97, 7328.

(19) Redmond, G.; Fitzmaurice, D.; Graetzel, M. *J. Phys. Chem.* 1993, 97, 6951.

(20) Schoenses, J.; Kanazawa, K.; Kay, E. *J. App. Phys.* 1977, 48, 2537.

(21) Eda, K. *J. App. Phys.* 1978, 49, 2964.

(22) Hirschwald, W. *Current Topics in Materials Science*; Kaldis, E., Ed.; North-Holland: New York, 1981; Vol. 7, Chapter 3.

(23) Gray, J. *J. Am. Ceram. Soc.* 1954, 37, 534.

scribed. The resulting device has a monochromatic IPCE( $\lambda$ ) of 13% at 520 nm and a simulated AM 1.5 solar conversion efficiency of 0.4%. Analysis of the components of the IPCE( $\lambda$ ) suggest that the lower efficiency compared with an analogous TiO<sub>2</sub>-based device is a consequence of reduced uptake of the sensitizing molecule and lower quantum yields for charge injection. The former is possibly due to reduced porosity of the semiconductor film and to reduced affinity of the sensitizer for the semiconductor substrate. The latter is due to weaker interaction of the dye with the electrode surface. The lowering of cell

efficiency due to reduced charge collection efficiency cannot be accurately estimated.

**Acknowledgment.** We thank Dr. M. K. Nazeeruddin for preparing the sensitizing molecule used in these studies and Dr. Shklover for measuring SEMs of the ZnO films. G.R. thanks Prof. M. Graetzel for the kind invitation to visit his laboratory. Work performed at EPFL was supported by a grant from the Swiss Federal Energy Office. Work performed at UCD was supported by Hewlett-Packard (Ireland) Ltd. and EOLAS.