

Highly efficient charge transfer from a *trans*-ruthenium bipyridine complex to nanocrystalline TiO₂ particles

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trans-Di(isothiocyanato)-[*N*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II)] acts as a very efficient charge-transfer sensitizer for nanocrystalline TiO₂ films. The incident photon-to-electron conversion efficiency (IPCE) for the dye-coated TiO₂ film exceeded 80% in the wavelength domain between 400 and 600 nm. A sandwich-type regenerative solar cell fabricated from a 10 μm thick TiO₂ film sensitized with this dye generated a short-circuit photocurrent of 19.6 mA cm⁻² and an open-circuit photovoltage of 720 mV in simulated AM1.5 solar light (924 W m⁻²) with an overall power conversion efficiency of 8.6%.

Much attention has been paid to dye-sensitized photoelectrochemical cells based on nanocrystalline semiconductor films since the advent of the Grätzel cell.¹ With the most outstanding photoelectric conversion properties and high stability, *cis*-di(isothiocyanato)-[*N*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)] ruthenium(II) (*cis*-Ru) was extensively studied^{2–6} during the past 10 years. In this period, although many ruthenium polypyridine complexes^{7–10} have been synthesized for the purpose of obtaining better dyes than *cis*-Ru in photoelectric conversion, so far few others have been comparable to it. Zakeeruddin *et al.* reported the synthesis of the isomer of *cis*-Ru, and prophesied it would be an attractive candidate as a panchromatic charge-transfer sensitizer in mesoporous oxide solar cells.¹¹ Herein we report its outstanding charge-transfer properties when anchored to the surface of nanocrystalline TiO₂ particles.

The absorption spectra for *trans*-Ru in DMF and nanocrystalline TiO₂ film, respectively, are shown in Fig. 1. Three absorption peaks assigned to MLCT appear in the UV-vis spectra for both dye-coated film and dye solution. Compared with the spectrum of *cis*-Ru, the lowest energy MLCT maximum is red-shifted by about 50 nm.¹¹ The enhanced red

absorption of *trans*-Ru renders it an attractive candidate as a panchromatic charge-transfer sensitizer in liquid junction solar cells based on nanocrystalline oxide. However, while the 590 nm peak is more intense than the 530 nm peak for dye solution, the opposite is seen for the dye-coated film. This phenomenon may result from the solvent effect.

Corrected IPCEs of *trans*-Ru are above 80% between 400 and 600 nm (Fig. 1). The close resemblance between the action spectrum and the UV-vis spectrum of the dye-coated film indicates that the dye is responsible for the photocurrent generation. We can see from the action spectrum that the sensitization of TiO₂ film at 590 nm is not as efficient as expected, compared with the sensitization at 530 nm, which is another example of “band selective” sensitization after the report of Ferrere and Gregg.¹²

A platinized CTO glass, as counter electrode, was placed on the dye-coated film and both were clamped together (see Experimental) after introducing the electrolyte into the inter-electrode space. Under irradiation of simulated AM1.5 solar light,² the *I*–*V* curves for *trans*-Ru and *cis*-Ru measured in a 2-electrode system are illustrated in Fig. 2. Under “one sun”

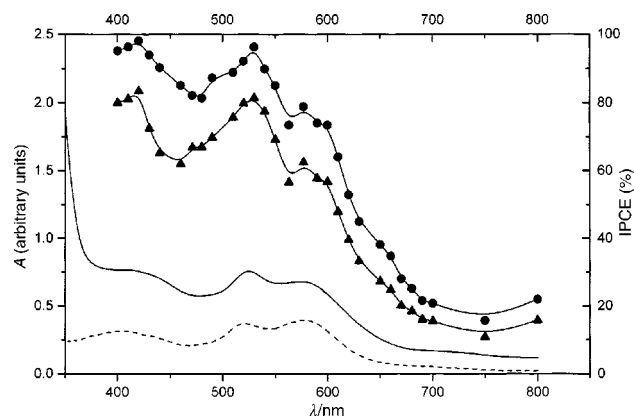
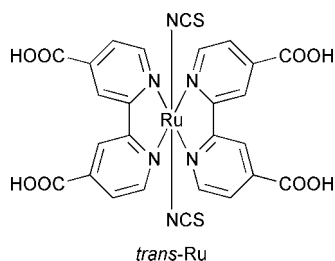


Fig. 1 Photocurrent action spectrum under zero bias voltage (vs. SCE): (●) corrected and (▲) uncorrected for the absorption and reflection loss of the bare CTO glass. UV-vis spectra of (—) *trans*-Ru-coated TiO₂ film, which was obtained by subtracting the spectrum of TiO₂ film together with CTO glass support from the original spectrum and (---) 2.5 × 10⁻⁵ M dye solution in DMF.

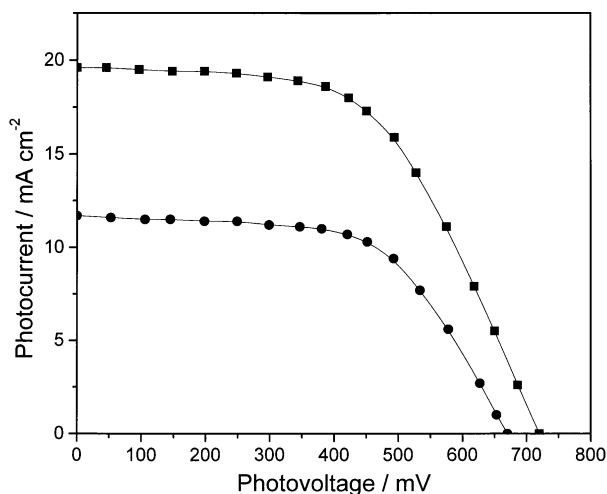
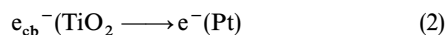
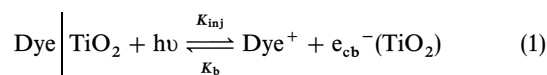


Fig. 2 I - V curves for a solar cell based on (■) *trans*-Ru and (●) *cis*-Ru in simulated AM1.5 sunlight (924 W m^{-2}).

irradiation (924 W m^{-2}), the cell based on *trans*-Ru gave 19.6 mA cm^{-2} of short-circuit photocurrent (I_{sc}), 720 mV of open-circuit photovoltage (V_{oc}) and 0.56 of fill factor (FF), corresponding to an overall power conversion efficiency of 8.6% , while the cell based on *cis*-Ru had 14.9 mA cm^{-2} I_{sc} , 692 mV V_{oc} and 0.60 FF, corresponding to an overall power conversion efficiency of 6.7% . Obviously, *trans*-Ru is more efficient in charge transfer than *cis*-Ru under the same conditions. No attempt has yet been made to optimize the solar cell, so it is of no doubt that the cell based on *trans*-Ru will be more efficient after optimizing FF.

We also examined the stability of the cell. After photoelectrochemical measurements, the dye-coated film was set in daylight for a week and then measured again. Results showed that the photocurrents remained unchanged within experimental deviation, confirming its high stability.

In order to explain the mechanism of photocurrent generation, we measured the HOMO energy level of *trans*-Ru by synchrotron radiation XPS (SRXPS). A HOMO energy level in vacuum of -5.2 eV , combined with an absorption threshold at 800 nm (1.55 eV) for *trans*-Ru, gives the first excited state energy level (under visible light excitation) at -3.65 eV , above the conduction band edge (CB) of TiO_2 (-4.4 eV). Therefore, an excited dye molecule on a TiO_2 particle could inject an electron into the CB of TiO_2 [eqn. (1)]. The electron injected into the CB of TiO_2 is subsequently directed to the back contact of the CTO glass and immediately flows to the counter electrode [eqn. (2)] under the photovoltage driving force. The process can be presented as follows:



The HOMO energy level of *cis*-Ru was also determined to be -5.2 eV by SRXPS, so the excited energy levels for both isomers should be similar under visible light illumination. Therefore, one can predict that the rate constant for electron injection (K_{inj}) is much larger than the rate constant for back electron transfer (K_b), resulting in very rapid electron transfer from *trans*-Ru to the CB of TiO_2 , otherwise, the values of IPCE and η would not be so high. Obviously, *trans*-Ru should also be an excellent sensitizer for TiO_2 . The study of the

kinetics of the charge-transfer process of *trans*-Ru coated films is in progress.

Experimental

cis-Ru was synthesized according to the literature procedure,² and at the same time its isomer, *trans*-di(isothiocyanato)-[*N*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)] ruthenium(II) (*trans*-Ru) was prepared by following the literature procedure.¹¹ ^1H NMR ($\text{D}_2\text{O}/\text{NaOD}$) for *trans*-Ru: 9.43 (4H, d, 6,6'-bpy); 8.76 (4H, s, 3,3'-bpy); 7.98 (4H, d, 5,5'-bpy); ^1H NMR ($\text{D}_2\text{O}/\text{NaOD}$) for *cis*-Ru: 9.50 (2H, d, 6-bpy), 8.87 (2H, s, 3-bpy), 8.70 (2H, s, 3'-bpy), 8.15 (2H, d, 5-bpy), 7.75 (2H, d, 6'-bpy), 7.44 (2H, d, 5'-bpy). TiO_2 colloid ($100\text{--}150 \text{ g dm}^{-3}$, $15\text{--}20 \text{ nm}$) was prepared by following the reported method.¹ TiO_2 films ($10 \mu\text{m}$ thick) were prepared by spreading the colloidal dispersion onto fluorine-doped conducting tin oxide glass (CTO, 20Ω per square) followed by sintering at 450°C for 30 min . The porous TiO_2 film was sensitized with *trans*-Ru by soaking it in the dye solution (in DMF) for at least 72 h .

UV-vis spectra were recorded on a Shimadzu UV-3100 spectrophotometer. With $0.3 \text{ M LiI} + 0.03 \text{ M I}_2$ in propylene carbonate-ethylene carbonate ($1:1 \text{ v/v}$) used as the redox electrolyte, the photocurrent action spectra were measured in a three-electrode system (CH 600 voltammetric analyzer, USA) in which dye-coated film, platinized CTO glass and a saturated calomel electrode were employed as working electrode, counter electrode and reference electrode, respectively. In order to increase light harvesting and catalyze the reduction of triiodide, the platinized CTO glass was placed on top of the dye-coated film and both were clamped tightly.

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References

- 1 B. O'Regan and M. Grätzel, *Nature (London)*, 1991, **353**, 737.
- 2 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
- 3 K. Tennakone, G. R. R. A. Kumara, I. R. M. Kottegoda and V. P. S. Perera, *Chem. Commun.*, 1999, 15.
- 4 A. Stanley, B. Verity and D. Matthews, *Sol. Energy Mater. Sol. Cells*, 1998, **52**, 141.
- 5 T. Hannappel, B. Burfeindt, W. Storck and F. Willig, *J. Phys. Chem. B*, 1997, **101**, 6799.
- 6 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer and M. Grätzel, *Nature (London)*, 1998, **395**, 583.
- 7 R. Argazzi, A. Bignozzi, T. A. Heimer, F. N. Castellano and G. J. Meyer, *J. Phys. Chem. B*, 1997, **101**, 2591.
- 8 P. Pechy, F. P. Rotzinger, M. K. Nazeeruddin, O. Kohle, S. M. Zakeeruddin, R. Humphry-Baker and M. Grätzel, *J. Chem. Soc., Chem. Commun.*, 1995, 65.
- 9 P. Bonhôte, E. Gogniat, S. Tingry, C. Barbe, N. Vlachopoulos, F. Lenzmann, P. Comte and M. Grätzel, *J. Phys. Chem. B*, 1998, **102**, 1498.
- 10 T. A. Heimer, S. T. D'Arcangelis, F. Farzad, J. M. Stipkala and G. J. Meyer, *Inorg. Chem.*, 1996, **35**, 5319.
- 11 S. M. Zakeeruddin, M. K. Nazeeruddin, R. Humphry-Baker and M. Grätzel, *Inorg. Chim. Acta*, 1999, **296**, 250.
- 12 S. Ferrere and B. A. Gregg, *J. Am. Chem. Soc.*, 1998, **120**, 843.