



ELSEVIER

Solar Energy Materials & Solar Cells 71 (2002) 261–271

www.elsevier.com/locate/solmat

Solar Energy Materials  
& Solar Cells

# Photoelectric behavior of nanocrystalline TiO<sub>2</sub> electrode with a novel terpyridyl ruthenium complex

Zhong-Sheng Wang<sup>a,b,c</sup>, Chun-Hui Huang<sup>a,b,\*</sup>, Yan-Yi Huang<sup>a,b</sup>,  
Bao-Wen Zhang<sup>d</sup>, Pu-Hui Xie<sup>d</sup>, Yuan-Jun Hou<sup>d</sup>,  
Kurash Ibrahim<sup>e</sup>, Hai-Jie Qian<sup>e</sup>, Feng-Qin Liu<sup>e</sup>

<sup>a</sup> State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, People's Republic of China

<sup>b</sup> The University of Hong Kong Joint Laboratory in Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871, People's Republic of China

<sup>c</sup> College of Science, Shandong Agricultural University, Tai'an 271018, Shandong Province, People's Republic of China

<sup>d</sup> Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, People's Republic of China

<sup>e</sup> Synchrotron Radiation Laboratory at Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Received 20 February 2001; received in revised form 18 April 2001; accepted 30 May 2001

## Abstract

The photoelectric behavior of a black dye, tris (isothiocyanato)-[*N*-(2,2':6',2''-terpyridine-4'-(4-carboxylic acid) phenyl)] ruthenium (II) complex, was examined under different conditions. The dye was adsorbed on nanocrystalline TiO<sub>2</sub> surface strongly and generated incident monochromatic photon-to-current conversion efficiency (IPCE) of about 90% at maximum absorption wavelength and greater than 20% in the near-IR region. A sandwich-type solar cell fabricated by this dye-sensitized nanocrystalline TiO<sub>2</sub> film generated 6.1 mA cm<sup>-2</sup> of short-circuit photocurrent, 0.58 V of open-circuit photovoltage and 2.9% of overall yield under irradiation of white light (78.0 mW cm<sup>-2</sup>) from a Xe lamp. Since the title dye shows better photoresponse than the N3 dye in the near-IR region, it would be a promising panchromatic sensitizer after optimization. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Grätzel cell; Black dye; TiO<sub>2</sub>; Nanocrystalline TiO<sub>2</sub>; Dye sensitized solar cell; Terpyridyl ruthenium dyes; Photoelectrochemical solar cells

\*Corresponding author. Tel.: +86-10-62757156; fax: +86-10-62751708.

E-mail address: hch@chem.pku.edu.cn (C.-H. Huang).

## 1. Introduction

The first efficient dye-sensitized nanocrystalline solar cell with an overall yield of 7.1% was reported in 1991 [1], which indicates that molecular photovoltaic converter has been a powerful alternative candidate for conventional silicon solar cells. Thereafter, many research groups started to investigate the sensitization of nanocrystalline TiO<sub>2</sub> electrode with inorganic [2–9] and organic dyes [11–17]. In recent years, *cis*-Ru(NCS)<sub>2</sub>(dcbpy)<sub>2</sub> (known as the N3 dye)<sup>2</sup>, where dcbpy is 4,4'-dicarboxylic acid-bipyridine, has been investigated extensively due to its unmatched performance in dye staff studied as solar cell sensitizer before 1997. Only recently, a black dye tri(cyanato)-2,2'2''-terpyridyl-4,4',4''-tricarboxylate ruthenium (II) was proved to exhibit better near-IR photoresponse than the N3 dye [18,19]. The discovery of this black dye [18,19] opens up the way to improve the overall yield of dye-sensitized solar cells. If the photoresponse in the 700–900 nm region is further enhanced, overall yield will be increased significantly [20]. Therefore, the challenge to search for a new more efficient dye remains.

In order to further broaden the photoresponse of sensitizer to longer wavelength of light, the 4'-position of terpyridine was substituted with *p*-carboxylphenyl group and a new ruthenium complex K[Ru(NCS)<sub>3</sub>(tlyphCOOH)] (hereafter denoted as tpyRu, structure as shown in Fig. 1), where tlyphCOOH is 2,2':6',2''-terpyridine-4'-(4-carboxylic acid)-phenyl, was synthesized. Its excited state energy level (under visible light excitation) lies above the edge of conduction band (CB) for TiO<sub>2</sub>, rendering electron injection to the CB of TiO<sub>2</sub> thermodynamically favorable. Here we report the photoelectrochemical properties of tpyRu-loaded nanocrystalline TiO<sub>2</sub> electrodes.

## 2. Experimental section

### 2.1. Materials

Optically transparent conducting glass (CTO glass, fluorine-doped SnO<sub>2</sub> overlayer, transmission > 70% in the visible, sheet resistance 20 Ω/square) was obtained

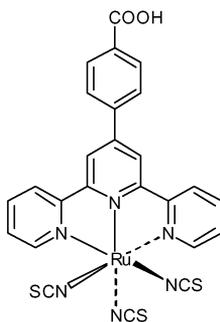


Fig. 1. Schematic structure of tpyRu.

from the Institute of Nonferrous Metals of China. Titanium tetraisopropoxide, 4'-(p-tolyl)-2,2':6,2''-terpyridine, 4-tert-butylpyridine, and propylene carbonate (PC) were purchased from Acros. All the other solvents and chemicals used in this work are of reagent grade (Beijing Chemical Factory, China) and used without further purification. Redox electrolyte used in this work is 0.5 M LiI + 0.04 M I<sub>2</sub> in PC.

*cis*-Ru(II)(NCS)<sub>2</sub>(dcbpy)<sub>2</sub> (N3 dye), where dcbpy is 4,4'-dicarboxylic acid-2,2'-bipyridine, was synthesized according to the literature [2], and its purity was confirmed by <sup>1</sup>H NMR and elemental analysis.

### 2.1.1. Synthesis of tpyRu

The oxidation of 4'-(p-tolyl)-2,2':6,2''-terpyridine (0.4533g) [21,22] was carried out in sulfuric acid (8.6 cm<sup>3</sup>) with chromium trioxide (0.562 g) at 75–80°C yielding 4'-(carboxyl-phenyl)-2,2':6,2''-terpyridine L.

The [RuLCl<sub>3</sub>] complex was synthesized by mixing a solution of 4'-(carboxy-phenyl)-2,2':6,2''-terpyridine (70.6 mg) in ethanol (20 cm<sup>3</sup>) with hydrated ruthenium trichloride (52.4 mg). The reaction mixture was refluxed for 3 h and the precipitated complex was collected and washed thoroughly with ethanol.

The complex K[RuL(NCS)<sub>3</sub>] was obtained by refluxing [RuLCl<sub>3</sub>] (0.224 g) and AgBF<sub>4</sub> in acetone for 3 h. A DMF/water (3:1 in volume, 20 cm<sup>3</sup>) solution of KSCN (0.44 g) was added to the above filtrate. The mixture was refluxed under Ar for 6 h at 130–140°C over reduced light. The isolated solid was recrystallized from acetone/ether.

Anal. Calcd. For K[RuL(NCS)<sub>3</sub>]·H<sub>2</sub>O : C, 43.80; H, 2.48; N, 12.26%. Found C, 43.75; H, 2.50; N, 12.28%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ (ppm): 8.93–8.78 (m, 6H, 3,3',5',3'',4,4''), 8.16–8.07 (m, 6H, 6,6''H<sub>o</sub>,H<sub>m</sub>), 7.79–7.77 (m, 2H, 5,5'').

### 2.2. Preparation of nanocrystalline TiO<sub>2</sub> films

100–150 g dm<sup>-3</sup> TiO<sub>2</sub> colloidal dispersion was prepared by following the procedure reported in the literature [1,2], but autoclaving was performed at 220°C. In order to improve the ohmic contact between TiO<sub>2</sub> particles and conducting glass, three drops of 1 × 10<sup>-3</sup> M titanium tetraisopropoxide in 2-propanol was spread on the conducting glass (2 × 8 cm) and dried naturally in air at room temperature followed by the preparation of TiO<sub>2</sub> films [2].

Coloration of the TiO<sub>2</sub> surface with the dye was carried out by immersing the film (10 μm thick) at least for 12 h in a 1 × 10<sup>-4</sup> M solution of tpyRu in DMF. After completion of the dye adsorption, the electrode was withdrawn from the solution, washed with dry ethanol, dried under a stream of dry air, and immediately wetted with redox electrolyte solution for testing.

### 2.3. Methods

The thickness of the film was determined with a DEKTAK 3 profilometer. Absorption spectra were recorded with a Shimadzu UV-3100 spectrophotometer. Photoelectrochemical experiments, including photocurrent action spectrum and

linear sweep voltammetry (LSV), were measured with a model 600 voltammetric analyzer (CH instruments Inc., USA). A three-electrode cell was comprised of a dye-coated film working electrode, a platinized conducting glass as counter electrode, which was placed on the face of the working electrode, and a saturated calomel electrode (SCE) as reference electrode. Before measurement, the redox electrolyte was degassed with ultra pure nitrogen for 15 min. The current–voltage characteristic curves were recorded in a 2-electrode-system described elsewhere [23]. A 500 W xenon lamp (Ushio Electric, Japan) was used as a light source. An IRA-25S filter (Toshiba, Japan) was used to cut off infrared light to protect the electrode from heating, meanwhile a GG420 filter (Toshiba, Japan) was used to cut off the light with wavelength less than 420 nm. Monochromatic light was obtained with a series of filters (Toshiba Co., Japan). Light intensities were measured with a light gauge radiometer/photometer (Coherent, USA). HOMO energy level of the ruthenium complex was determined through the synchrotron radiation photoelectron spectroscopy (SRPES) in Synchrotron Radiation Laboratory at the Institute of High Energy Physics. Under ultrahigh vacuum ( $3\text{--}4 \times 10^{-8}$  Pa), photoelectron spectra were recorded using 60 eV radiation light, from which the first ionization energy, the HOMO energy level, was derived.

### 3. Results and discussion

#### 3.1. Absorption and photoelectrochemical properties of tpyRu

Absorption properties of tpyRu both in solution and on  $\text{TiO}_2$  film are listed in Table 1, while the absorption spectrum for the dye in ethanol solution is shown in Fig. 2. We can see from Fig. 2 that three peaks and a shoulder peak appear in the UV-visible range. Peaks at 287 and 323 nm are attributed to  $\pi\text{--}\pi^*$  intraligand transitions, while peaks at 389 and 560 nm are assigned to  $t_2\text{--}\pi^*$  MLCT bands. Interestingly, the peak at 560 nm is very broad, its half-peak-width being ca. 110 nm; it is expected to harvest visible light very efficiently. In order to compare the photoresponse between tpyRu and the N3 dye, the absorption spectrum of the N3 dye is also shown in Fig. 2. One can conclude from the comparison of both spectra that tpyRu exhibits better photoresponse than the N3 dye in the visible. However, after tpyRu dye was adsorbed onto nanostructured  $\text{TiO}_2$  film, the peak in the visible

Table 1  
Absorption properties of tpyRu

	Abs. max <sup>a</sup> (nm)			Abs. max <sup>b</sup> (nm)	
	287	323	389	560	500
$\epsilon$ ( $M^{-1} \text{ cm}^{-1}$ )	$7.55 \times 10^3$	$3.87 \times 10^3$	$1.60 \times 10^3$	$1.24 \times 10^3$	—

<sup>a</sup> Dye solution in ethanol ( $3.70 \times 10^{-5}$  M).

<sup>b</sup> Bare dye-coated  $\text{TiO}_2$  film corrected for the absorption of  $\text{TiO}_2$  and conducting glass support.

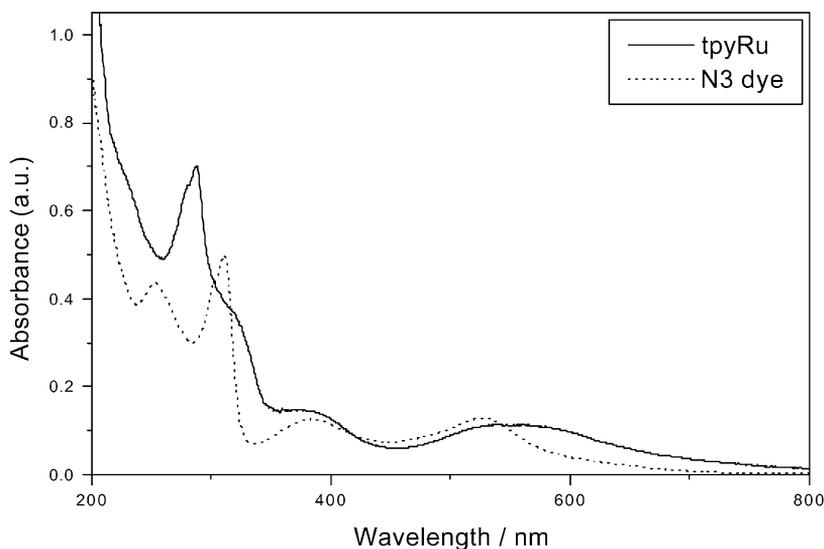


Fig. 2. Absorption spectra of tpyRu (a) and the N3 dye (b) in ethanol.

was blue-shifted (see Fig. 3a), which is disadvantageous to the conversion of red light. This phenomenon implies that tpyRu form H-aggregates on the TiO<sub>2</sub> surface [24]. The absorption threshold of tpyRu on TiO<sub>2</sub> film extends well to 800 nm, which is in agreement with that of the dye solution. The photocurrent was measured under illumination through substrate with zero bias voltage (vs. SCE) applied to tpyRu-coated TiO<sub>2</sub> electrode. The incident monochromatic photon-to-current conversion efficiency (IPCE), defined as the number of electrons generated by light in the external circuit divided by the number of incident photons (calculated by Eq. (1)), is plotted as a function of excitation wavelength shown in Fig. 3b.

$$\text{IPCE (\%)} = \frac{1240 I_{\text{sc}} (\mu\text{A}/\text{cm}^2)}{\lambda (\text{nm}) P_{\text{in}} (\text{W}/\text{m}^2)}, \quad (1)$$

where  $\lambda$  and  $P_{\text{in}}$  are the wavelength of incident monochromatic light and its power, respectively, and  $I_{\text{sc}}$  is the short-circuit photocurrent generated under illumination of the related monochromatic light. Photocurrent action spectrum (Fig. 3b) and the absorption spectrum for the dye-coated film (Fig. 3a) match well, indicating the dye is responsible for the anodic photocurrent generation. Data from action spectrum show that the IPCE values exceed 80% in the wavelength range between 400 and 600 nm, and decrease gradually above 600 nm. The IPCEs above 20% in the red region (650–800 nm) should result from the absorption of the dye in the red region.

### 3.2. Current–voltage characteristics of regenerative cells

The counter electrode, a platinized conducting glass, was placed directly on the dye-coated TiO<sub>2</sub> film (working electrode), then a sandwich-type solar cell was

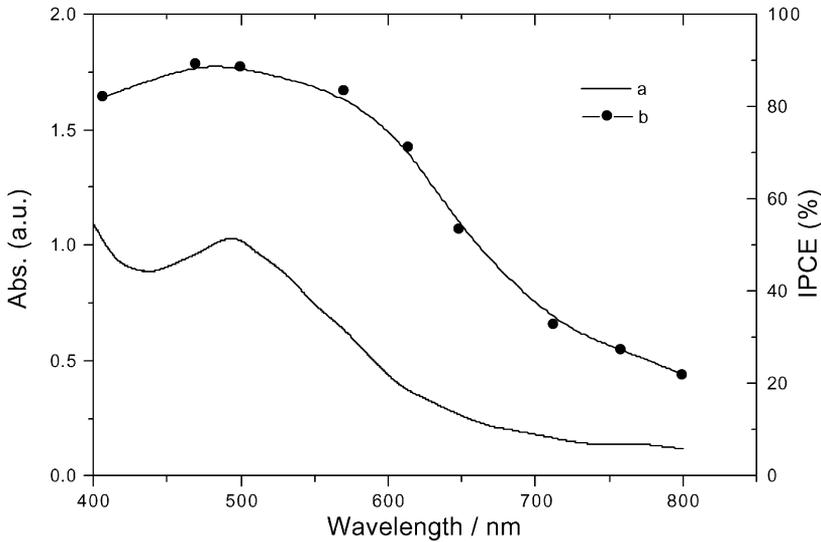


Fig. 3. (a) Absorption spectrum of tpyRu on TiO<sub>2</sub> film (10 μm) without any electrolyte, which is obtained by the subtraction of absorption spectrum for TiO<sub>2</sub> and substrate glass from that for tpyRu-coated TiO<sub>2</sub> film; (b) photocurrent action spectrum for tpyRu (corrected for the absorption of light by CTO glass) with zero bias voltage (vs. SCE).

fabricated after the electrolyte was introduced into the interelectrode space by capillary force. In order to examine the performance of tpyRu-coated TiO<sub>2</sub> electrode, the N3-dye-sensitized electrode was also tested under the same conditions. Fig. 4 shows the  $I$ - $V$  curves obtained with a tpyRu or N3-dye-modified solar cell under illumination of white light from a Xe lamp. One can see from Fig. 4 that the N3 dye is more outstanding than tpyRu in both short-circuit photocurrent and photovoltage. Photocurrent-voltage characteristic parameters are listed in Table 2 for the purpose of comparison. Under illumination of white light (78.0 mW cm<sup>-2</sup>), tpyRu-sensitized electrode gave  $I_{sc} = 6.1$  mA cm<sup>-2</sup>,  $V_{oc} = 0.58$  V, FF = 0.62, corresponding to an overall energy conversion efficiency ( $\eta$ ) of 2.9%. However, under the same conditions as those for tpyRu, the N3 dye-based solar cell generated 6.8% of overall yield ( $I_{sc} = 14.5$  mA cm<sup>-2</sup>,  $V_{oc} = 0.66$  V, FF = 0.55). The fill factor (FF) is defined as follows:

$$FF = V_{opt}I_{opt}/V_{oc}I_{sc}, \quad (2)$$

where  $V_{opt}$  and  $I_{opt}$  are, respectively, voltage and current for maximum power output.  $\eta$  is defined as follows:

$$\eta = \frac{I_{sc}V_{oc}FF}{P_{in}}, \quad (3)$$

where  $P_{in}$  is the power of incident white light. The effect of light intensity on the cell performance was also studied, the results are listed in Table 2.  $I_{sc}$  is not linearly

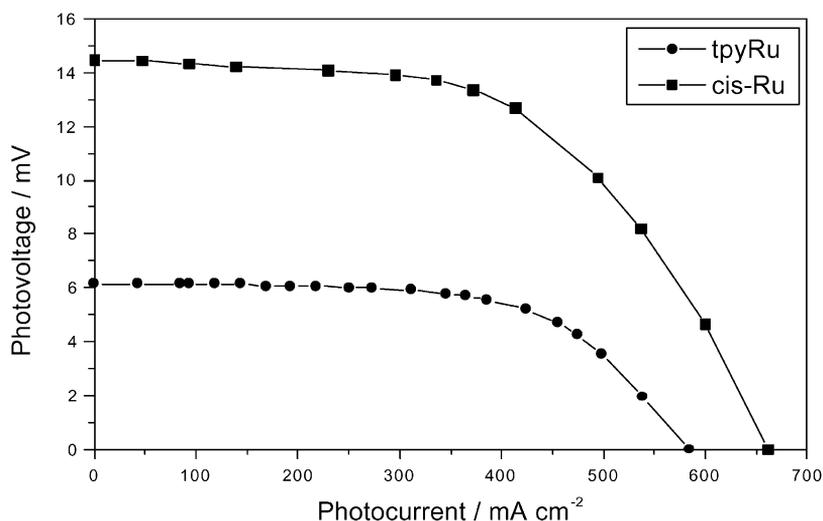


Fig. 4.  $I$ - $V$  curves of tpyRu or the N3 dye-coated TiO<sub>2</sub> film under illumination of 78.0 mW cm<sup>-2</sup>; effective area for illumination is 0.14 cm<sup>2</sup>.

Table 2

Performance parameters of solar cells based on nanocrystalline TiO<sub>2</sub> films sensitized with tpyRu or the N3 dye<sup>a</sup>

	Light intensity <sup>b</sup> (mW cm <sup>-2</sup> )	$I_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	$\eta$ (%)
tpyRu	78.0	6.1	584	0.62	2.9
	52.6	4.7	576	0.66	3.3
	15.6	1.6	542	0.71	3.9
N3	78.0	14.5	662	0.55	6.8

<sup>a</sup> Dye-sensitized TiO<sub>2</sub> electrodes were immersed in 4-tertbutylpyridine for 15 min before measurement.

<sup>b</sup> An IRA-25S filter and a GG-420 filter were used to cut off infrared light and light with wavelength less than 420 nm.

proportional to the light intensity, increasing less than expected with the increase of light intensity. The nonlinearity indicates that photocurrents generated by this solar cell are limited by diffusion of the iodide or triiodide ions within the nanostructured film [2]. The overall power conversion yield ( $\eta$ ) and fill factor (FF) decreases with the increase of light intensity (Table 2) due to the increase in ohmic loss in the TiO<sub>2</sub> film with the increase of light intensity. Additionally,  $I_{sc}$  almost remained constant under continuous 6-h illumination, confirming that the dye is stable.

### 3.3. Effect of applied potential on photocurrent

In order to understand the effect of applied potential on charge recombination, the current-bias voltage curves were recorded via LSV from the photoelectrochemical

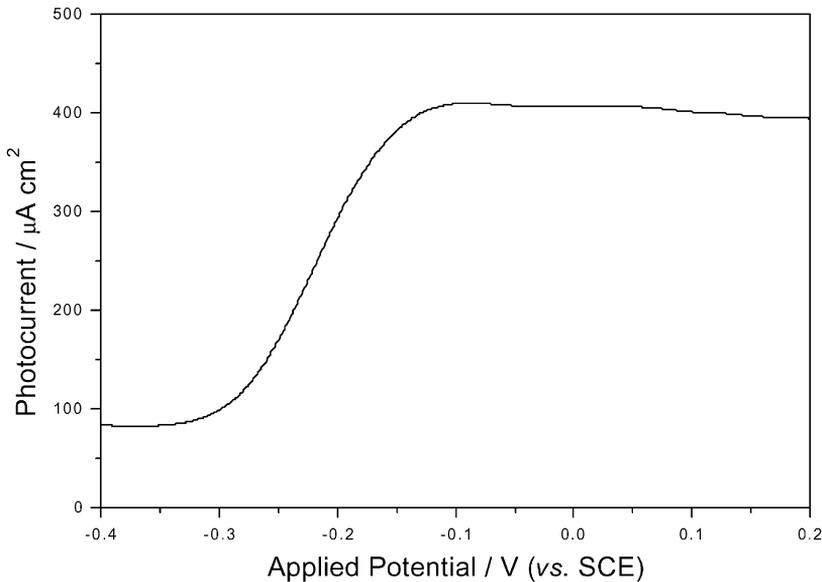


Fig. 5. Photocurrent-applied potential (vs. SCE) curve, the subtraction of the curve in dark from that under 570 nm illumination of  $1382 \mu\text{W cm}^{-2}$ .

experiments employing the same dye-coated  $\text{TiO}_2$  film under light illumination and dark, respectively. The subtraction of the curve under dark from that under light illumination gave the photocurrent–bias voltage curve, shown in Fig. 5. One can see from Fig. 5 that photocurrents rise steeply with increasing bias voltage from  $-0.3 \text{ V}$  and level off at  $-0.1 \text{ V}$ . It is seen from the steep edge and rapid attainment of plateau for the photocurrent–potential characteristic curve that the charge separation, but not the charge recombination, is the controlling step under present conditions. Generally, applying negative potential will decrease the anodic photocurrent and finally reverse the current flow because negative bias can increase the concentration of electrons in conduction band (CB) [25,26]. After the CB of  $\text{TiO}_2$  is filled with electrons due to negative bias voltage, electron injection from the dye will be hindered. Strangely, the photocurrent onset was not observed even if applying negative potential up to  $-0.6 \text{ V}$ , that is, the photocurrents were much greater than zero in the applied negative potential range. This phenomenon implies that electron injection is so favorable that negative bias voltage cannot reverse the current flow within the potential range studied.

#### 3.4. Mechanism

As for photosensitization of semiconductor, the position of the excited state energy level of the dye is an important factor because electron injection from the dye molecule to the CB of semiconductor requires that the first excited state energy level of the dye be higher than the edge of CB for  $\text{TiO}_2$ , and meanwhile both match well in

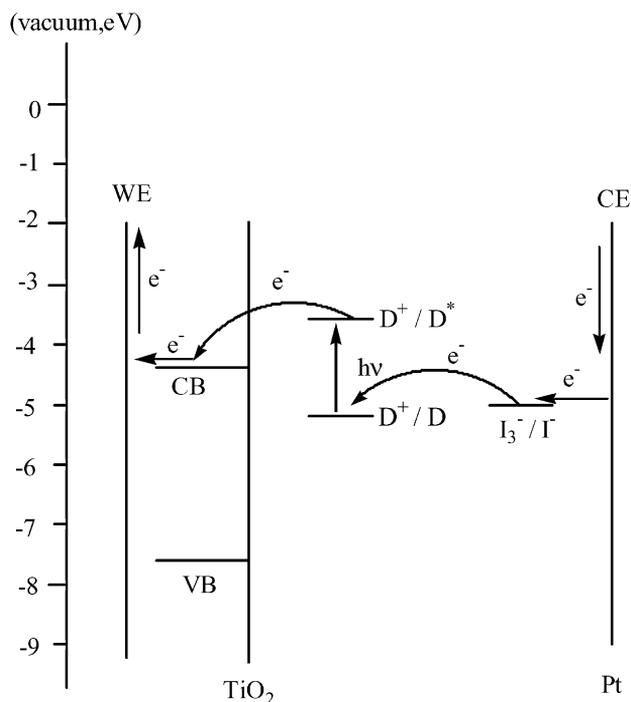
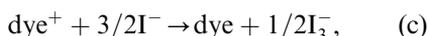
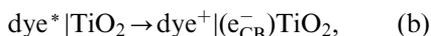
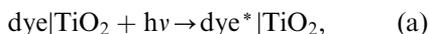
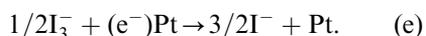
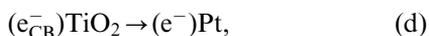


Fig. 6. Schematic representation of the processes for the photocurrent generation in tpyRu-sensitized solar cell.

energy level. Therefore, the HOMO energy level of tpyRu was determined to be  $-5.2$  eV by SRPES. Combining HOMO energy level of tpyRu with its UV-vis spectrum (Fig. 3), absorption threshold being around 800 nm (1.55 eV), one can derive its first excited state energy level to be  $-3.65$  eV, which is higher than the edge of CB for  $\text{TiO}_2$  ( $-4.4$  eV) [25]. On the basis of energy levels for both  $\text{TiO}_2$  and tpyRu and the experimental results, the mechanism (Fig. 6) proposed for the photocurrent generation [1] holds for tpyRu-modified  $\text{TiO}_2$  electrode too. Current is generated in the cell as a result of the monolayer of the dye on the surface of  $\text{TiO}_2$  being excited by light (a) and injecting an electron to the CB of  $\text{TiO}_2$  (b). The oxidized dye is reduced back to its prototype by the iodide ions in the pores of  $\text{TiO}_2$  (c), meanwhile electrons are taken to the back contact and flow, through external circuit, to the counter electrode (d), where triiodide ion accepts an electron to be reduced to iodide ion (e). Consequently, current circulation is completed.





Obviously, under illumination of light, electricity is generated, but no net chemical reaction occurs in the solar cell device.

#### 4. Conclusions

A novel terpyridyl ruthenium sensitizer was synthesized, which has broad absorption in the visible. Although the absorption of tpyRu is red shifted to longer wavelength compared with that of the N3 dye, its overall efficiency is much lower than that of the latter. Compared with its similar complex, the triscarboxyterpy complex [18,19], the overall yield generated by this dye is also much lower. However, tpyRu should be an ideal black dye in terms of its broad absorption in the visible, and its overall energy conversion yield would be improved further after optimization. The experimental results we obtained will be helpful for the molecular design of dyes based on ruthenium-polypyridine unit for photovoltaic devices.

#### For further reading

[10]

#### Acknowledgements

We gratefully acknowledge the financial support from the State Key Program of Fundamental Research (G 1998061308), the NNSFC (59872001, 20023005, 29733100 and 29971031), and the Doctoral Program Foundation of Higher Education (99000132).

#### References

- [1] B. O'Regen, M. Grätzel, *Nature (London)* 353 (1991) 737.
- [2] M.K. Nazeerudin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* 115 (1993) 6382.
- [3] P. Bonhote, J.E. Moser, M. Grätzel, et al., *Chem. Commun.* (1996) 1163
- [4] R. Argazzi, C.A. Bignozzi, T.A. Heimer, F.N. Castellano, G.J. Meyer, *J. Phys. Chem. B* 101 (1997) 2591.
- [5] H. Rensmo, K. Keis, S.-E. Lindquist, et al., *J. Phys. Chem. B* 101 (1997) 2598.
- [6] Zhong-Sheng Wang, Chun-Hui Huang, Bao-Wen Zhang, Yuan-Jun Hou, Pu-Hui Xie, Hai-Jie Qian, Kurash Ibrahim, *New J. Chem.* 24 (2000) 567.
- [7] Zhong-Sheng Wang, Chun-Hui Huang, Yan-Yi Huang, Yuan-Jun Hou, Pu-Hui Xie, Bao-Wen Zhang, Hu-Min Cheng, *Chem. Mater.* 13 (2001) 678.

- [8] Zhong-Sheng Wang, Chun-Hui Huang, Fu-You Li, Shi-Fu Weng, Kurash Ibrahim, Feng-Qin Liu, *J. Phys. Chem. B*, in press.
- [9] Zhong-Sheng Wang, Chun-Hui Huang, Fu-You Li, Shu-Ming Yang, Shi-Fu Weng, *Sci. China Ser. B* 3 (2001) 103–108.
- [10] F. Nuesch, J.E. Moser, V. Shklover, M. Grätzel, *J. Am. Chem. Soc.* 118 (1996) 5420.
- [11] D.M. Martino, H.V. Willigen, M.T. Spitler, *J. Phys. Chem. B* 101 (1997) 8914.
- [12] Wei Zhao, Yuan Jun Hou, Xue Song Wang, Bao Wen Zhang, et al., *Sol. Energy Mater. Sol. Cells* 58 (1999) 173.
- [13] P. Bonhote, E. Gogniat, M. Grätzel, *J. Phys. Chem. B* 102 (1998) 1498.
- [14] Zhong-Sheng Wang, Fu-You Li, Chun-Hui Huang, Lu Wang, Min Wei, Lin-Pei Jin, Nan-Qiang Li, *J. Phys. Chem. B* 104 (2000) 9676.
- [15] Zhong-Sheng Wang, Fu-You Li, Chun-Hui Huang, *Chem. Commun.* (2000), 2063.
- [16] Zhongsheng Wang, Yanyi Huang, Chunhui Huang, Jie Zheng, Humin Cheng, Shujian Tian, *Synthet. Met.* 114 (2000) 201.
- [17] Zhong-Sheng Wang, Chun-Hui Huang, Fu-You Li, Shi-Fu Weng, Shu-Ming Yang, *J. Photochem. Photobiol. A: Chem.* 140 (2001) 255–262.
- [18] Md.K. Nazeeruddin, P. Péchy, M. Grätzel, *Chem. Commun.* (1997) 1705.
- [19] Md.K. Nazeeruddin, P. Péchy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* 123 (2001) 1613.
- [20] A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.* 33 (2000) 269.
- [21] F.H. Case, T. Kaspens, *J. Am. Chem. Soc.* 80 (1958) 2745.
- [22] W. Spahni, G. Calzaferri, *Helv. Chem. Acta* 67 (1984) 450.
- [23] G.P. Smestad, M. Grätzel, *J. Chem. Educ.* 75 (1998) 752.
- [24] A.C. Khazraji, S. Hotchandani, S. Das, P.V. Kamat, *J. Phys. Chem. B* 103 (1999) 4693.
- [25] A. Hagfeldt, M. Grätzel, *Chem. Rev.* 95 (1995) 49.
- [26] B. O'Regan, M. Grätzel, D. Fitzmaurice, *Chem. Phys. Lett.* 183 (1991) 89.