

NOVEL DYES TO SENSITIZE PHOTOELECTROCHEMICAL SOLAR CELLS: RESEARCHES ON DYE-CELLS FOR A SUSTAINABLE ENERGY

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Abstract

Photoelectrochemical solar cells based on dye-sensitization of TiO_2 by novel ruthenium polypyridinic complexes are presented in this work. Sunlight harvesting and energy conversion to electricity assisted by a new class of complexes, having the hydroxamic acid, $\text{dobH}_2 = 4,4'-(\text{CONHOH})_2-2,2'$ -bipyridine, as an anchoring group to be attached on the mesoporous nanostructured surface of the semiconductor oxide, are being investigated. The current-potential profile for solar cells, as well as $I_{\text{sc}} = 4.58 \text{ mA cm}^{-2}$ and $V_{\text{oc}} = 0.595 \text{ V}$ with fill factor = 0.56 for the *cis*- $[\text{Ru}(\text{dobH}_2)_2\text{Cl}_2]$ complex as one dye and $I_{\text{sc}} = 4.36 \text{ mA cm}^{-2}$ and $V_{\text{oc}} = 0.612 \text{ V}$ with fill factor = 0.59 for the *cis*- $[\text{Ru}(\text{dobH}_2)_2(\text{H}_2\text{O})_2]^{2+}$ complex as a second dye, show that these new sensitizers efficiently promote electron injection into the TiO_2 conduction band upon light absorption. The results can be significantly improved by appropriate engineering of this new class of molecular sensitizers by using adequate ancillary ligands in order to modulate their properties for maximum absorption of visible light and its conversion to electrical output.

Keywords: Energy conversion, Solar cells, Dye-sensitized photoelectrochemical cells, Ruthenium polypyridinic dyes, Dye-cells

1. Introduction

Solar photovoltaic cells, capable of directly converting sunlight into electrical power, are one of the most promising devices in the search for sustainable and renewable sources of clean energy (Green, 2000, Yamaguchi, 2001). Although the field had been dominated until the last years of the past century by technology based on the solid-state p-n junction devices, a new generation of photovoltaics is nowadays emerging. One of them is the dye-sensitized nanocrystalline solar cell, (Garcia et al., 2002, 2000, Garcia and Murakami Iha, 2001a,b, Grätzel, 2001, 2000) registered by USP as Dye-Cell[®]. It has a different approach from the conventional systems, where the semiconductor performs both the task of light absorption and charge carrier transport. These two functions are separated in a Dye-cell[®] by having the light absorbed by sensitizers (dyes) chemically attached to the surface of a nanostructured wide band-gap semiconductor (mesoporous oxides) and, therefore, does not require an intrinsic electric field. Among several other advantages, the low environmental impact (de Vries et al., 2000, Greijer et al., 2001) and reduced energy factor in the production process of dye-sensitized solar cells, (Murakami Iha et al., 2003), are certainly worth to be emphasized.

The Dye-Cell[®] technology is based on sensitization of a wide band-gap semiconductor (typically oxide films, which are stable against photocorrosion) of nanocrystalline morphology to allow an efficient harvesting of sunlight. Added to this advantage, the separation of the optical absorption and the charge separation processes gives a near quantitative conversion of incident photons into current. This photovoltaic device has electric conversion efficiencies over 10% under standard AM 1.5 solar radiation (Grätzel, 2001).

It also has other advantages: the manufacturing processes are relatively simple, requiring low cost capital equipment, non-toxic materials with a low environmental impact and a low energy production with embodied energy as low as 32 kWh/m² (Smestad, 1998, Murakami Iha et al., 2003). One of the positive features of a dye-sensitized solar cell is its performance, which is quite insensitive to temperature change. No effects on the power conversion efficiency can be observed by raising the temperature from 20 to 60 °C (Grätzel, 2000, Nazeeruddin et al., 1993), in contrast to the conventional cells that exhibit *ca.* 20% decrease under the same conditions. The effect of augmenting dark current, which implies loss in open circuit voltage, is compensated by the increase in the mobility of I₃⁻, that function as hole carriers, and the decrease of counter electrode charge transfer resistance, resulting in gain in photocurrent and fill factor.

This technology is also particularly adequate to indoor applications due to its voltage and power output stability over a wide range of low sunlight conditions, but it is also an attractive option for outdoor photovoltaics. For instance, it provides the possibility of being translucent and can be easily incorporated into buildings as power windows capable to harvest electricity from sunlight (Murakami Iha et al., 2003, Grätzel, 2001, 2000).

Following this approach, the *Laboratory of Inorganic Photochemistry and Energy Conversion* at the Chemistry Institute of the University of São Paulo has been conducting investigations on Dye-cells[®] including the pathway from the scientific knowledge acquired from fundamental academic research (Garcia et al., 2003a,b, 2002, 2000, 1998a,b, Garcia and Murakami Iha, 2001a, Murakami Iha, 2000, Polo et al., 2004) to technological innovation and intellectual protection by patents (Garcia and Murakami Iha, 2001b). A straightforward example of the association of both molecularly engineered chemical systems and photoinduced tasks for energy conversion is the photoelectrochemical solar cell based on dye-sensitization of *n*-TiO₂. Compounds with the general formula *cis*-[(dcbH₂)₂RuLL'], Figure 1A, where dcbH₂ = 4,4'-(COOH)-2,2'-bipyridine and L/L' = substituted pyridines, CN⁻, SCN⁻, H₂O, etc. are successfully employed as molecular sensitizers in such cells. In this work, we extend our investigations by employing ruthenium polypyridinic dyes with a new class of anchoring group (hydroxamic acid) to porous TiO₂, which has never been reported in the literature, *cis*-[(dobH₂)₂RuX₂], Figure 1B, where X = Cl⁻ or H₂O and dobH₂ = 4,4'-(CONHOH)-2,2'-bipyridine.

2. Experimental Section

2.1 Materials

All solvents and chemicals employed for preparations were reagent or HPLC grade.

2.2 Synthesis of 4,4'- dihydroxamic-2,2'bipyridine

The 4,4'-dihydroxamic-2,2'-bipyridine ligand, dobH₂, was synthesized as described in the literature (Donnici et al., 1998)

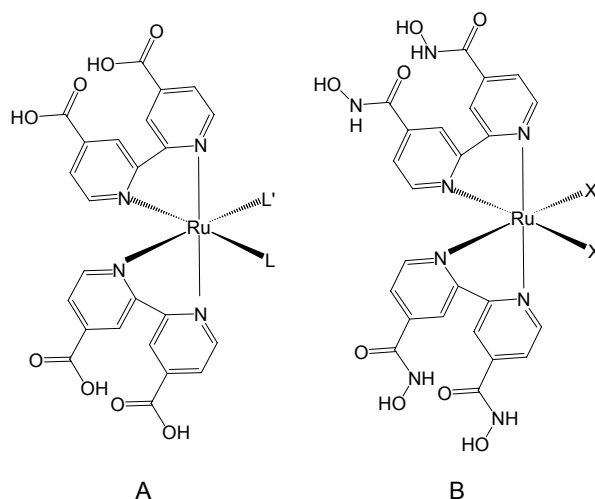


Figure 1. Structure of ruthenium(II) complexes with dcbH₂ (A) and dobH₂ (B) anchoring ligands.

2.3 Synthesis of *cis*-[Ru(dobH₂)₂Cl₂]

The *cis*-[Ru(dobH₂)₂Cl₂] dye was obtained (Polo et al., 2003) by suspending dobH₂ in N,N'-dimethylformamide, DMF. After heating and argon bubbling, hydrated ruthenium(III) chloride, dissolved in DMF, was added and the mixture was refluxed for 20-24h. The solid was purified by selective protonation of hydroxamic group. Yields 55%.

2.4 Synthesis of *cis*-[Ru(dobH₂)₂(H₂O)₂](CF₃SO₃)₂

The *cis*-[Ru(dobH₂)₂(H₂O)₂]²⁺ complex was prepared (Polo et al., 2003) suspending *cis*-[Ru(dobH₂)₂Cl₂] in water, raising the pH by adding NaOH (0.1 mol L⁻¹) until a complete dissolution of the solid. The *cis*-[Ru(dobH₂)₂(H₂O)₂](CF₃SO₃)₂ complex was precipitated by adding triflic acid (0.1 mol L⁻¹) until the isoelectric point.

2.5 Synthesis of *cis*-[Ru(dcbH₂)₂(NCS)₂]

The *cis*-[Ru(dcbH₂)₂(NCS)₂] complex, named N3, and employed as a standard, was prepared following the reported procedure (Nazeeruddin et al., 1993).

2.6 Preparation of TiO₂

The colloidal TiO₂ was prepared by hydrolysis of titanium(IV) isopropoxide as described in the literature (Garcia et al., 1998b, Nazeeruddin et al., 1993).

2.7 Thin layer solar cell

The regenerative solar cell consists of dye-sensitized TiO₂ photoanode and a counter electrode sandwiching the mediator electrolyte. Transparent photoanodes were obtained by deposition of a TiO₂ thin film onto an FTO conducting glass (Asahi Glass Co., Fluorine doped Tin Oxide - 7 Ω square⁻¹) by doctor blade technique and sintering its particles at 450 °C for 30 min. The processed electrode was immersed into the dye solution to result in a dye-sensitized photoanode. The counter electrode is a transparent Pt-coated ITO conducting glass (Asahi Glass Co., Indium doped Tin Oxide – 10-20 Ω square⁻¹). These electrodes set up solar cells in a sandwich arrangement having a layer of mediator, I⁻/I₃⁻ in 90/10 acetonitrile/3-methyl-2-oxazolidinone, NMO, previously distilled, in between, as can be seen in Figure 2.

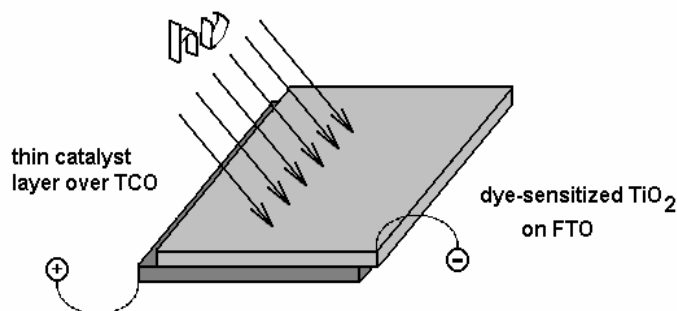


Figure 2. Thin layer Dye-Sensitized Solar Cell.

2.8 Measurements

Absorption spectra were recorded on a Hewlett Packard 8453 UV-Vis spectrophotometer. Short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) were obtained as previously described (Garcia et al. 1998a,b).

The experiments for determination of current-voltage data were carried out by an Eco-Chemie PGSTAT-30 Potentiostat/Galvanostat. The I-V curves were obtained with a dye sensitized solar cell under irradiation provided by an overhead projector (Garcia et al., 2003a). The data were normalized according to reported values for N3 (Nazeeruddin et al., 1993).

3 Results and Discussion

3.1 Absorption Spectra

The absorption spectra of the new compounds, *cis*-[Ru(dobH₂)₂Cl₂] and *cis*-[Ru(dobH₂)₂(H₂O)₂]²⁺, are presented in Figure 3. The absorption maxima in the visible region are centered at 405 and 576 nm for the chloro complex and at 393 and 561 nm for the aqua complex. These broad and intense bands are ascribed to MLCT (metal to ligand charge transfer) transitions and cover a wide range of the visible spectrum with an efficient harvest of sunlight.

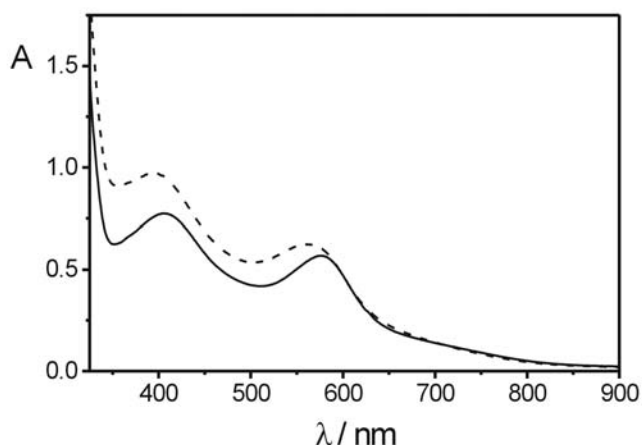


Figure 3. Absorption spectra of *cis*-[Ru(dobH₂)₂Cl₂] (—) and *cis*-[Ru(dobH₂)₂(H₂O)₂]²⁺ (---) in N,N'-Dimethylformamide.

3.5 Photoelectrochemistry

The current-potential profile of 0.5 cm² cells sensitized by *cis*-[Ru(dobH₂)₂Cl₂] and *cis*-[Ru(dobH₂)₂(H₂O)₂]²⁺ dyes are presented in Figure 4. The average values of I_{sc}, V_{oc}, and fill factor are, respectively, 4.58 mA cm⁻², 0.595 V and 0.56 for *cis*-[Ru(dobH₂)₂Cl₂] and 4.36 mA cm⁻², 0.612 V and 0.59 for *cis*-[Ru(dobH₂)₂(H₂O)₂]²⁺.

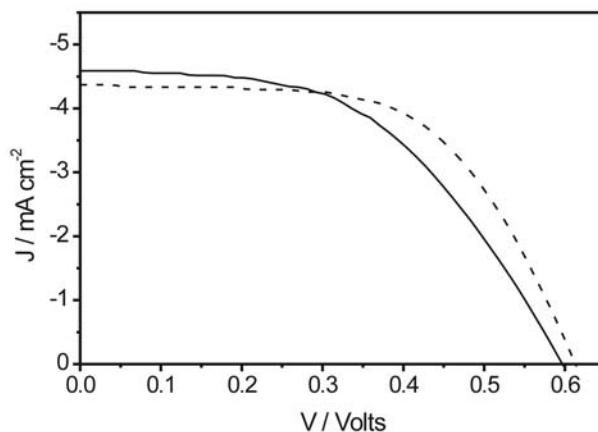


Figure 4. Current-potential profile of the dye-cell using *cis*-[Ru(dobH₂)₂Cl₂] (—) or *cis*-[Ru(dobH₂)₂(H₂O)₂]²⁺ (---) as sensitizers.

The data clearly point out that the new dyes are strongly adsorbed to the mesoporous TiO₂ and promote an efficient electron injection to the semiconductor conducting band upon light absorption. These results show that these sensitizers having the complexes with hydroxamic anchoring groups to be attached directly onto the semiconductor surface are a new class of dyes, which can provide novel molecular sensitizers by engineering various ancillary ligands to modulate their properties conveniently in order to absorb visible light to be converted into electrical output.

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