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Article

Sensitization of n-Type TiO_2 Electrode by a Novel Isoquinoline Ruthenium(II) Polypyridyl Complex

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A sensibilização de TiO_2 à luz visível pela espécie *cis*-$[(dcbH_2)_2Ru(isq)_2](ClO_4)_2$, onde $dcbH_2$ = 4,4'-$(CO_2H)_2$-2,2'-bipiridina e isq = isoquinolina, é relatada. O espectro de ação de fotocorrente, obtido para células solares regenerativas com filmes de TiO_2 nanocristalinos recobertos com o corante, resultou em valores de IPCE de até 40%. Este novo composto atua eficientemente como sensibilizador de fotoanodo de TiO_2 em células solares do tipo sanduíche constituídas de camada delgada.

The effective sensitization of TiO_2 to visible light by *cis*-$[(dcbH_2)_2Ru(isq)_2](ClO_4)_2$, where $dcbH_2$ = 4,4'-$(CO_2H)_2$-2,2'-bipyridine and isq = isoquinoline, is reported. The photocurrent action spectrum obtained for the regenerative solar cell with dye coated nanocrystalline TiO_2 films resulted in IPCE values up to 40%. This novel compound acts as an efficient TiO_2 photoanode sensitizer in thin-layer sandwich-type solar cells.

Keywords: *TiO_2 sensitization, solar cell, energy conversion, Ru-dye*

Introduction

The development of efficient systems for the conversion of solar energy into electricity is a very active research field. Spectral sensitization of wide band-gap semiconductors in photoelectrochemical cells has been an attractive approach, with efficient results.[1-4] Many *cis*-$[(dcbH_2)_2RuLL']$ complexes have been studied for this purpose[5-8], and the best solar to electric power conversion has been achieved by thiocyanate derivatives[5,6]. In the present work we extended our investigations on semiconductor sensitization to the Ru(II) complex with isoquinoline as the ancillary ligand. Previous studies on the *fac*-$[ClRe(CO)_3(isq)_2]$ complex have revealed interesting spectral, photophysical and photochemical properties[9] which could be conveniently extended to another compound. In order to verify if the use of this azine ligand leads to a good ruthenium carboxylate dye, we have prepared the novel sensitizer, *cis*-$[(dcbH_2)_2Ru(isq)_2](ClO_4)_2$, and determined its effectiveness. This species has the requirements for the sensitization of n-type TiO_2 semiconductors and can present promising efficiency in TiO_2-based solar cells.

Experimental

The *cis*-$[(dcbH_2)_2RuCl_2]$ complex was synthesized following a slight modification of the procedure previously described[5]. To a solution of 37 mg (15.2 mmol) of $dcbH_2$ (Aldrich) in 10 mL of DMF (Aldrich), 53 mg (2.6 mmol) of $RuCl_3.xH_20$ (Aldrich) was added. The reaction mixture was refluxed for 8 h, then concentrated to 2 mL and cooled. The complex was precipitated by addition of acetone (Merck). The solid product was filtered off and dried under vacuum.

The *cis*-$[(dcbH_2)_2Ru(isq)_2](ClO_4)_2$ complex was obtained starting from the anionic form of $[(dcbH_2)_2RuCl_2]$[6]. To a solution of 200 mg (0.27 mmol) of $Na_4[(dcb)_2RuCl_2]$

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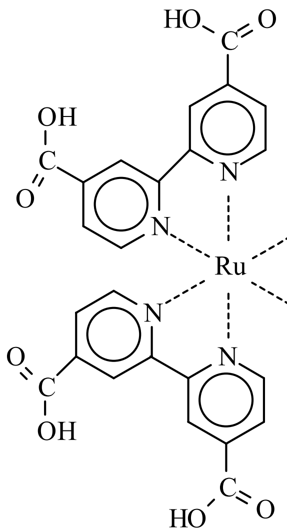

Scheme 1. *cis*-[$(dcbH_2)_2Ru(isq)_2$]

in 50 mL of methanol (Merck), 1.38 g (10.7 mmol) of isoquinoline (Aldrich) was added. The reaction mixture was refluxed for 14 h, rotary-evaporated to 3 mL, and then added to acetone (Aldrich). The solid was filtered off, redissolved in water and precipitated by addition of $HClO_4$ (Mallinckrodt). After washing with a pH 1.9 $HClO_4$ solution, the solid was dried under vacuum. Anal. Calcd. for $RuC_{42}H_{30}N_6O_{16}Cl_2.3H_2O$: C, 45.83; N, 7.63; H, 3.30. Found: C, 45.90; N, 8.02; H, 3.55.

Spectra and photocurrent measurements were performed as described elsewhere[6,10].

Results and Discussion

The absorption spectrum of the *cis*-[$(dcbH_2)_2Ru(isq)_2]^{2+}$ complex in methanol is shown in Fig. 1. Analogously to similar complexes, it exhibits $\pi \rightarrow \pi^*$ intra ligand transition in the UV region and metal to ligand (MLCT), $d\pi \rightarrow \pi^*$ bands in the visible range[5,6,11,12].

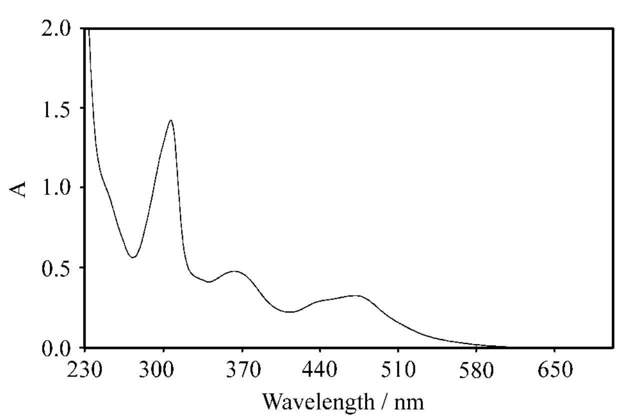

Figure 1. UV-Vis absorption spectrum of $[(dcbH_2)_2Ru(isq)_2]^{2+}$ in a methanolic solution.

Transparent, nanocrystalline TiO_2 electrodes for photoelectrochemical measurements were prepared using titanium isopropoxide as previously described[5]. The complex was attached to the TiO_2 surface by immersing the processed electrode in a $\sim 10^{-4}$ M solution of the dye in ethanol. Photoelectrochemical experiments were carried out using the dye sensitized TiO_2 film in a thin-layer sandwich-type solar cell. This cell consists of a TCO, fluorine doped SnO_2 glass, with the TiO_2 film sensitized by the complex, as a photoanode, I_2/LiI solution in acetonitrile, as an electrolyte relay and a transparent Pt film on a conducting TCO glass as a counter electrode. The spectrum for the dye adsorbed on the electrode is shown in Fig. 2.

Figure 3 shows the photocurrent action spectrum of the solar cell where the incident photon to current conversion efficiency (IPCE) is plotted as a function of the irradiation wavelength. The IPCE values were calculated by using the equation

$$\text{IPCE\%} = (1239.8)\ \frac{\text{photocurrent density } (\mu A/cm^2)}{\text{wavelenght (nm)}\ \ \text{irradiance } (W/m^2)} \text{ x } 100$$

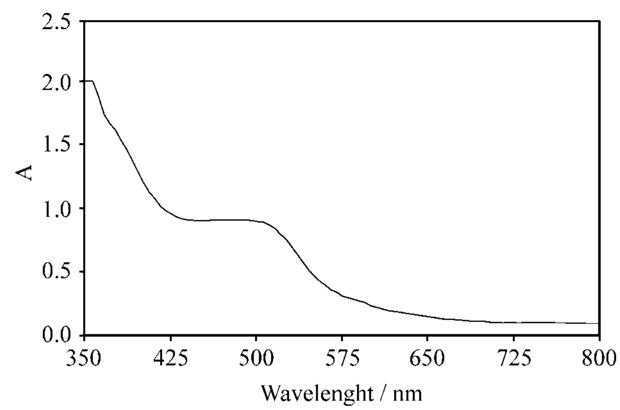

Figure 2. Optical densities of $[(dcbH_2)_2Ru(isq)_2]^{2+}$ adsorbed on a TiO_2 photoanode.

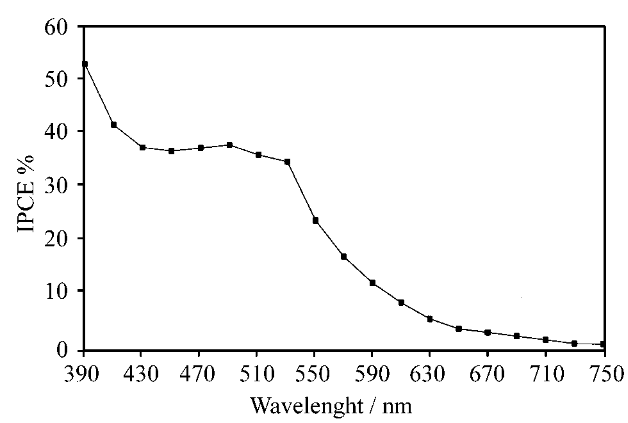

Figure 3. Photocurrent action spectrum obtained for the regenerative nanocrystalline TiO_2 cells using $[(dcbH_2)_2Ru(isq)_2]^{2+}$ as a sensitizer in 0.03 M I_2 and 0.3 M LiI in acetonitrile.

A comparison between Figs. 2 and 3 shows that the photocurrent action spectrum closely resembles the optical density spectrum for the dye adsorbed on the electrode. The photocurrents obtained in the wavelength region up to 540 nm are quite good, with efficiencies ranging up to 40%. These values confirm that the dye adsorbs efficiently to the nanoporous TiO_2 with large internal surface area, and are comparable to those obtained by other ruthenium(II) polypyridyl-based sensitizers previously studied[6,11,13].

Conclusions

Enhanced spectral response of TiO_2 to visible light has been accomplished with the use of *cis*-$[(dcbH_2)_2Ru(isq)_2](ClO_4)_2$ as a dye. This novel compound presents good light harvesting properties and performs efficiently in the charge-transfer sensitization of nanocrystalline TiO_2. When employed in regenerative solar cells, this complex converts light into electricity effectively, showing a good spectral sensitization of the wide band-gap semiconductor to the visible light. This has been an attractive strategy for the conversion of sun light to electricity with efficiencies close to those obtained with traditional solid-state photovoltaic devices.

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