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Photoelectrochemical solar cells based on SnO_2 nanocrystalline films

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Abstract

Dye-sensitized solar cells (DSSCs) fabricated using nanocrystalline SnO_2 films sensitized by the $Ru(dcbpy)(NCS)_2$ dye (N3) were compared to the corresponding nanocrystalline titania cells. Although the light-to-power energy conversion efficiency of SnO_2 cells is low with respect to the nc-TiO_2 DDSCs, their general characteristics are similar. The influence of the addition of 4-*tert*-butylpyridine (4TBP) or acetic acid to the electrolyte was investigated. 4TBP increased the cell's open-circuit voltage and stability. Raman spectroscopy confirmed the presence of new vibration bands; their intensity depends on the additives and characterizes the amount of tri-iodides at the photoactive interface, as well the complex formed between dye and iodide. ***To cite this article: N. Nang Dinh et al., C. R. Chimie 9 (2006)***.

Résumé

Des cellules solaires utilisant l'oxyde d'étain nanocristallin, sensibilisées par le complexe de ruthénium N3: Ru(dcbpy)$(NCS)_2$ ont été comparées à leurs homologues utilisant l'oxyde de titane. Deux adjuvants, 4-*tert*-butylpyridine (4TBP) ou acide acétique, ont été ajoutés à l'électrolyte pour augmenter le potentiel en circuit ouvert de la cellule et sa stabilité à long terme. L'addition de 4TBP améliore nettement ces deux caractéristiques. On a utilisé la spectroscopie Raman pour caractériser les espèces à l'interface photoélectrode–électrolyte. L'apparition de nouvelles bandes de vibration (dont l'intensité dépend de l'adjuvant) permet de caractériser le complexe formé entre le colorant et l'oxyde, et d'estimer la quantité de tri-iodures présente à l'interface photoactive. ***Pour citer cet article : N. Nang Dinh et al., C. R. Chimie 9 (2006)***.

Keywords: Dye-sensitized solar cells; DSSC; SnO_2; N3; Raman spectroscopy; Photoelectrochemical efficiency

Mots-clés : Cellules solaires sensibilisées par colorant ; SnO_2 ; N3 ; Spectroscopie Raman ; Rendement photoélectrochimique

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1. Introduction

Taking into account the value of its bandgap, SnO_2 seems to be a good candidate for the dye-sensitized solar cells (DSSC); it can also be prepared in a convenient nanocrystalline form (nc-SnO_2) [1,2]. However, we will confirm here that the photoelectrochemical efficiency of nc-SnO_2 DSSCs is noticeably lower than the efficiency of nc-TiO_2 cells [3–11]. In the case of the nc-TiO_2 cells using N3 dye [N3: (*cis*-bis(isothiocyanato)bis(2,2′-bipyridine-4,4′-dicarboxylic acid)-Ru(II)], one knows that one of the reasons for their high efficiency is the excellent grafting between the terminal group of the bridging ligand, COOH, and the surface of anatase, which optimizes the electron injection.

We tried to add different additives in the electrolyte, able to improve the cell efficiency by modifying in particular the tri-iodides amount at the interface. The most studied additive is 4-*tert*-butylpyridine (4TBP), it was shown that the exposure of the dye-photoelectrode to 4TBP improves the fill factor (FF) and open-circuit voltage (V_{oc}) of the device without affecting the short-circuit photocurrent (J_{sc}). The increase of V_{oc} is due to the suppression of the dark current (arising from the reduction of triiodide by conduction band electrons, which occurs despite the fact that the TiO_2 surface is covered by a dye monolayer) at the semiconductor electrolyte interface. 4TBP is adsorbed at the TiO_2 surface and this blocks surface states, thus resulting to a decrease in the rate of reduction of triiodide by conduction band electrons [12,13]. Here, we will study also the influence of the acetic acid (AcH) which blocks the semiconductor surface and hinders the charge transfer process between the injected electron and the triiodides [14].

2. Experimental

2.1. SnO_2

To obtain high conversion efficiency, the preparation of rough, high surface area nano-structured thin films is necessary. Transparent nc-SnO_2 thin film electrodes were prepared by doctor-blading a colloid solution of 15 wt % tin oxide (Nyacol Products) in water on SnO_2:F conductive glass substrates, followed by a thermal treatment of sintering at 450 °C in air for 30 min. The investigation of their morphological properties by SEM showed that uniform and well-crystallized nc-SnO_2 films were obtained, with good adherence and a critical thickness, which is not larger than 2.0 µm. We have compared the photoelectrochemical properties of 1.5µm- and 2.46µm-thick films, the thicker film are better, but the differences are not so great. The results given here were obtained with a 1.5µm-thick film. Fractal analysis leads to a fractal dimension of 2.368, proving a self-similar and self-affine character of significant complexity.

2.2. Surface modification

Here we have used exclusively N3 dye from Solaronix. Surface derivatization of tin oxide was achieved by immersing the SnO_2 thin-film electrodes (heated at 120 °C) overnight in a 10^{-4} M ethanolic solution of this complex. It is noteworthy that a red coloration color developed immediately after immersion, confirming the dye grafting on the semiconductor surface. After completion of the dye adsorption the modified materials were thoroughly washed with ethanol and dried. Thus, any dye in excess (physically adsorbed) was eliminated and a monolayer coverage was ensured.

2.3. Electrolyte and cell elaboration

Counter electrode is a similar SnO_2:F coated substrate that had been platinized by DC-sputtering deposition, to give a catalytic effect on the electron donor reduction. The electrolyte is sandwiched between the dye-sensitized tin oxide photoelectrode and the counter electrode. A spacer (thickness about 50 µm) is placed between the two electrodes to avoid short-circuiting and to ensure the thickness of the electrolyte. The liquid electrolyte consists of propylene carbonate (PC), in which the redox couple $LiI + I_2$ is added. Here, we used a total amount of iodine of 0.12: 0.1 M LiI + 0.01 M I_2. Respectively 0.17 M acetic acid (AcH) or 0.1 M 4TBP were added.

We must point that the electrolyte composition was chosen in order to allow the best Raman and optical analysis, which requires to have a not too optically absorbing electrolyte, and therefore to limit the iodine concentration. In the present experiments, the electrolyte is therefore far from to be optimized in iodine, and the efficiencies will be subsequently very low.