



Assessment of dye distribution in sensitized solar cells by microprobe techniques



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ABSTRACT

Dye sensitized solar cells (DSCs) have received considerable attention once this technology offers economic and environmental advantages over conventional photovoltaic (PV) devices. The PV performance of a DSC relies on the characteristics of its photoanode, which typically consists of a nanocrystalline porous TiO₂ film, enabled with a large adsorptive surface area. Dye molecules that capture photons from light during device operation are attached to the film nanoparticles. The effective loading of the dye in the TiO₂ electrode is of paramount relevance for controlling and optimizing solar cell parameters. Relatively few methods are known today for quantitative evaluation of the total dye adsorbed on the film. In this context, microprobe techniques come out as suitable tools to evaluate the dye surface distribution and depth profile in sensitized films. Electron Probe Microanalysis (EPMA) and Ion Beam Analytical (IBA) techniques using a micro-ion beam were used to quantify and to study the distribution of the Ru organometallic dye in TiO₂ films, making use of the different penetration depth and beam sizes of each technique. Different 1D nanostructured TiO₂ films were prepared, morphologically characterized by SEM, sensitized and analyzed by the referred techniques. Dye load evaluation in different TiO₂ films by three different techniques (PIXE, RBS and EPMA/WDS) provided similar results of Ru/Ti mass fraction ratio. Moreover, it was possible to assess dye surface distribution and its depth profile, by means of Ru signal, and to visualize the dye distribution in sample cross-section through X-ray mapping by EPMA/EDS. PIXE maps of Ru and Ti indicated an homogeneous surface distribution. The assessment of Ru depth profile by RBS showed that some films have homogeneous Ru depth distribution while others present different Ru concentration in the top layer (2 μm thickness). These results are consistent with the EPMA/EDS maps obtained.

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1. Introduction

The world is in great need of technologies providing renewable energy. Solar energy which is abundant and clean is of great interest among the choices of sustainable and renewable energy. Dye sensitized solar cells (DSCs) based on polypyridyl ruthenium(II) complex dyes adsorbed on TiO₂ electrode have received considerable attention since the pioneering work of Gratzel and O'Regan [1]. This technology offers economic and environmental advantages over conventional photovoltaic (PV) devices because they can be manufactured with low-cost technologies and in an energy-efficient and eco-friendly manner.

Along the last two decades, significant progress has been made and best power conversion efficiency of the DSCs at the laboratory scale has surpassed 12% [2].

A typical DSC is constructed with a dye-sensitized mesoporous wide band gap semiconductor electrode, such as TiO₂ or ZnO, a liquid electrolyte containing I⁻/I³⁻ redox couple and platinum coated fluorine doped tin oxide (FTO) counter electrode.

The PV performance of a DSC relies on the characteristics of its photoanode, which plays a central role in converting light into electrical energy. A DSC photoanode usually consists of a nanocrystalline porous TiO₂ film, enabled with a large adsorptive surface area. Dye molecules that capture photons from light during device operation are attached to the film nanoparticles. Thus, an oxide film with a large interfacial surface area and superior electron transport properties is vital for strong light harvesting and efficient device

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performance [3]. The effective loading of the dye in the TiO₂ electrode is of paramount relevance for controlling and optimizing solar cell parameters. In particular, the cell short-circuit current density (J_{sc}) is directly proportional to the light harvesting ability of the cell, which in turn is strictly dependent on dye concentration on the TiO₂ adsorptive surface [4]. In addition, the dye adsorption behavior directly affects the cell open circuit voltage (V_{oc}) as well [5].

Dye adsorption on the TiO₂ is considered one key step of DSCs manufacturing, and various procedures have been developed to improve dyeing. Nevertheless, relatively few methods are known and used today for quantitative evaluation of the total dye adsorbed in the film. Generally, the amount of adsorbed dye is determined by desorbing the dye from TiO₂ with a hydroalcoholic solution of NaOH and then measuring the desorbed dye concentration by UV–Vis spectroscopy. This method gives the total amount of dye that has been desorbed from the film without taking into account the dye distribution profile.

Other methods have been proposed for quantitative estimation of dye loading [6] including Photoelectron Spectroscopy (PES) [7], Diffuse Reflectance UV–Vis Spectroscopy and Digital Imaging [8] and Optical Waveguide Spectroscopy (OWS) [9]. Gómez et al. [10] presented a distribution profile study of the dye on TiO₂ film using Secondary Ion Mass Spectroscopy (SIMS), concluding that Ru/Ti ratio in sputtered films decreased in depth while an uniform distribution in mesoporous films was observed.

More recently, Electron Probe Microanalysis (EPMA) technique has been applied to analyze the adsorption depth and control the desorption process of organometallic dyes on TiO₂ films [11–13].

In this work, a new approach combining microprobe techniques namely, nuclear microprobe (Rutherford Backscattering Spectrometry (RBS), Particle Induced X-ray Emission (PIXE)) and Electron Probe Micro-Analysis (EPMA) is carried out to assess dye distribution in TiO₂ films and the dye load based on Ru/Ti mass ratio. This study is performed in a comparative manner based on advantages and complementarities of each technique. The Ru/Ti mass ratios obtained by EPMA wavelength dispersive spectrometry (WDS), PIXE and RBS analyses are compared to estimate the consensus value for dye load on TiO₂ sensitized films, providing reliability to measurements and clarifying their suitability to assess dye quantification of the oxide semiconductor film. Dye distribution across film surface is checked by PIXE maps and in cross section is visualized by EPMA energy dispersive spectrometry (EDS) maps. The information obtained from EDS maps is compared with the RBS results for Ru depth profile in an integrated perspective to confirm data obtained.

2. Experimental

2.1. TiO₂ films preparation and sensitization

1D nanostructured titanium dioxide (TiO₂) films were deposited by pulsed DC magnetron reactive sputtering [14] onto commercial fluorine-doped tin oxide (FTO) coated glass plates (TEC15 – 2 mm thick from Pilkington) cut to form electrodes of 25 × 15 mm². The target consists of a pure titanium (99.99%) plate with 75 mm in diameter and is located 150 mm above the substrate holder. Pure argon and oxygen (99.99%) were used as sputtering and reactive gases, respectively, being the gas flow controlled by two mass flow controllers from Bronkhorst Hi-Tec. The power source used is a DC Pinnacle Plus unit from Advanced Energy. The depositions were carried out with a total sputtering pressure of 1.2 × 10⁻² mbar (with a fixed gas ratio (GR) of argon to oxygen of 2:1) and a current of 0.3, 0.5 and 1 A (pulsed DC frequency = 200 kHz), at 60 °C (substrate temperature). Deposition times were 18, 24 and 48 h.

The deposited titanium dioxide films were sensitized with the commercial dyes: N719 [cisbis(isothiocyanato)bis(2,2-bipyridil4,

4-dicarboxylate) ruthenium(II) bis tetrabutylammonium] and N749 [tris(isothiocyanato)-(2,2':6',6''-terpyridyl-4,4',4''-tricarboxylate) ruthenium(II) tris(tetra-butylammonium)] by immersion in acetonitrile/ethanol solution of N719 (0.14 mM) and ethanolic solution of N749 (0.2 mM) for 24 h at room temperature in the dark.

2.2. Characterization and analytical techniques

For morphological characterization, the equipment used was a Philips XL30 FEG (field emission electron source). SEM secondary electron images were obtained at an acceleration voltage between 5 and 10 kV from films surface and cross-section. For this study, the samples were not coated with any conductive surface layer.

EPMA microanalysis was achieved with a JEOL JXA-8500F equipment [15] with 5 WD spectrometers and an EDS Oxford Instruments INCA X-act. EPMA/EDS was used to obtain X-ray maps imaging with elemental cross sectional distribution information. Ru/Ti mass ratio was obtained by WDS to assess dye concentration in the different sensitized films.

IBA analyses were conducted with an Oxford Microbeams Nuclear Microprobe installed at one of the beam lines of the CTN's 2.5 MV Van de Graaff accelerator [16]. Comprising an OM150 quadrupole triplet the experimental setup includes an X-ray and a backscattered particle detection system for PIXE and RBS analysis, respectively. X-rays are detected with a 30 mm² Bruker SDD detector positioned at 135° with the beam direction while a 200 mm² PIPS detector, positioned at a backward angle of 40° in Cornell geometry, is used for RBS analysis.

Combining the PIXE and RBS data simultaneously accumulated for each of the analyzed samples it is expected to gather information on the samples surface homogeneity and the dye depth distribution.

For maximizing the RuS_x ($x = 2$ for N719 and $x = 3$ for N749) containing organometallic dye PIXE/RBS signal, two different approaches were accomplished and combined: irradiation with a 1.8 MeV proton beam – this allows a good PIXE yield for Ru, S and Ti and at the same time profit from the C proton resonance at 1.75 MeV for establishing the dye depth distribution or content at sample layers below the surface layer; irradiation with a 2 MeV He⁺ beam for obtaining a clear RBS signal from Ru.

Surface homogeneity was accessed through 530 × 530 μm² wide elemental distribution maps whereas PIXE quantitative data for S, Ru and Ti was obtained with the GUPIX [17] programme while NDF software [18] was used for RBS analysis.

For simulating the RBS spectra [19] for almost all samples it was enough to consider three different layers: the glass substrate; the FTO layer with adjustable thickness; the TiO₂ film layer with molecular formula of the organometallic dye. For the fit of the surface layer only the ratio TiO₂/dye molecule and its thickness were allowed to change. The layers thicknesses obtained were used for the multilayer GUPIX analysis.

3. Results and discussion

3.1. Dye load assessment

The Ru organometallic dyes, N719 and N749, were used to sensitize two different 1D nanostructured TiO₂ films obtained with a sputtering current of 0.3 A (films A with 1 μm thickness) and 0.5 A (films B with 4 μm thickness), both with a deposition time of 24 h. These four different sensitized films were analyzed by PIXE and RBS. Films B were also analyzed in cross section by WDS. To convey reliability to the quantification of Ru and relate it to the dye load, the mass fraction ratio Ru/S was determined once its

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