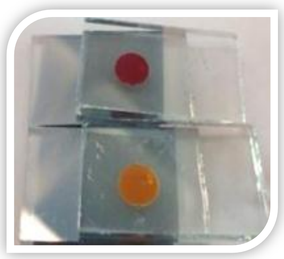
Dye assessment in nanostructured TiO_2 sensitized films by microprobe techniques



M. A. Barreiros[1*], J.Mascarenhas[1], V. Corregidor[2], L. C. Alves[2], F. Guimarães[1], E. Torres[1], M. J. Brites[1]

(1) Laboratório Nacional de Energia e Geologia, Portugal; (2) Instituto Superior Técnico, Universidade de Lisboa, Portugal

DSCs

✓The dye sensitized solar cell (DSC) is the only photovoltaic cell using molecules that generate charge carriers after photo-excitation without the need for excitonic transport

Motivation

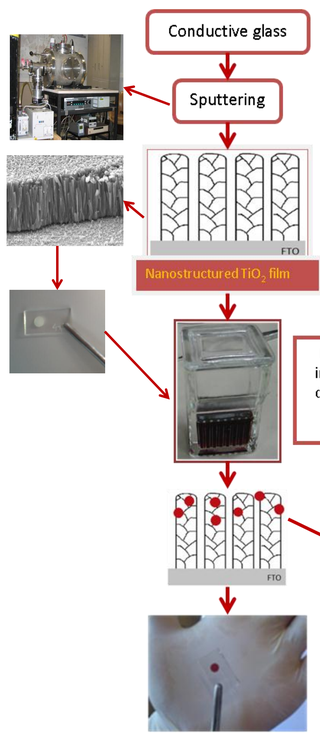
✓Dye adsorption on the TiO_2 is considered one key step of DSCs manufacturing

✓Effective loading of the dye in the TiO_2 electrode is important for controlling and optimizing solar cell parameters (J_{SC}, V_{OC}, …)

✓Few methods known and used today for quantitative evaluation of the total dye adsorbed in the film, but without taking into account the dye distribution profile

✓Microprobe techniques can be powerful tools to evaluate the dye distribution and dye depth profile in sensitized films

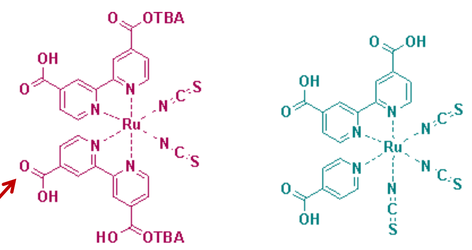
Sample Preparation



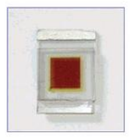
Films were immersed in dye solution during 24 hours

Dye molecules adsorbed on the surface of nanocrystalline TiO_2

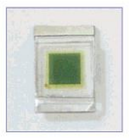
Commercial dyes – ruthenium polypyridyl complexes



N719



N749 "Black dye"



Analytical Techniques

SEM / EDS

- PHILIPS XL 30 FEG
- Acceleration voltage 7 - 10 kV
- EDS microanalysis EDAX

EPMA/ WDS / EDS

- JEOL JXA – 8500F
- Acceleration voltage 15 kV
- 5 WD Spectrometers
- EDS Oxford Instruments INCA X-act

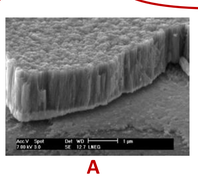
Nuclear Microprobe - RBS set-up

- 1.8 and 2.0 MeV proton or alpha beam
- Resolution ~ 3x3 μm^2
- PIPS RBS detector
- Si(Li) X-ray detector
- Software: Gupix Win for PIXE and WiNDF for RBS spectra

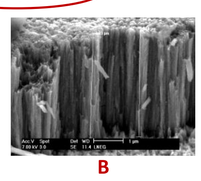
RESULTS AND DISCUSSION

Dye load assessment

Two films



A — 1 μm thickness



B — 4 μm thickness

Two dyes

N719 – $C_{58}H_{86}N_8O_8RuS_2$ – Ru/S=1.6

N749 – $C_{69}H_{117}N_9O_6RuS_3$ – Ru/S=1.10

Mass fraction ratio in dye compound

Ru/Ti mass fraction ratio (%) and Ru/S obtained		N719 Ru/S=1.6			N749 Ru/S=1.1		
		PIXE	RBS	WDS	PIXE	RBS	WDS
film A	Ru/Ti [%]	1.1	0.9	-	0.7	1	-
	Ru/S	1.6	*	-	1.3	*	-
film B	Ru/Ti [%]	0.8	0.9	0.9	0.7	0.6	0.5
	Ru/S	1.6	*	1.7	1.1	*	1.2

* Values kept constant during RBS simulation

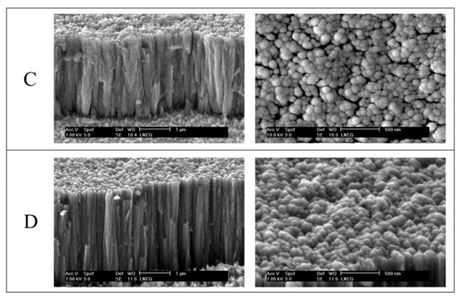
➢ Ru/S - Experimental values agree with this ratio in N719 and N749 dyes

➢ suitability to assess dye load in TiO_2

- nine 1D nanostructured TiO_2 films (1 to 4 μm thickness) sensitized by N719 and N749
- normal beam incidence to the sample surface analyses:
  PIXE (1.8 MeV H^+ ion beam)
  RBS (1.8 MeV H^+ and 2.0 MeV He^+ ion beams)
- cross section analyses:
  WDS (only five samples)

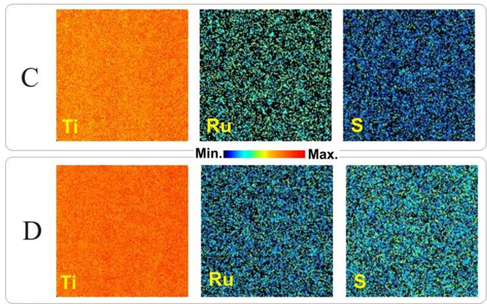
Dye distribution

- C and D TiO_2 films (4 μm thickness)
- different sputtering deposition conditions
- sensitized with N719



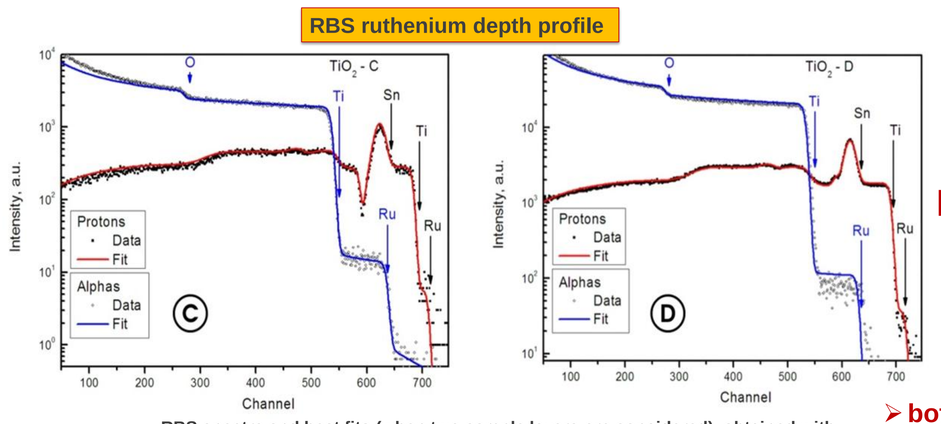
SEM secondary electrons images of films C and D

✓homogeneous surface distribution of the dye Ru and S



PIXE 2D X-ray maps for Ti, Ru and S recorded with an H^+ beam on the films surface (530 x 530 μm^2 scan)

RBS ruthenium depth profile



RBS spectra and best fits (when two sample layers are considered), obtained with 2 MeV alpha particle beam and 1.8 MeV proton beam for C and D films

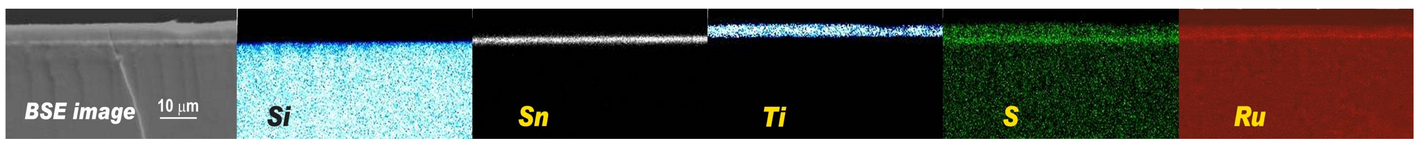
RBS quantitative results

Ru/Ti [%]	Film C	Film D
Top layer	1.1%	1.1%
Bottom layer	1.3%	1.6%

➢ bottom layer (close to the FTO) has higher dye load

➢ Ru/Ti difference between top and bottom layers: 18% in film C and 45 % in film D

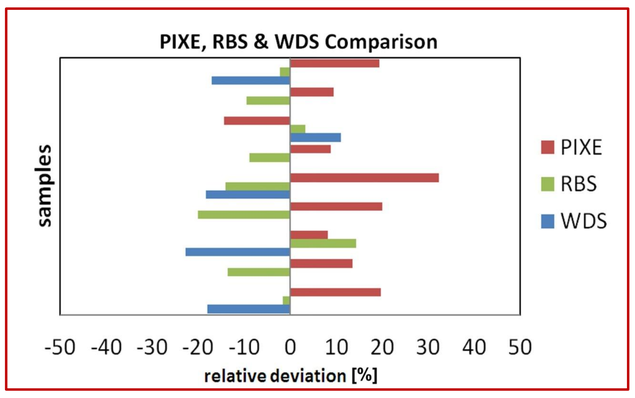
The same observed in the X-ray maps in cross sectional analysis by EPMA/EDS of film C



Backscattered electrons image and Si, Sn, Ti, S and Ru X-ray maps of film C (cross section) obtained by EPMA/EDS

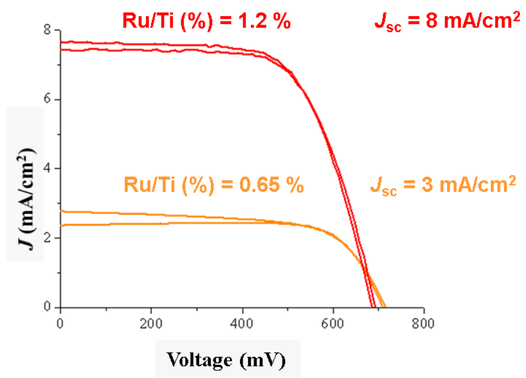
➢ S and Ru maps exhibit increased signal in the lower part of the TiO_2 film

Consensus value for the Ru/Ti mass fraction ratio determined average of all the results (σ <20%)



➢ **Relative deviations** (from consensus value) **< 20%**
except for one sample by PIXE (30%)
and another by WDS (23%)

DSCs based on two sensitized films with Ru/Ti (%) values of 1.2% and 0.65% prepared and characterised under standard conditions



➢ confirming the importance of the dye load evaluation

Concluding remarks

✓IBA techniques together with EPMA (WDS and EDS) proved to positively contribute for dye sensitized TiO_2 films characterisation

✓One of the IBA most important features is its versatility and the complementary information obtained when combining data from different techniques such as RBS and PIXE

✓The sensitivity of the techniques used allowed to evaluate Ru/Ti mass fraction ratio with similar results, in different TiO_2 films

✓It was possible to assess dye surface distribution and depth profile and to visualise the dye distribution in sample cross-section

✓Dye assessment by microprobe techniques may contribute to study the photoanode preparation of the DSCs photovoltaic devices

*alexandra.barreiros@lneg.pt

INTERNATIONAL IBERIAN NANOTECHNOLOGY LABORATORY