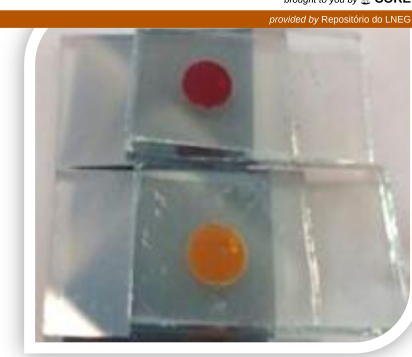
Dye assessment in nanostructured TiO_2 sensitized films by microprobe techniques



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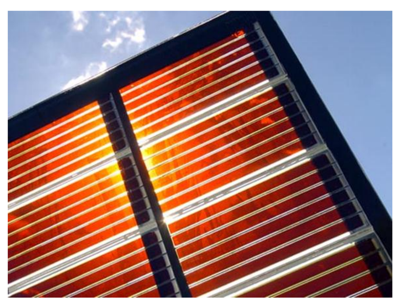
DSCs

✓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

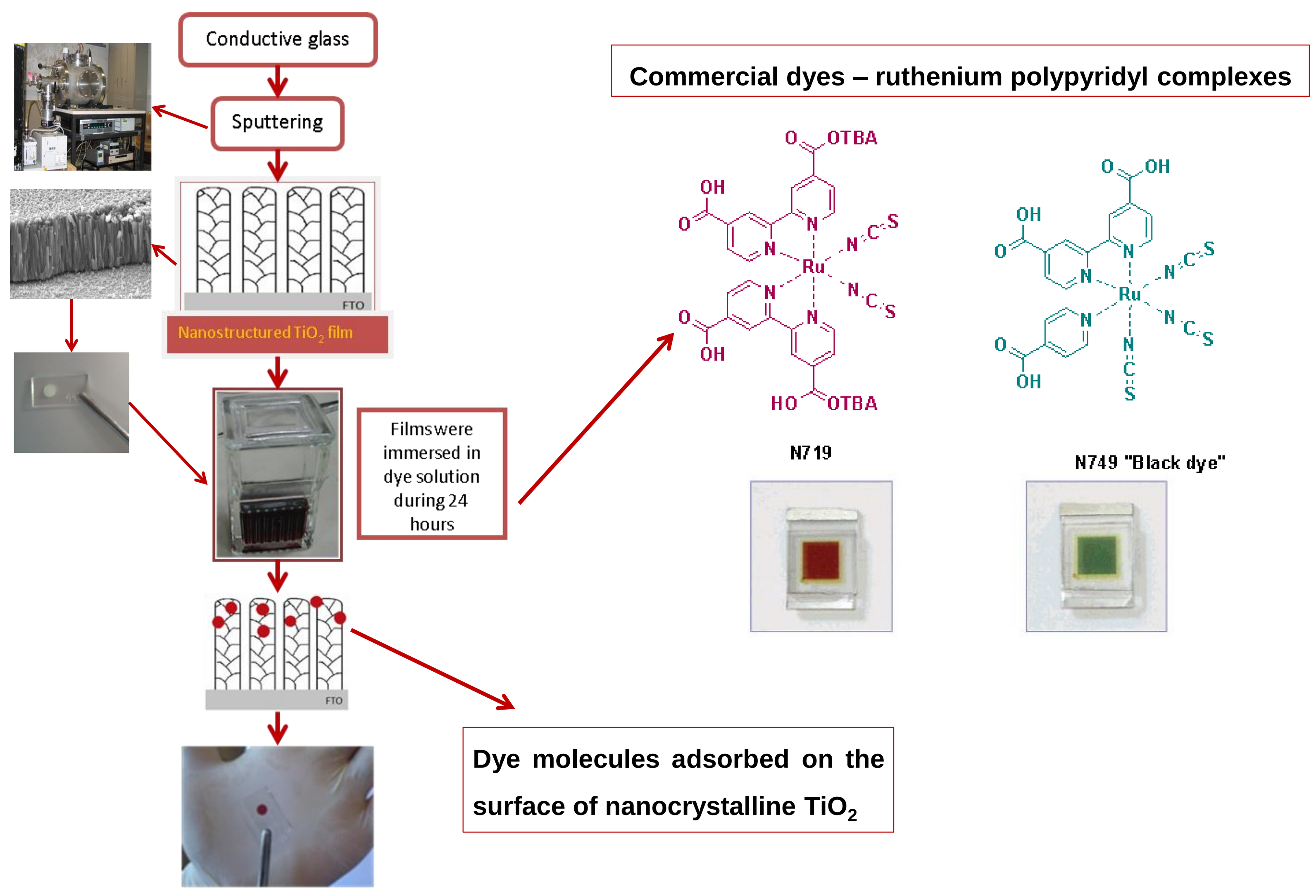
✓Dye adsorption on the TiO_2 is considered one key step of DSCs manufacturing

✓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



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

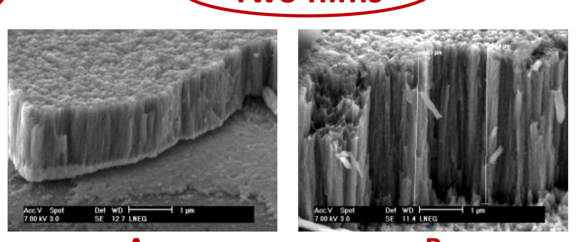
Nuclear Microprobe - RBS set-up

- 1.8 and 2.0 MeV proton or alpha beam
- Resolution ~ 3x3 μm²
- 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

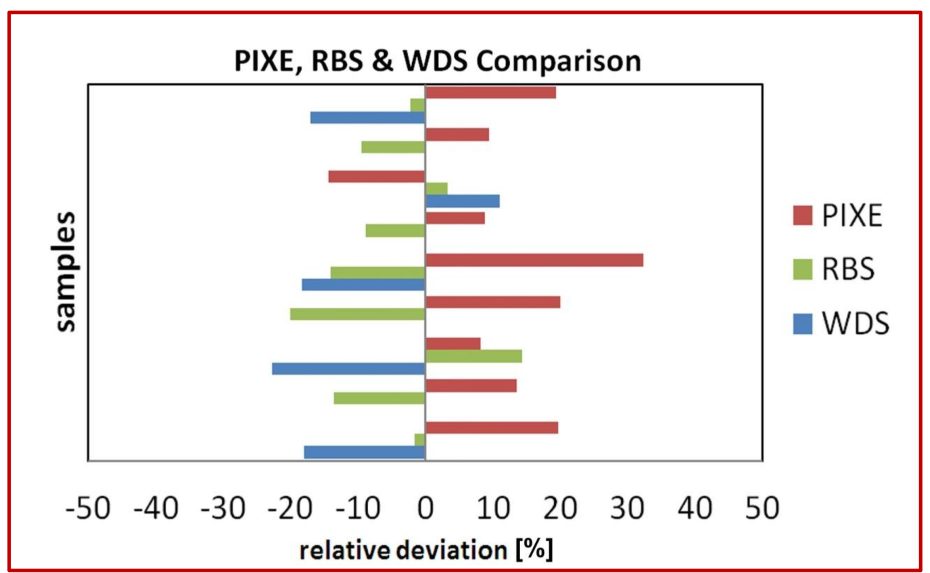
* Values kept constant during RBS simulation

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

➢ suitability to assess dye load in TiO_2

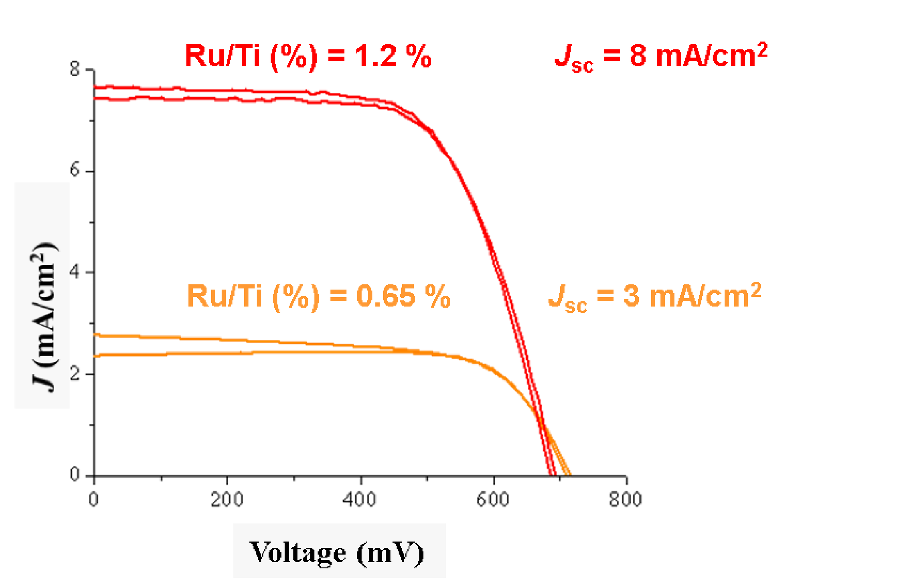
- nine 1D nanostructured TiO_2 films (1 to 4 μm thickness) sensitized by N719 and N749
- normal beam incidence to the sample surface analyses:
  PIXE (1.8 MeV H⁺ ion beam)
  RBS (1.8 MeV H⁺ and 2.0 MeV He⁺ ion beams)
- cross section analyses:
  WDS (only five samples)

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

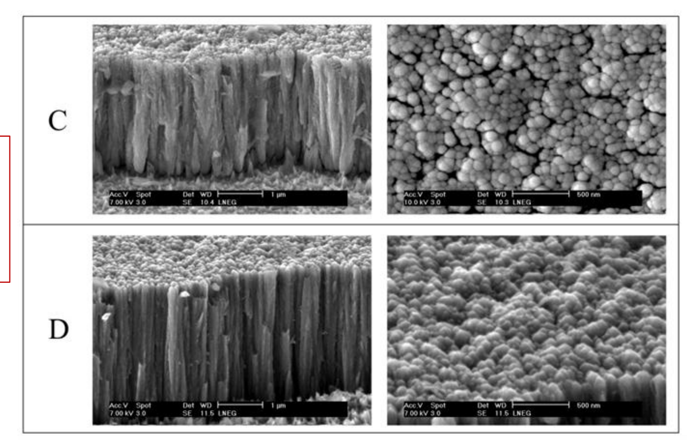


➢ confirming the importance of the dye load evaluation

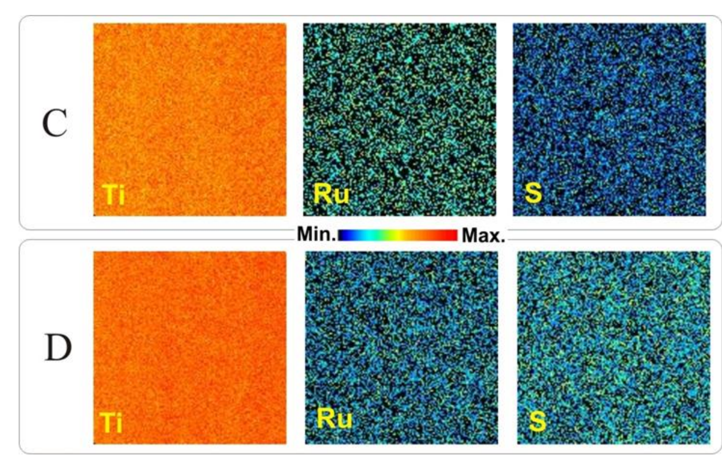
Dye distribution

✓homogeneous surface distribution of the dye Ru and S

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

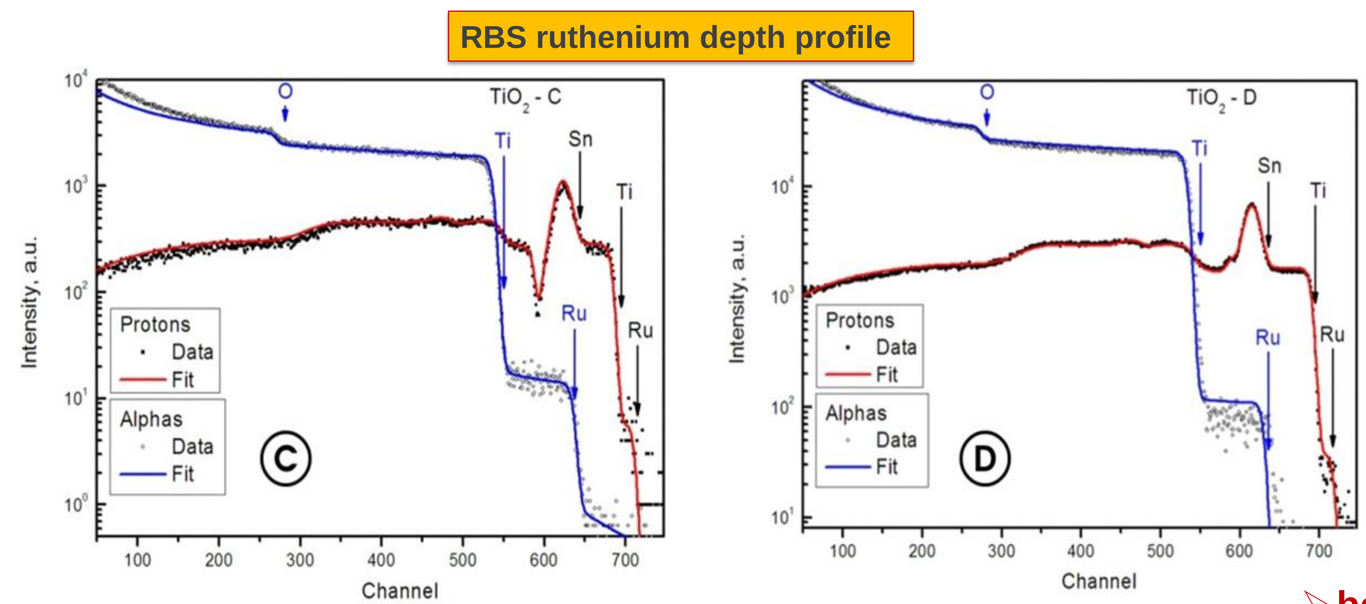


SEM secondary electrons images of films C and D



PIXE 2D X-ray maps for Ti, Ru and S recorded with an H⁺ beam on the films surface (530 x 530 μm² 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

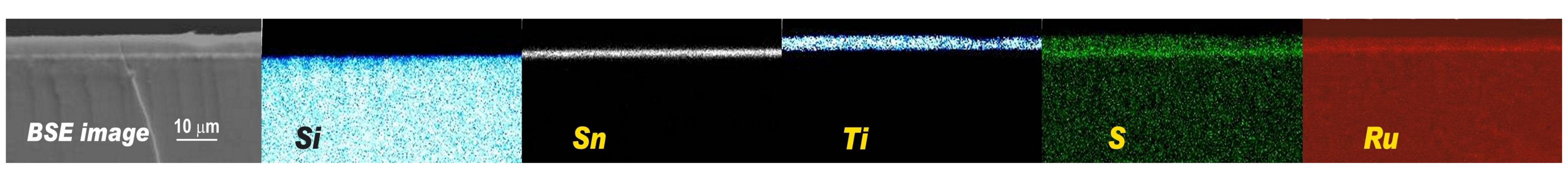
RBS quantitative results

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

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

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