Dynamic EIS- and Photo-electrochemical Measurements on TiO_2-Nanotube Based Photo-anodes for Dye Sensitized Solar Cells - The Influence of the Annealing Temperature.

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Outline

- Electrochemical solar energy conversion: expectations, problems, and the idea of dynamic techniques as improvement tools.
- The three dynamic transfer function variables: light intensity, cell current and cell voltage leading to IMPS and IMVS, analogue to EIS.
- The drawbacks of literature-known IMPS in comparison to new CIMPS.
- The primary aim for IMPS & IMVS: improvement of DSSC kinetics.
- Improving TiO_2-based DSSC: nano-tubes and nano-wires, preparation and curing techniques.
- The influence of the annealing temperature on the efficiency of TiO_2-nano-tube based DSSC: thin film cell measurement results.
- Measurements on an isolated photo-anode in a three-electrode arrangement: the porous photo-electrode model after Bay & West applied in an equivalent circuit modeling and fitting procedure.

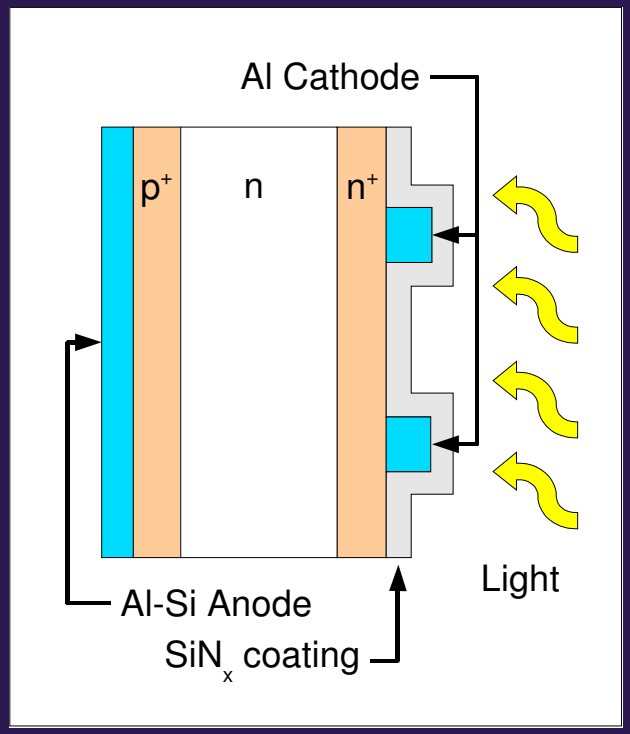
Introduction

Global warming – CO_2-production – renewable energy sources – environmental protection - they are the talk of the town.

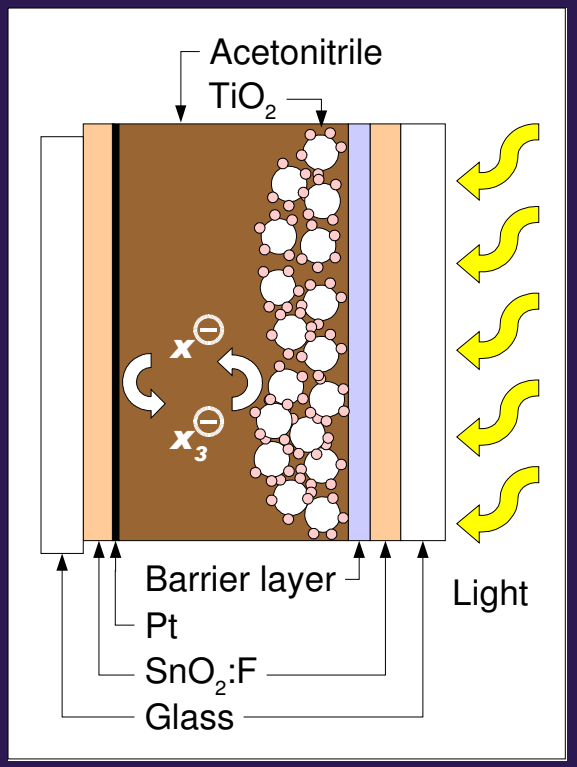
New SC technologies allowing cheap mass production by printing, spraying, spin coating, out of roll lamination techniques, flexible shape SC, and renouncement on clean room procedures are of great demand.

- Expensive mono-crystalline SC: high efficiency, clear structure, easy data interpretation
- Cheaper DSSC and OSC: low efficiency, complex morphology, difficult data interpretation

Silicon Solar Cell vs. Dye Sensitized SC.



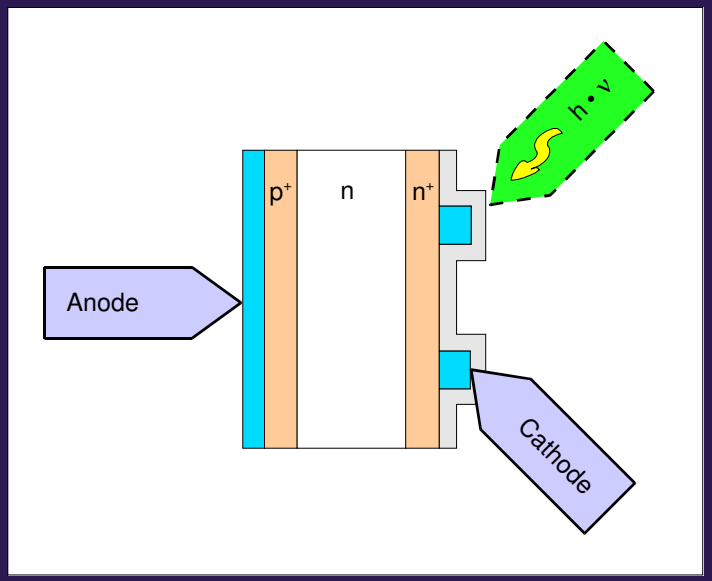
Silicon SC: fast drift of the photo-induced charge from the room charge zone immediately to the metallic current collectors.



DSSC: large band-gap ⇒ mediating dye necessary ⇒ porous layer ⇒ slow diffusion of the photo-electrons to the anode. Hole transport needs supporting electro-chemical reactions. Slow electron diffusion is in competition with recombination process at the Oxide-Solution interface.

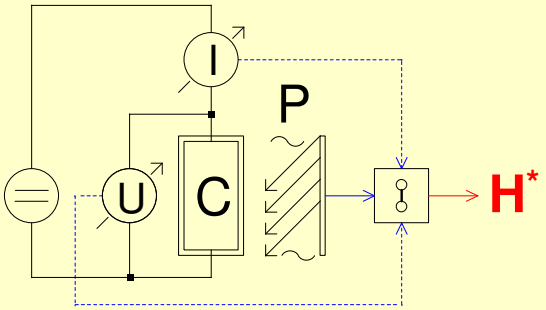
The Three "Terminals" of a Solar Cell

- No information about the photoelectric process through EIS
- Two additional force-response couples can be used for further transfer function analysis:
  - Dynamic Photocurrent vs. Intensity IMPS
  - Dynamic Photovoltage vs. Intensity IMVS



- Each transfer function emphasizes different parts of the system!

IMPS



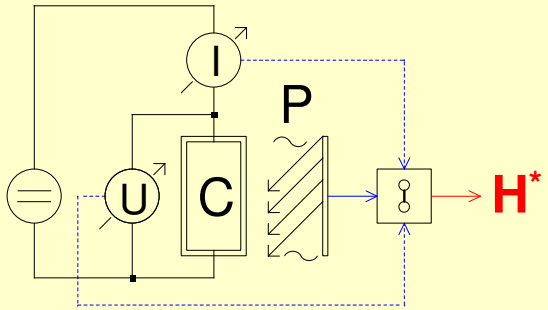
$$H_{IP}(\omega) = \frac{I^*}{P^*}, \quad [H_{IP}] = 1\frac{A \cdot m^2}{W}$$

$$H_{UP}(\omega) = \frac{U^*}{P^*}, \quad [H_{UP}] = 1\frac{V \cdot m^2}{W}$$

The Aim of IMPS / IMVS

- The electron-recombination and the electron-diffusion process are assumed to determine the efficiency of a DSSC.

IMPS

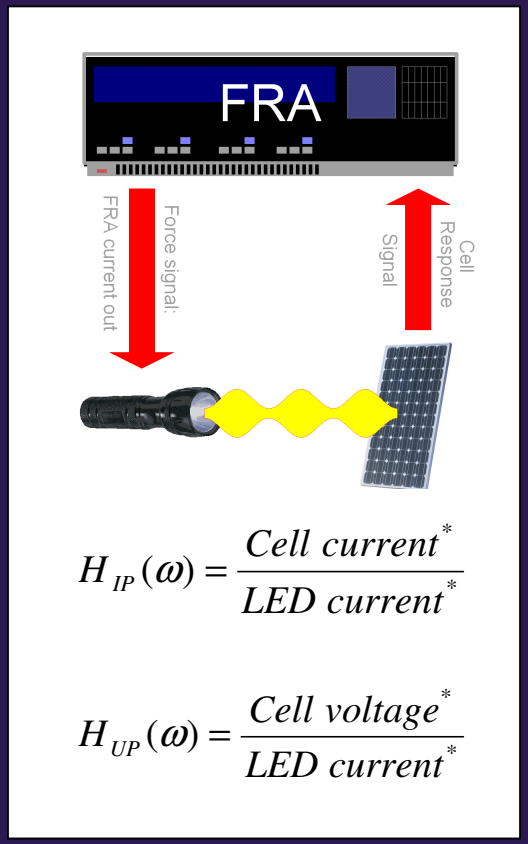


$$H_{IP}(\omega) = \frac{I^*}{P^*}, \quad [H_{IP}] = 1\frac{A \cdot m^2}{W}$$

$$H_{UP}(\omega) = \frac{U^*}{P^*}, \quad [H_{UP}] = 1\frac{V \cdot m^2}{W}$$

- Dynamic Photovoltage vs. Intensity IMVS: electron recombination time constant τ_r dominates at OCP under illumination
- Dynamic Photocurrent vs. Intensity IMPS: electron diffusion time constant τ_c dominates at short-circuit under illumination
- The ratio 1 - τ_c/ τ_r determines the efficiency

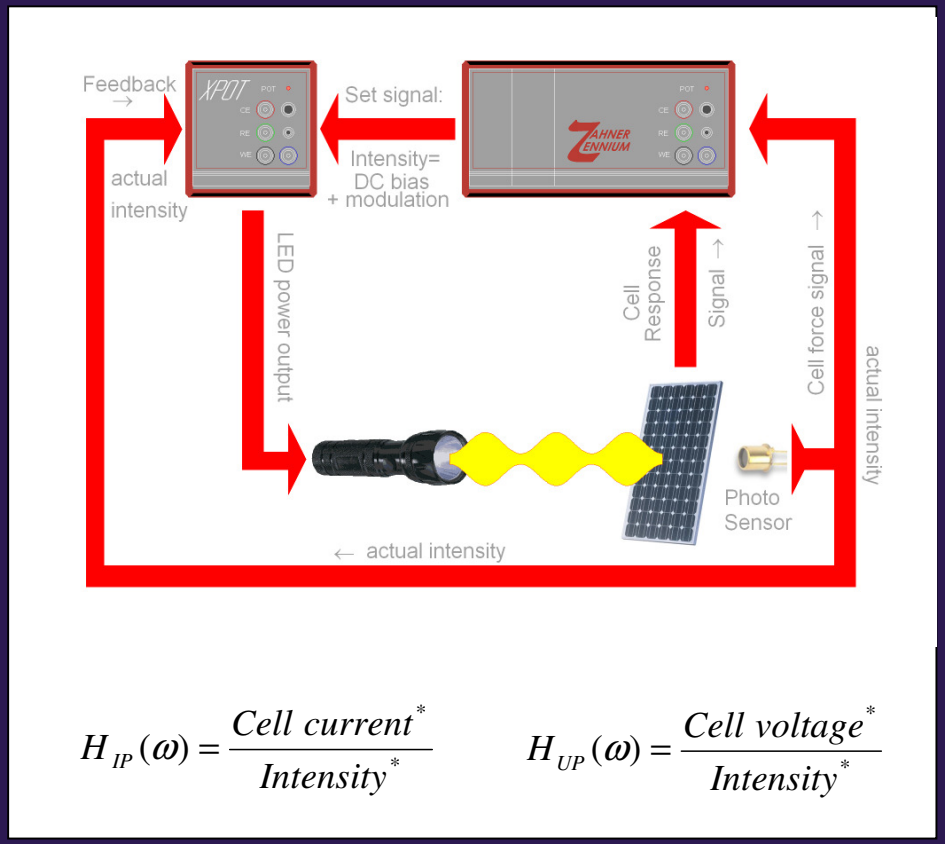
Comparison Between Conventional IMPS and CIMPS



$$H_{IP}(\omega) = \frac{Cell\ current^*}{LED\ current^*}$$

$$H_{UP}(\omega) = \frac{Cell\ voltage^*}{LED\ current^*}$$

Conventional IMPS: The LED control current is used as force signal information. The actual intensity and modulation is uncertain.



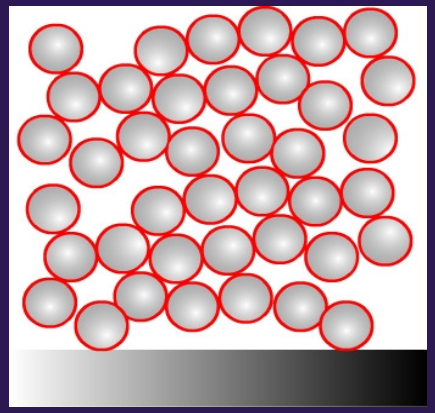
$$H_{IP}(\omega) = \frac{Cell\ current^*}{Intensity^*}$$

$$H_{UP}(\omega) = \frac{Cell\ voltage^*}{Intensity^*}$$

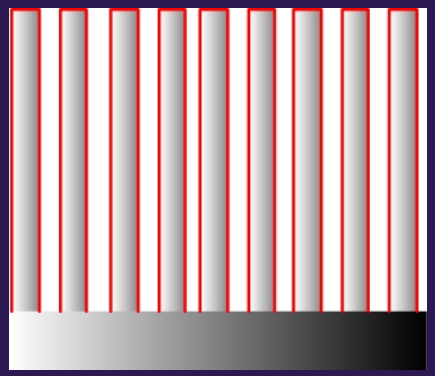
CIMPS: The measured intensity is used as force signal information.The actual intensity is controlled with a photo-sensor at the site of the cell and regulated by means of an operational amplifier feedback circuit.

The Structure of The Nanotube Thin Film DSSC

a)

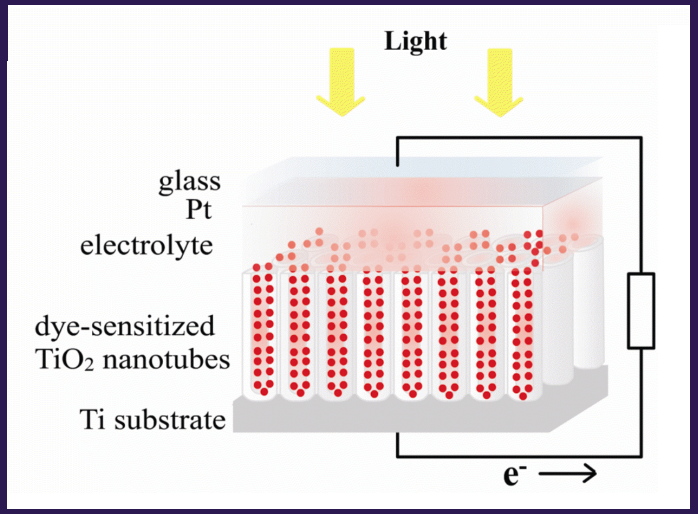


b)



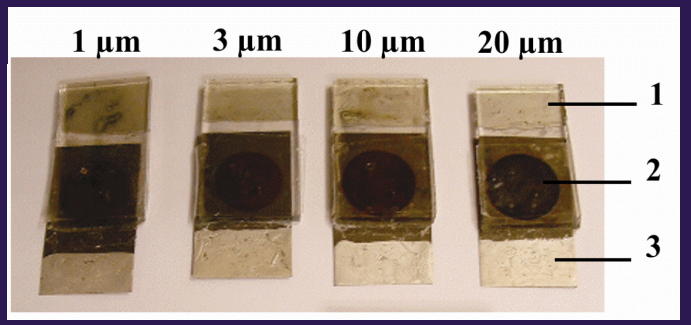
Sketch of nanoporous TiO_2 (a) compared with one-dimensional structures like nano-tubes (b).

c)



Schematic of the DSSC based on TiO_2-nano-tubes used for testing (c)

d)



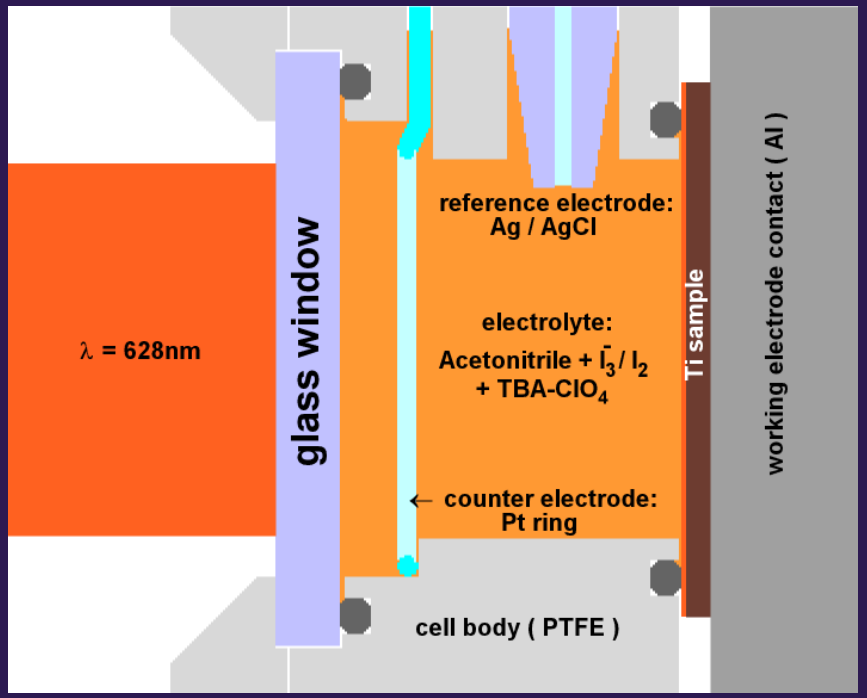
Photograph of the thin film DSSC based on TiO_2-nano-tubes built for testing (d).

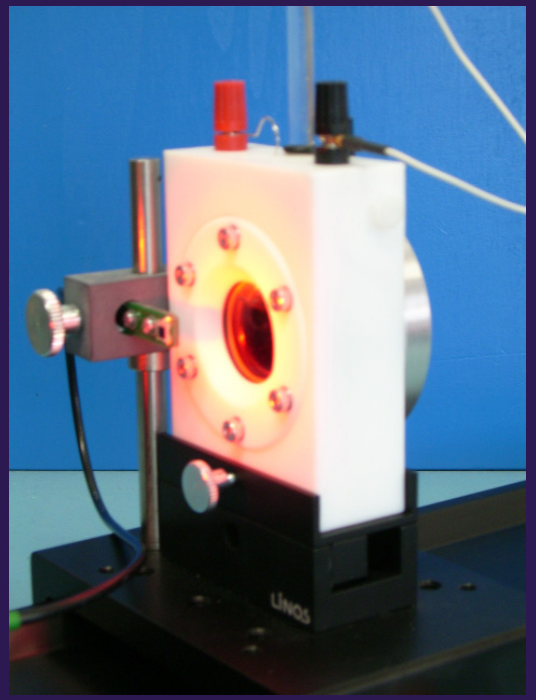
1 cathode: ITO with Pt on glass

2 dye loaded TiO_2 nano-tubes of different length in J/J_3^- containing electrolyte.

3 Ti-foil as oxide carrier and anode

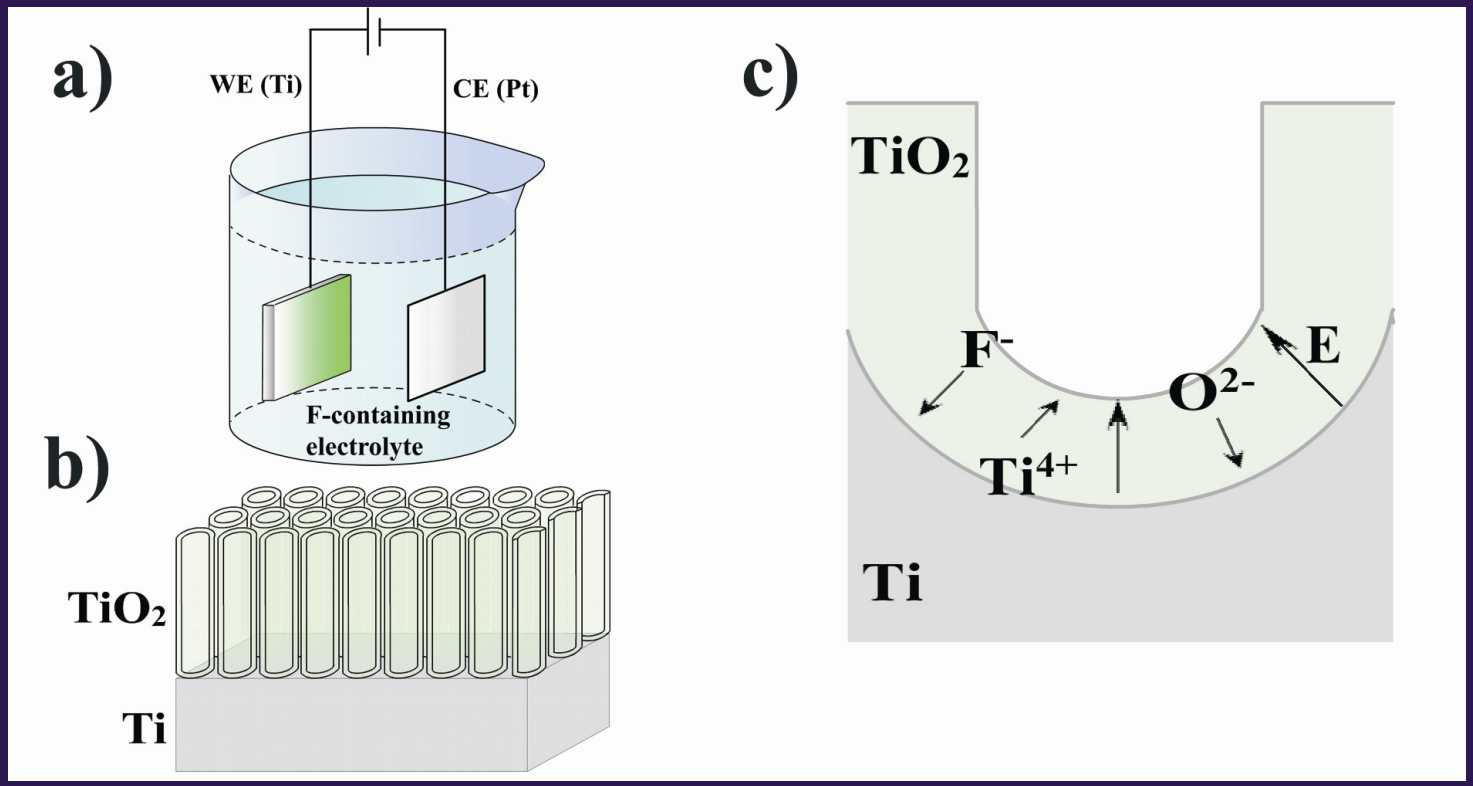
Three-electrode Photo-Electrochemical Cell (PECC) Set-Up





Cross-section scheme (left) of the Photo-electrochemical cell PECC (right) used for the measurements in three-electrode arrangement. The TiO_2-Nanotubes annealed at 450ºC for one hour in air had an average length of 10 to 15 µm. Dye-sensitizing was performed for one day with N179 300 µmol in ethanol. Light: 628nm. Electrolyte is moderate transparent for orange light. The transmission was about 20%.

Preparation of the TiO_2 Nano-Tubes

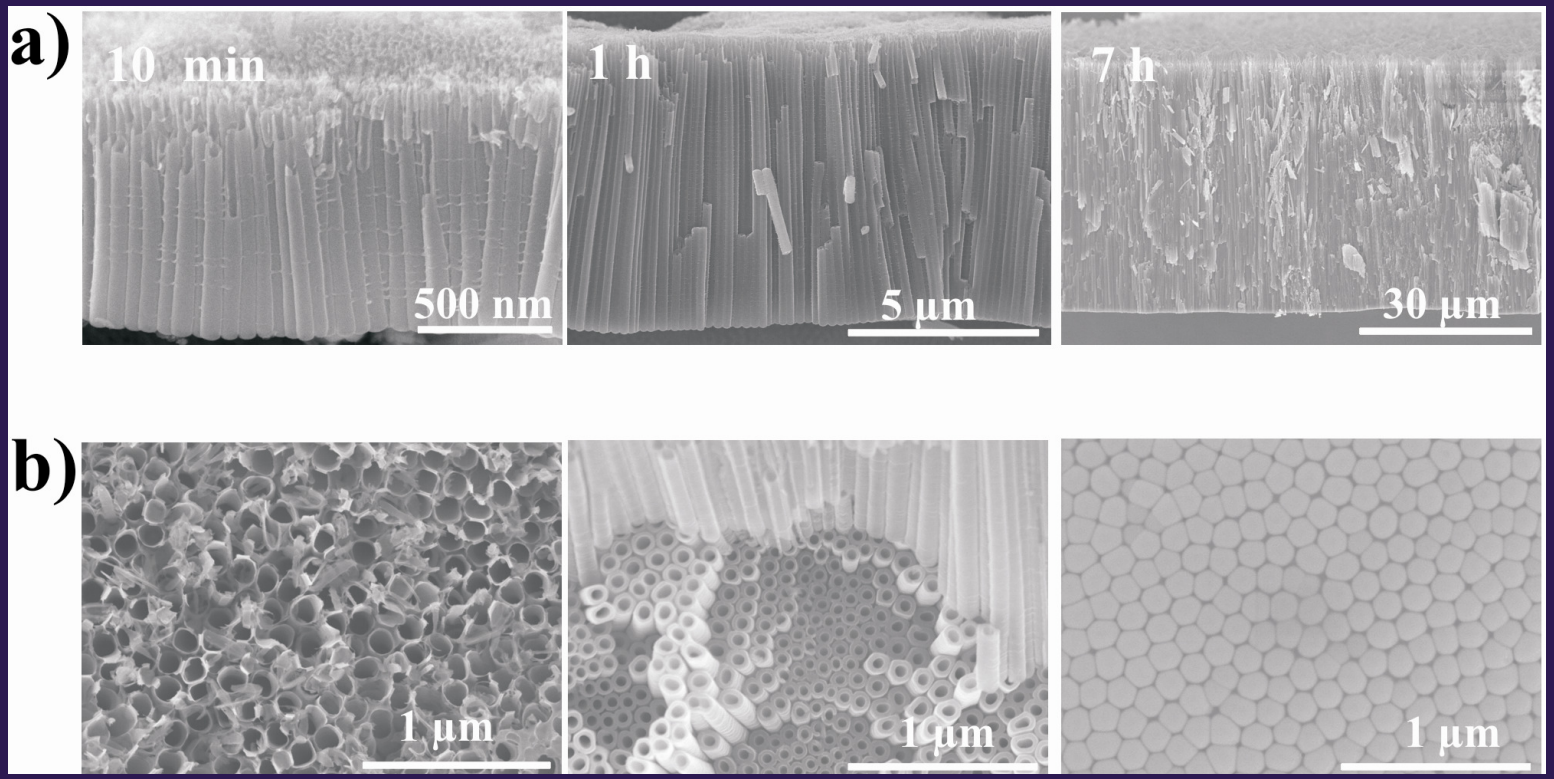


a) Schematic of the high-voltage (≈100V) anodization procedure. Electrolyte was based on ethylene glycol, containing 0.5M HF.

b) Sketch of the TiO_2-nano-tube layer on Ti.

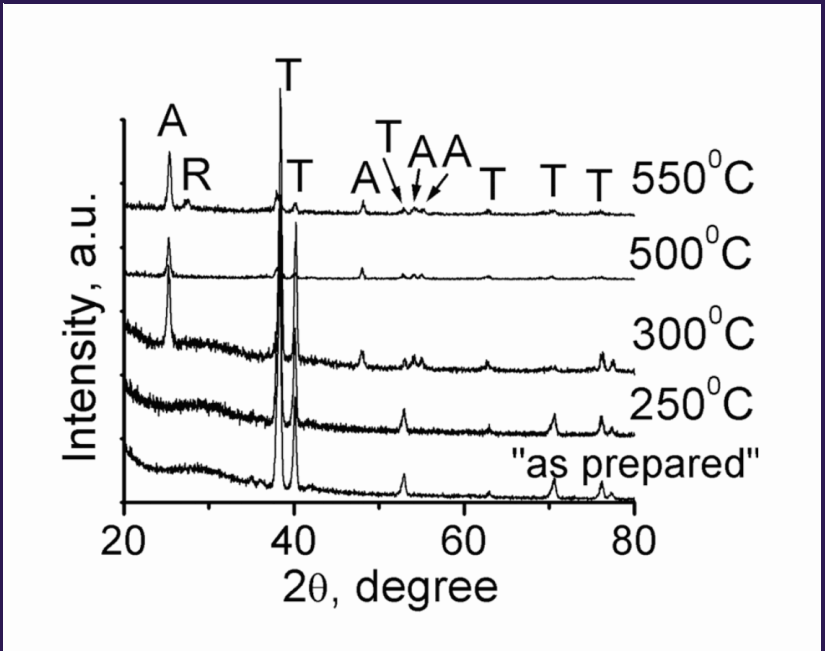
c) Scheme of the self organizing process controlled by the competition of anodic formation and F^--induced etching of TiO_2.

Preparation Results of TiO_2 Nano-Tubes

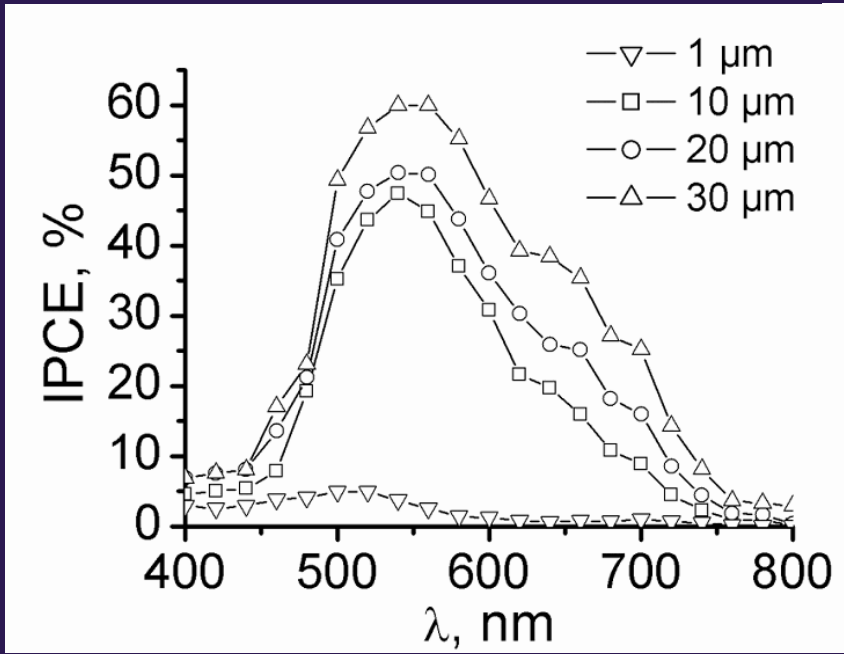


a) SEM cross-sections of typical nanotubular layers prepared in Ethylene Glycol based electrolyte at 120 V for different times. b) SEM top-view (left), view from an intentionally cracked layer (middle) and bottom-view (right). The measured BET surface area for the nanotubes (with diameter of 160±20 nm), used in this work, is 29.8 m^2/g, which is slightly higher than the calculated value of 25 m^2/g, for ideal nanotube structures.

Preparation Results of TiO_2 Nano-Tubes (2)

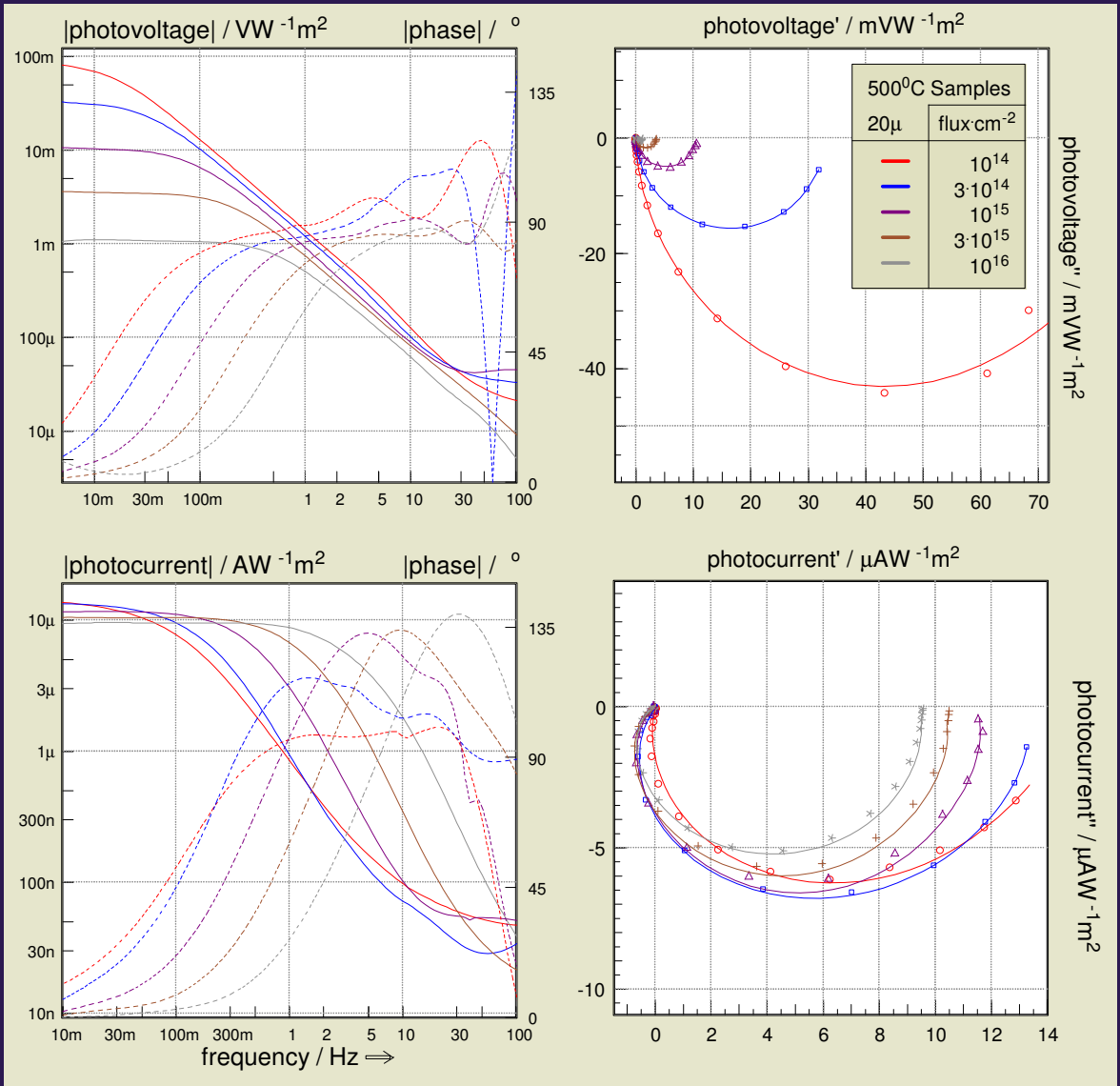


XRD results from “as prepared” nanotube layers and after annealing at 4 different temperatures for 1h in air (A, R and T denote Anatase, Rutile and Ti reflexes).



Normalized PCS (IPCE diagram) measured from four different thickness nanotube samples. The quantum efficiency increases with the tube length.

CIMPS Measurements – Samples Annealed at 500°C



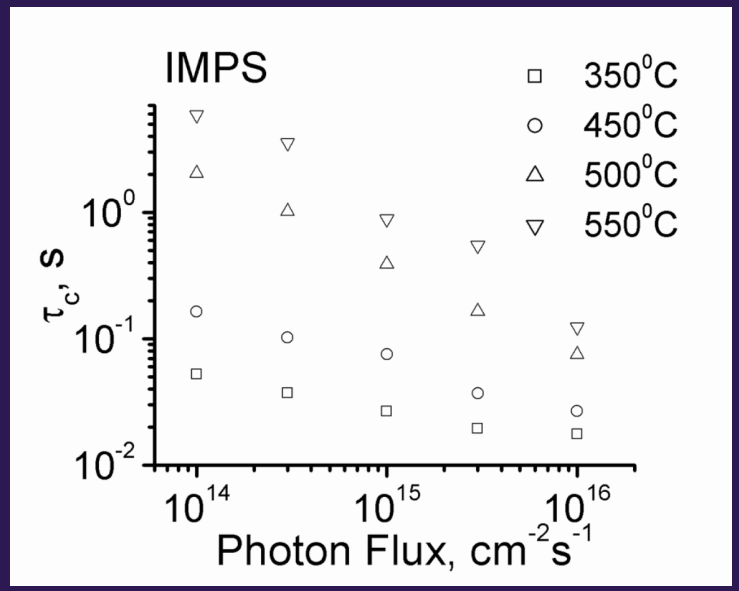
IMVS (upper) and IMPS (lower) spectra of 20µm length TiO_2 nanotubes annealed at 500°C. Bode diagrams at the left, complex plane diagrams at the right hand side.

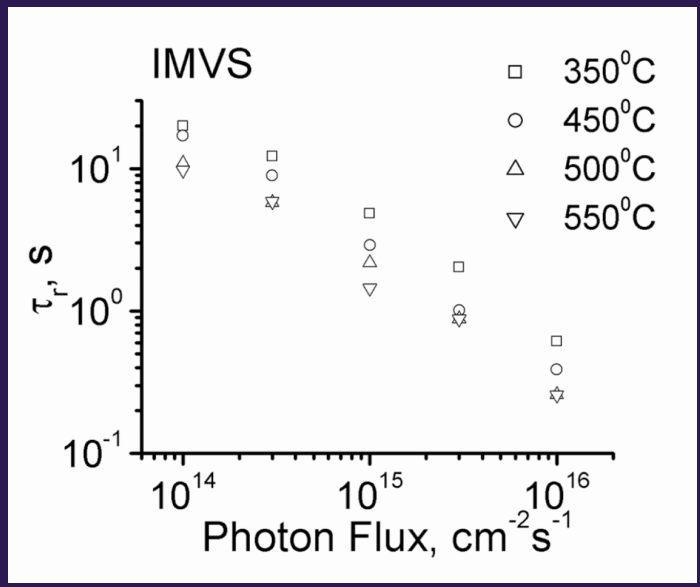
IMVS was done at OCP, IMPS under short circuit conditions. The samples were illuminated with a photon flux between 10^{14} and 10^{16}.

Estimate dynamic efficiency parameter:

$1 - \tau_c/\tau_r \approx 0.66.$

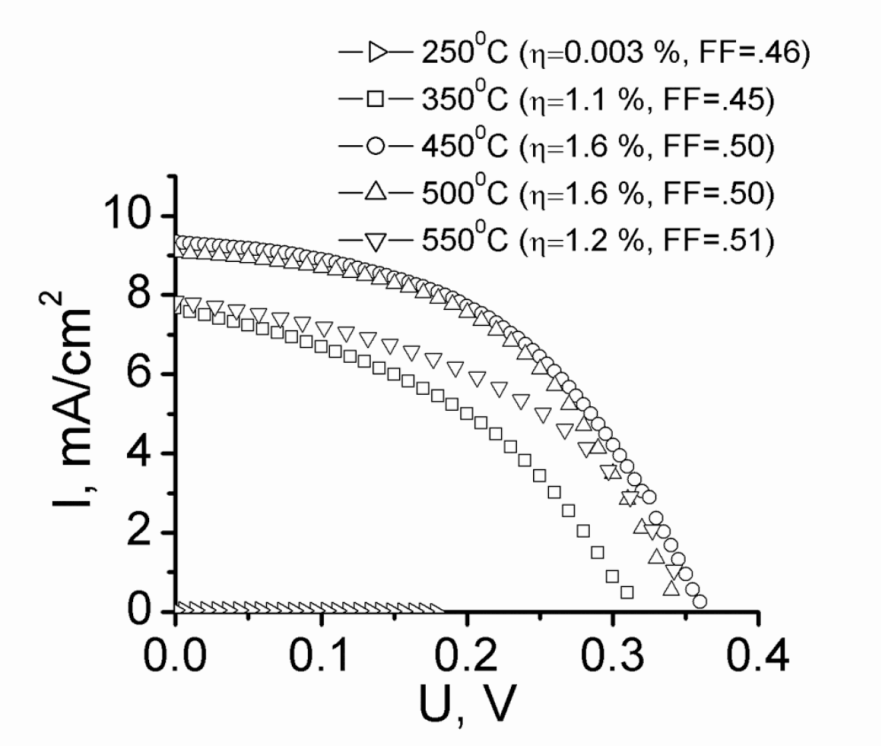
The Results of IMPS / IMVS





Transport (left) and recombination time (right) extracted from the dominating time constants of CIMPS and CIMVS for the thin film nanotube DSSC. The dynamic efficiency parameter 1 - τ_c/τ_r decreases with increasing annealing temperature.

DC-AC-Performance of the Nanotube DSSC



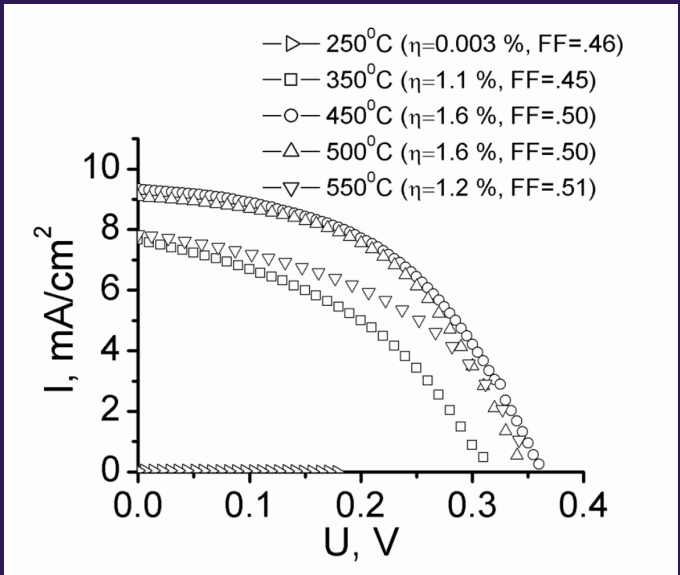
Annealing Temperature / Cº	IMPS τ_c / s	IMVS τ_r / s
350	0.018	0.6
450	0.027	0.29
500	0.077	0.25
550	0.12	0.25

AM 1.5 I-V curves from cells with nanotubes annealed in the range 250-550^0 C.

Temperature-dependence of diffusion time constant τ_c and recombination time constant τ_r.

DC-Performance of the Nanotube DSSC

	Annealing temperature, ^{0} C (20 µm, 4 days)			**Nanotubes length, µm** (450^0 C, 4 days)			**Soaking time, days** (20 µm, 450^0 C)		
	350	450	500	10	20	30	1	4	7
Dye-loading, mM	27	61	60	49	61	52	50	61	59

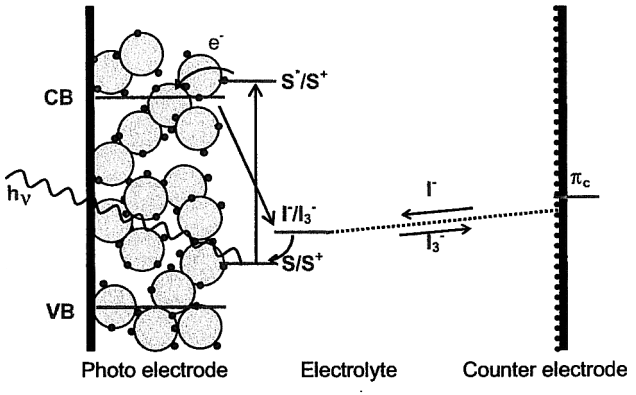


I-V curves from nanotube carriers annealed in the range 250-550^0 C.

Dye loading was determined by desorption and photometry.

Modeling and Fit of the DSSC in the Three Electrode Set-Up

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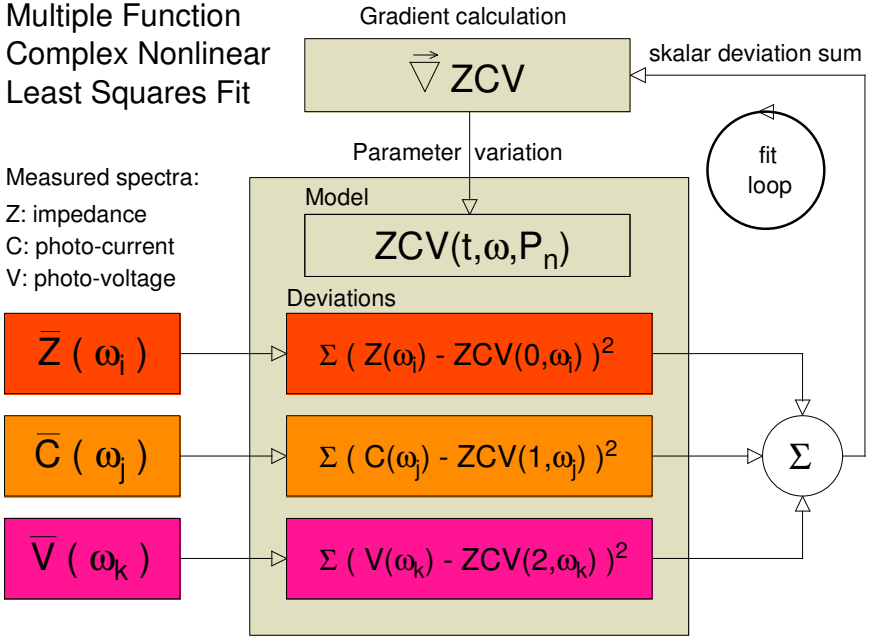
$$Z_{EC} = (R_e + R_i)\ell \frac{\coth(\alpha\ell)}{\alpha\ell} + \frac{R_e R_i}{R_e + R_i}\ell\left(1 - \frac{\tanh(\alpha\ell/2)}{\alpha\ell/2}\right)$$

$$V_P(R_i, R_e) = \frac{BAR_i}{A^2 - \alpha^2}\left(e^{-A\ell}\left[1 + \frac{A}{\alpha}\coth(\alpha\ell)\right] - \frac{A}{\alpha\sinh(\alpha\ell)}\right)$$

$$+ \frac{BAR_i}{A^2 - \alpha^2}\left(\left[1 - \frac{A}{\alpha}\coth(\alpha\ell)\right] + \frac{Ae^{-A\ell}}{\alpha\sinh(\alpha\ell)}\right)$$

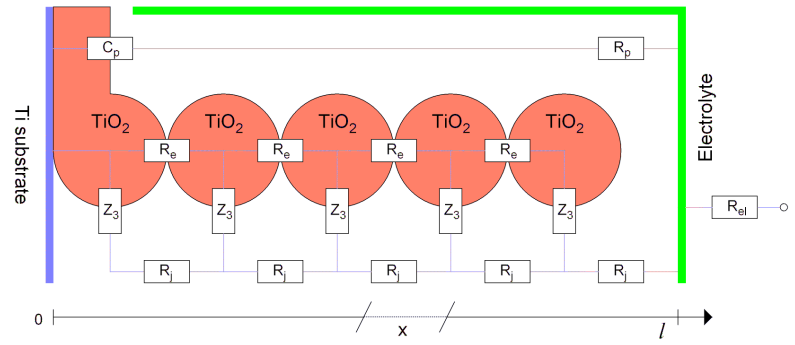
Porous Photo-Electrode Model after:

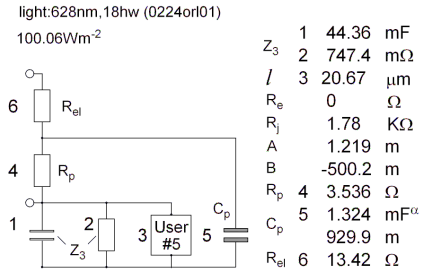
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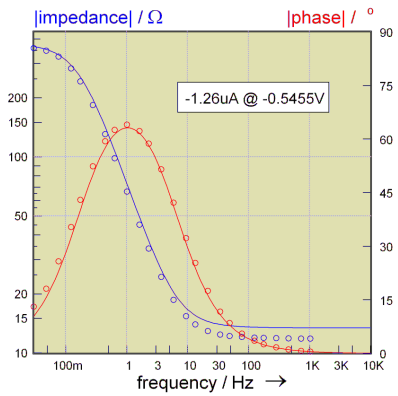
Scheme of the Thales SIM software joint fitting procedure for three different kinds of spectral transfer functions: impedance, dynamic photo current and dynamic photo voltage.

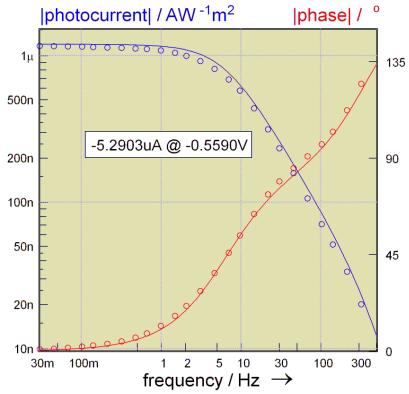
Modeling and Fit Result of the Photo-Anode Applying the Porous Photo-Electrode Model After Bay & West

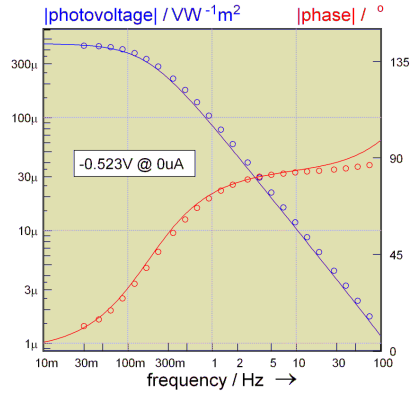




Z_3	1	44.36	mF
	2	747.4	mΩ
l	3	20.67	µm
R_e		0	Ω
R_j		1.78	KΩ
A		1.219	m
B		-500.2	m
R_p	4	3.536	Ω
C_p	5	1.324	mF$^\alpha$
		929.9	m
R_{el}	6	13.42	Ω







Schematic of the porous photo-electrode model (upper left), the equivalent circuit used in the SIM software (upper right) and the three transfer functions: impedance (lower left), dynamic photo-current (lower middle) and dynamic photo-voltage (lower right). Samples represent the measurement data, solid lines the fit result.

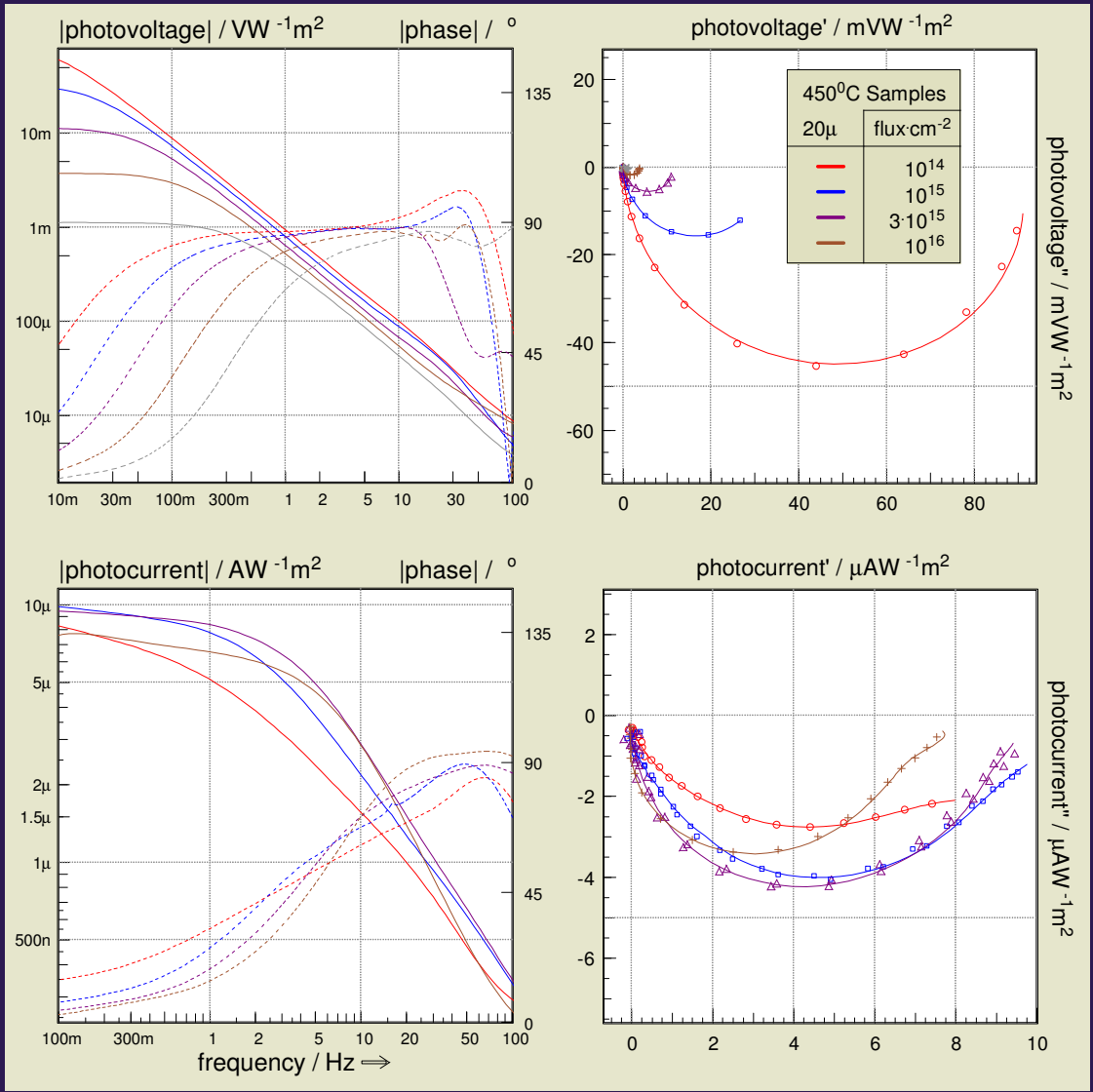
Summary and Conclusion

- Thin-film Graetzel-type DSSC on the base of TiO_2-nanotubes were produced and tested.
- The nanotubes were prepared by high-voltage anodization of Ti-foils. A Fluoride-containing electrolyte based on ethylene glycol mediated the self organizing process.
- The conversion of the tubular oxide from the initially amorphous state by thermal annealing lead to Anatase crystals with an increasing Rutile content at higher temperatures.
- Except for the highest one, the DSSC efficiency increased with increasing annealing temperature. This is in contradiction with the kinetic data determined with IMPS/IMVS.
- A possible explanation may be the better light absorption property of samples annealed at higher temperature. Such samples exhibited a significantly higher dye loading.
- The dynamic behavior of a nanotube sample tested in a three electrode set-up could be understood by means of the porous photo-electrode model after Bay & West. Future endeavor will be made to apply this model to the thin film DSSC as well.

Acknowledgement

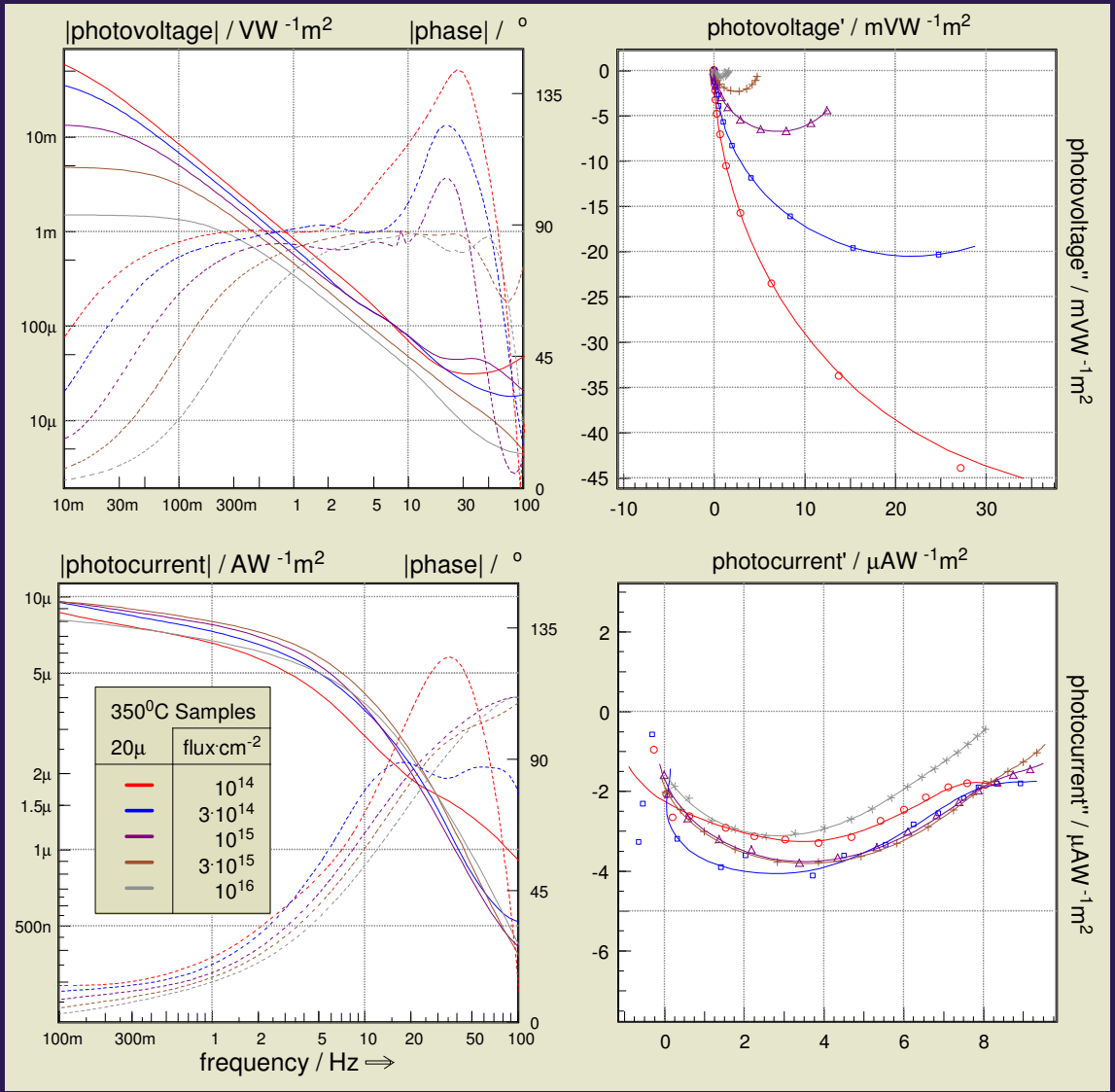
Thank you for your attention !

CIMPS Measurements – Samples Annealed at 450°C



IMVS (upper) and IMPS (lower) spectra of 20µm length TiO_2 nanotubes annealed at 450°C.

CIMPS Measurements – Samples Annealed at 350°C



IMVS (upper) and IMPS (lower) spectra of 20µm length TiO_2 nanotubes annealed at 350°C.