Il ruolo della chimica nei temi tecnologici dell'energia

ROMA – 21 Giugno 2011

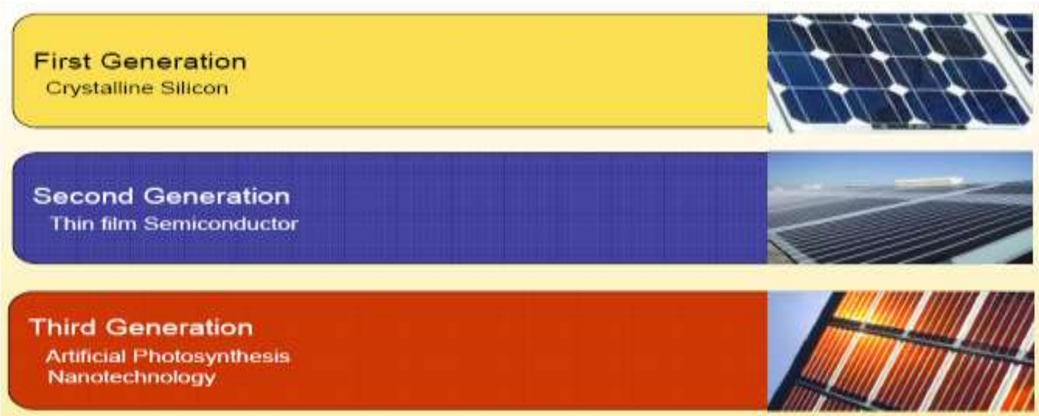
Dispositivi fotovoltaici a sensibilizzatore organico: nanomateriali a geometria controllata e architetture intelligenti

Ing. MICHELE MANCA

Center for Biomolecular Nanotechnologies - Italian Institute of Technology

http://cbn.iit.it/

PRODUCTION FORECASTS FOR DIFFERENT TECHNOLOGIES

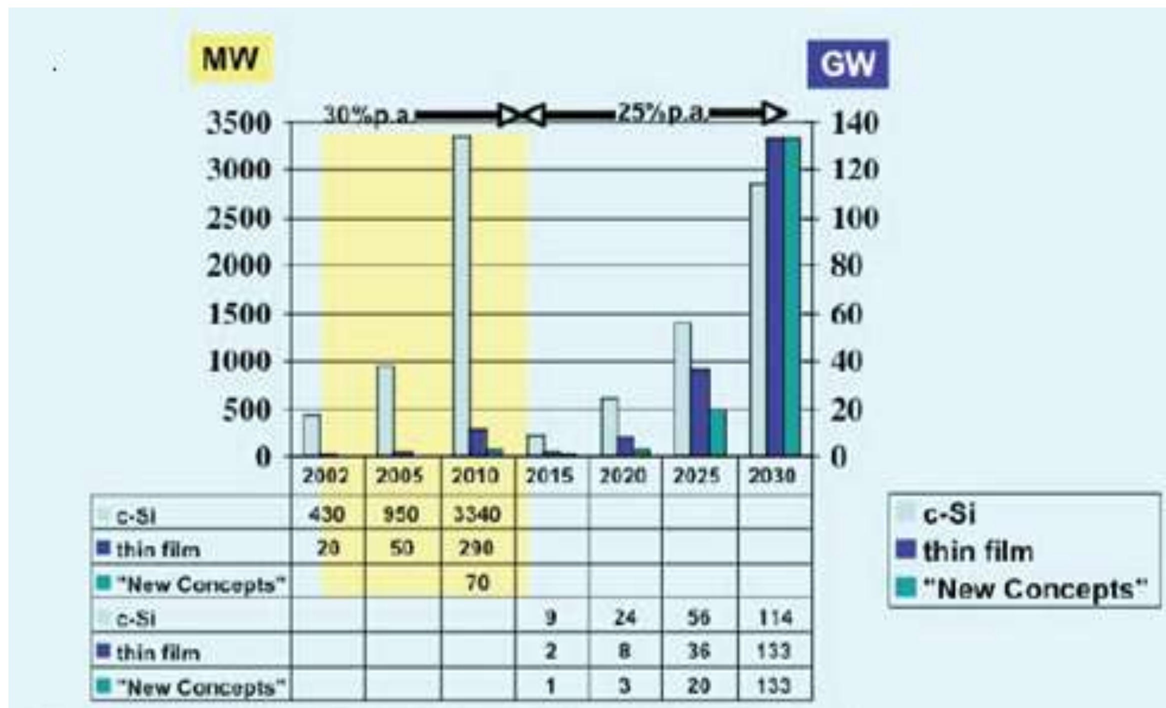


MARKET REQUIREMENTS:

- ❑ high efficiency
- ❑ low cost of the kWh produced
- ❑ high lifetime of the devices
- ❑ application flexibility

The present technologies mainly meet two of the above-mentioned parameters:

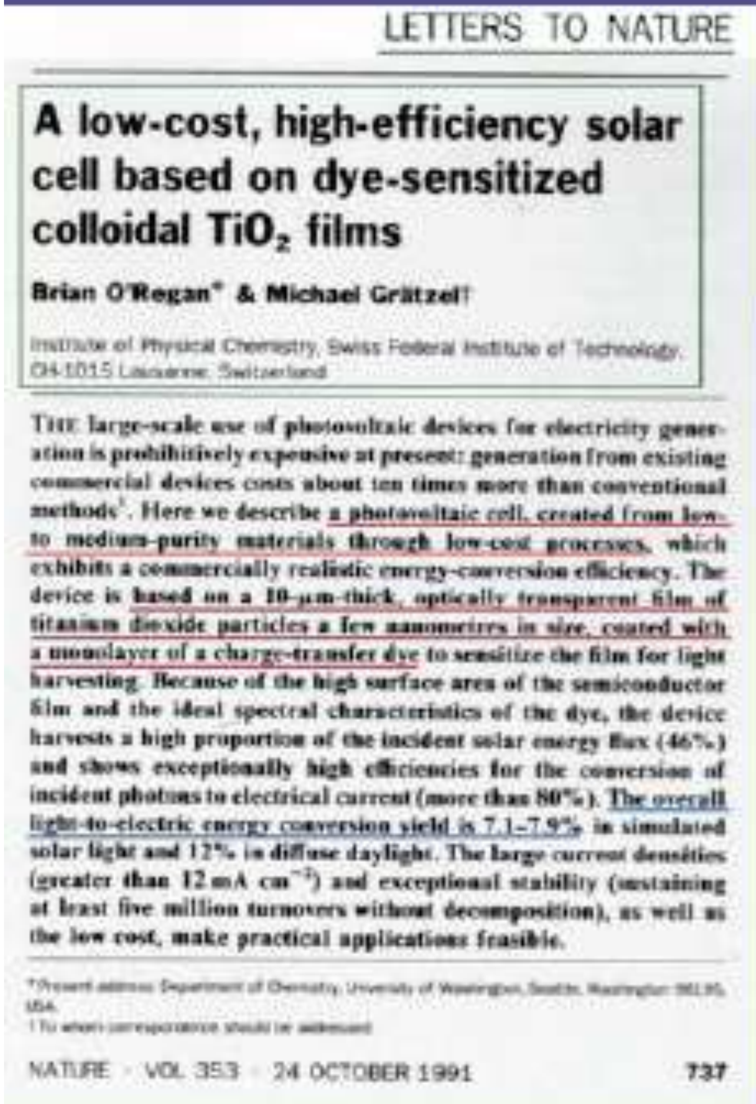
- good efficiency ➔ 8-18%
- high cell duration➔ >25 years
- still high costs ➔ 2.5 €/Wp
- applications are optimized nearly exclusively for systems installed on the ground or roofing



Courtesy Dr. Winfried Hoffman, CEO, RWE, SCHOTT Solar GmbH

DYE-SENSITIZED SOLAR CELLS

A promising technology for 3rd generation photovoltaics



A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films

Brian O'Regan* & Michael Grätzel†

Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

THE large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods[1]. Here we describe a photovoltaic cell, created from low- to medium-purity materials through low-cost processes, which exhibits a commercially realistic energy-conversion efficiency. The device is based on a 10-μm-thick, optically transparent film of titanium dioxide particles a few nanometres in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current (more than 80%). The overall light-to-electric energy conversion yield is 7.1–7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12 mA cm^{-2}) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make practical applications feasible.

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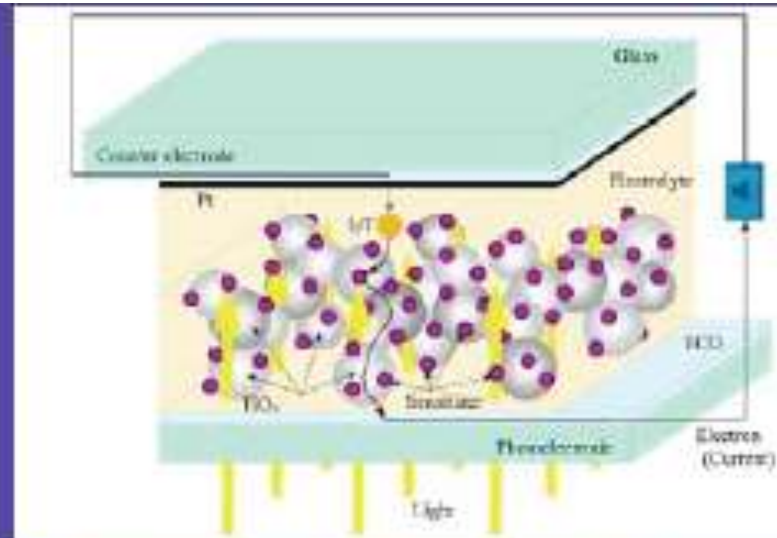
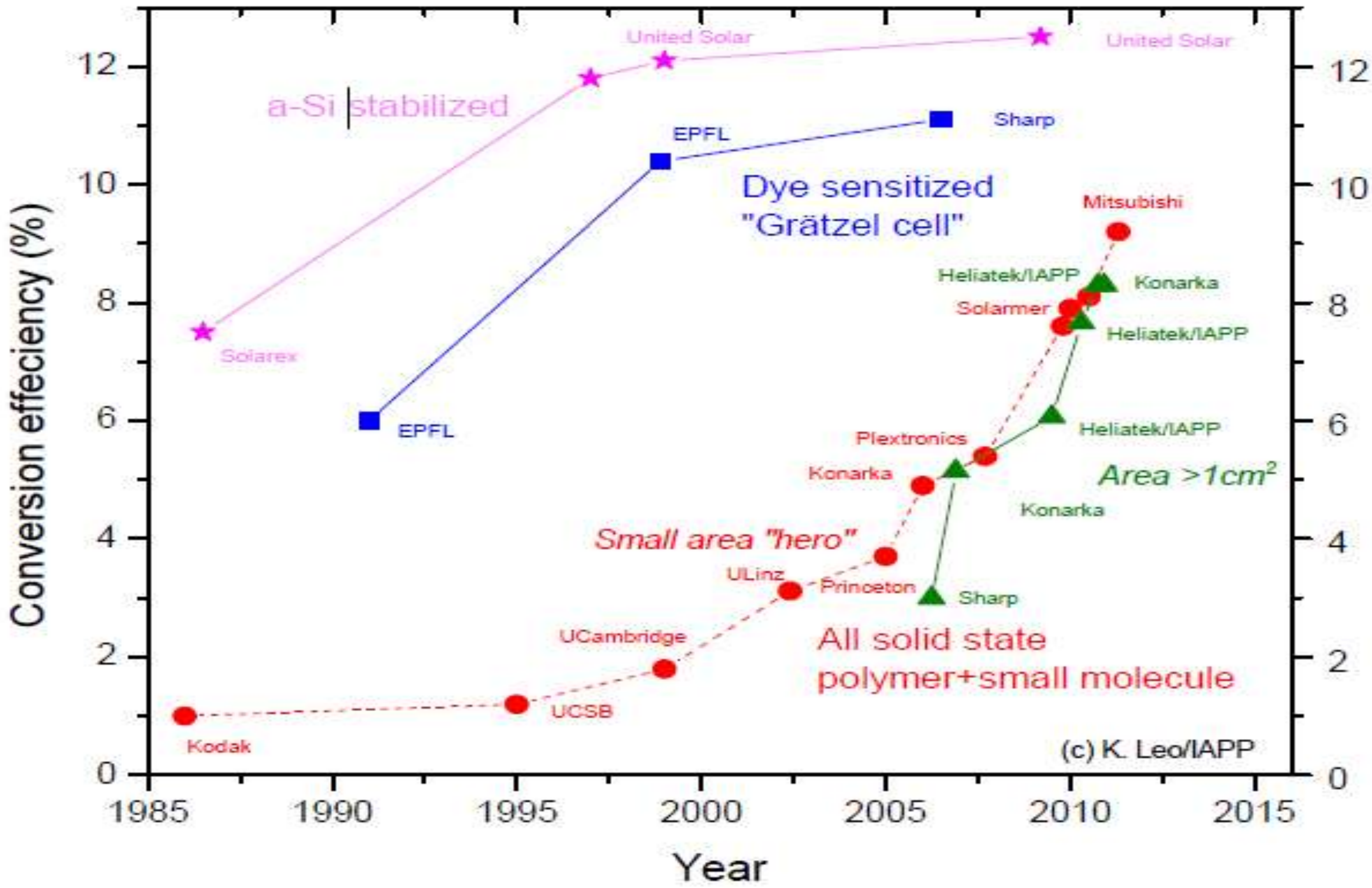
† To whom correspondence should be addressed.



PV TECHNOLOGIES
Efficiency and Cost Trends



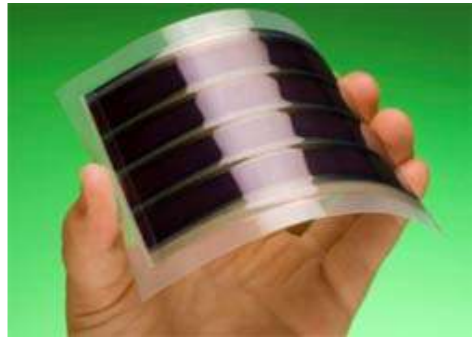
DYE-SENSITIZED SOLAR CELLS

A promising technology for 3rd generation photovoltaics

- ❑ Lowest embodied energy
- ❑ Environmentally benign manufacturing and materials
- ❑ Can be engineered to the environment and application
- ❑ Energy security
- ❑ Better than Silicon in low-light conditions (haze, overcast , shading , indirect light)
- ❑ Modest capital required to establish manufacturing
- ❑ Possibility for various colors ➔ aesthetic appeal
- ❑ Flexibility suits new product development
- ❑ Bifacial feature of semi-transparent PV windows

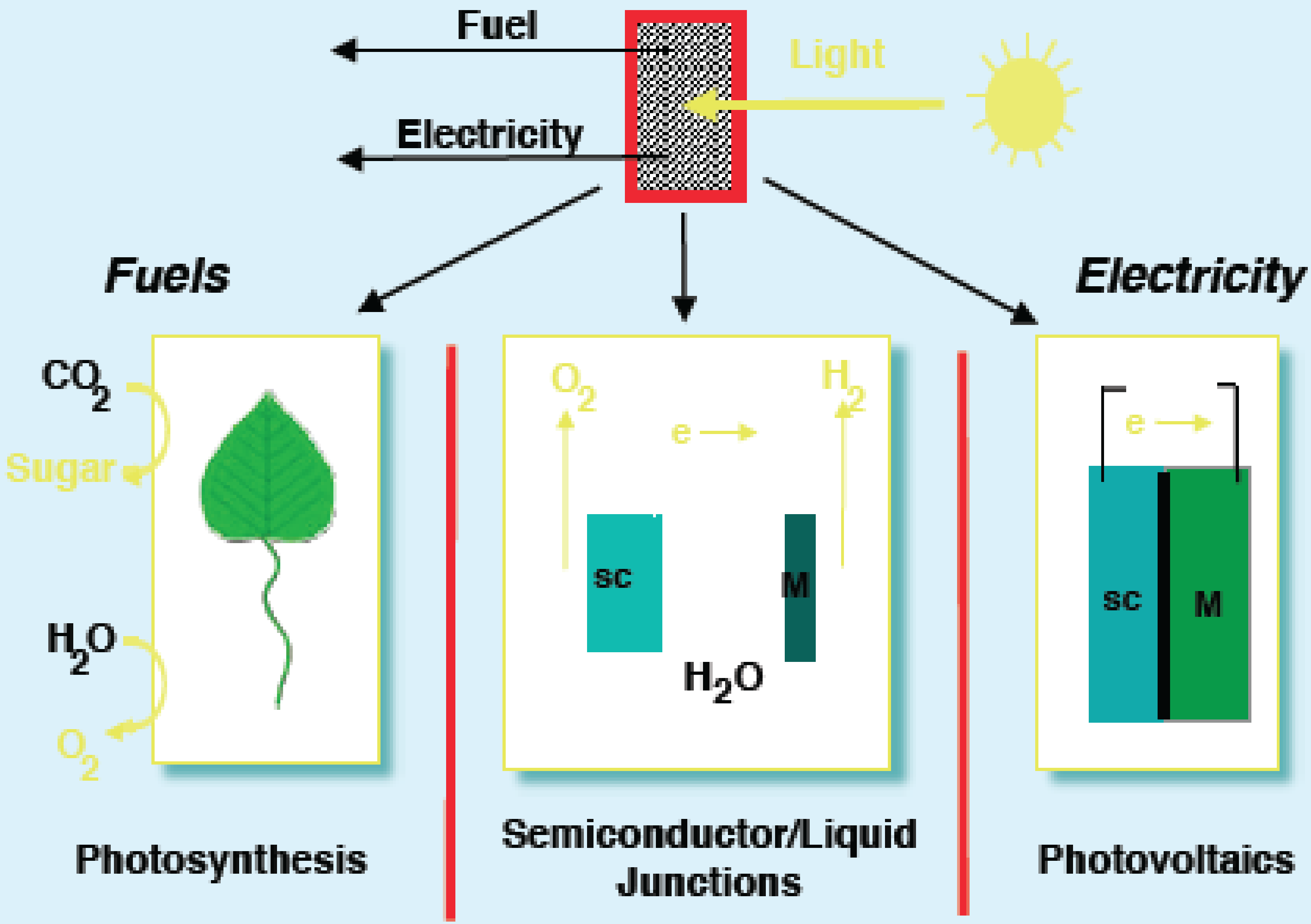
DYE-SENSITIZED SOLAR CELLS

A promising technology for 3rd generation photovoltaics

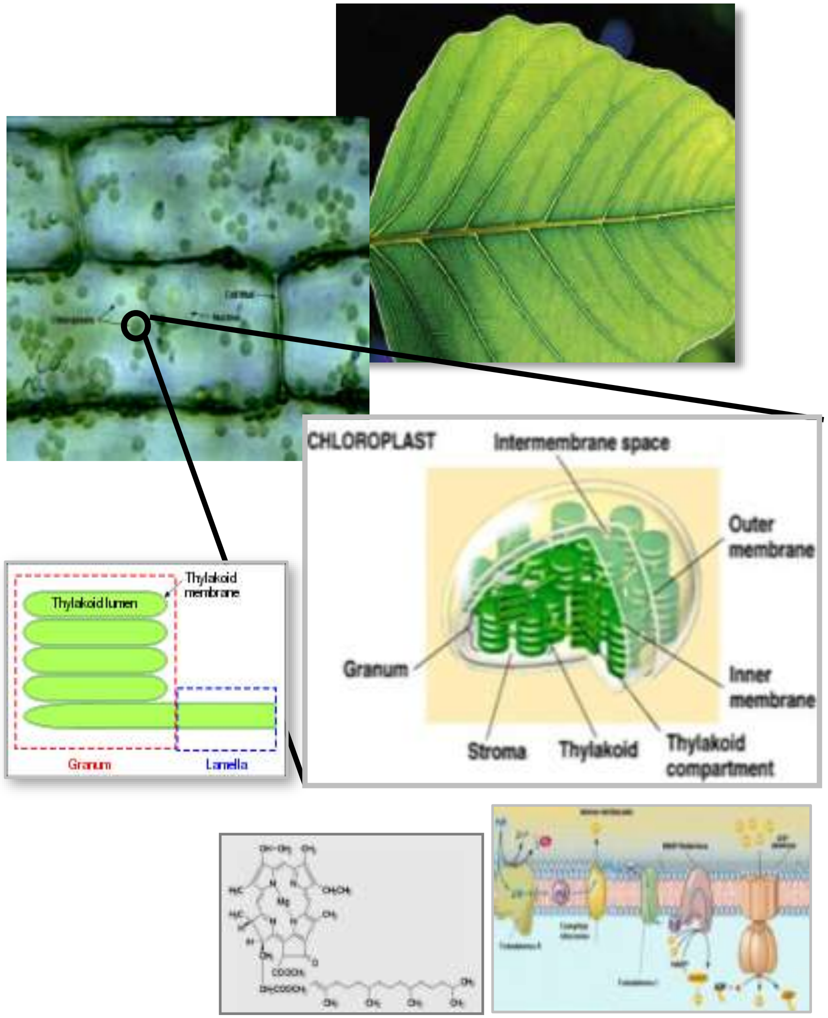


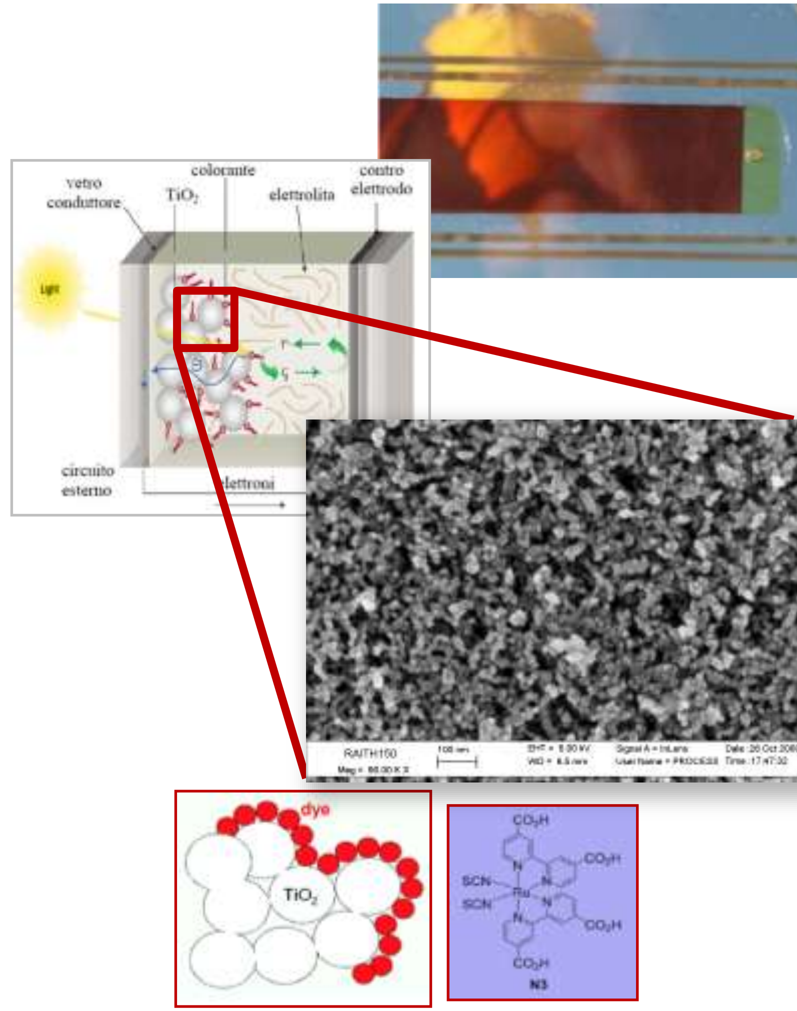
✓Building integrated
✓Consumer products
✓Grid connected solar farms
✓Remote industrial
✓Remote communities

QUANTUM ENERGY CONVERSION STRATEGIES



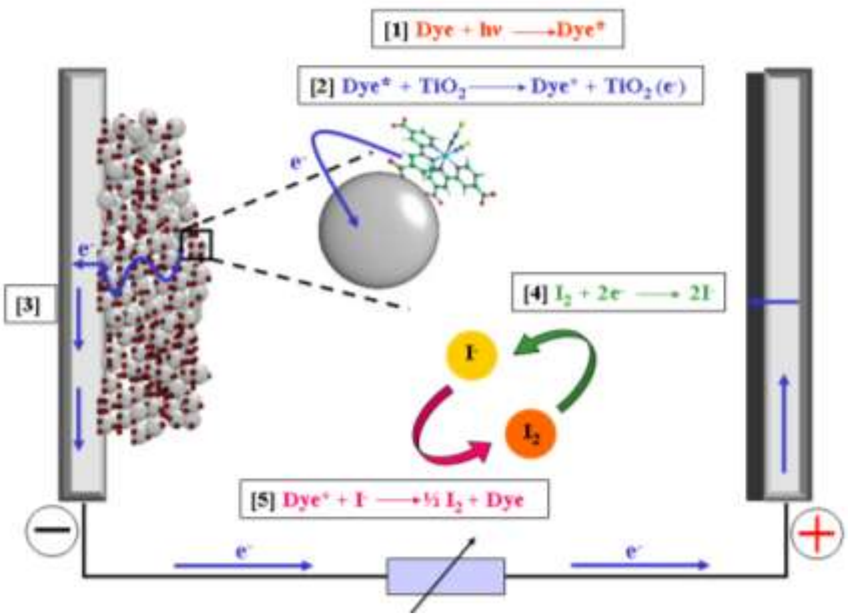
QUANTUM ENERGY CONVERSION STRATEGIES

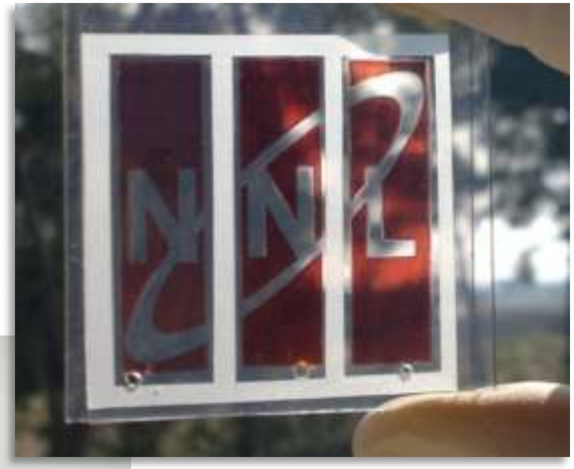


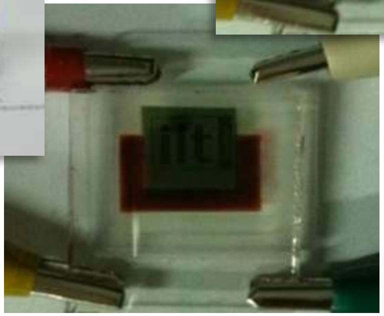


DYE-SENSITIZED SOLAR CELLS
Ongoing R&D activities @ CBN-IIT & NNL-CNR

- Photoelectrodes based on shape-tailored NCs
- Flexible composite nanocarbon-based plates
- Highly stable gel electrolytes
- Smart photovoltachromic devices







KEY COMPONENT #1 :PHOTOELECTRODE

- Optical and electronic properties of the photoelectrode are mainly governed by the nanocrystals morphology and by the sinter necks
- The main transport mechanism for electrons in the TiO_2 layer is diffusion
- The electron mobility of a mesoporous layer is more than two orders of magnitude lower than in the corresponding bulk crystals

k_1= ns- μs

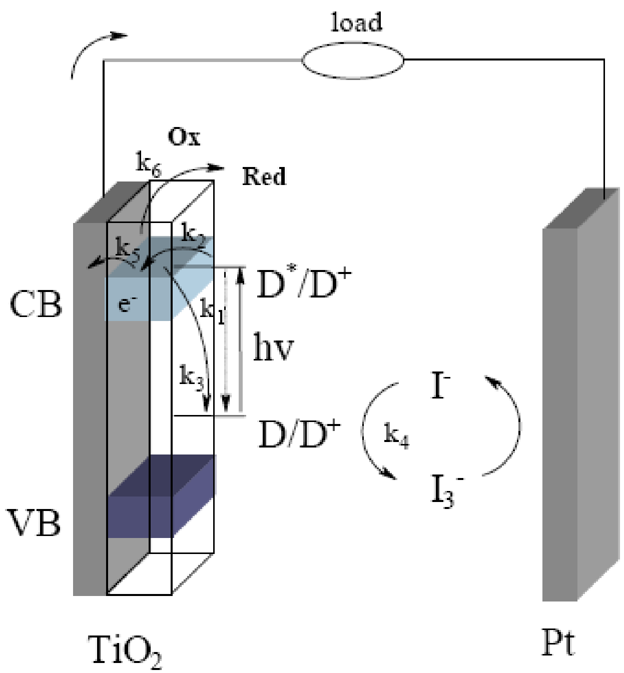
k_2= fs- ps

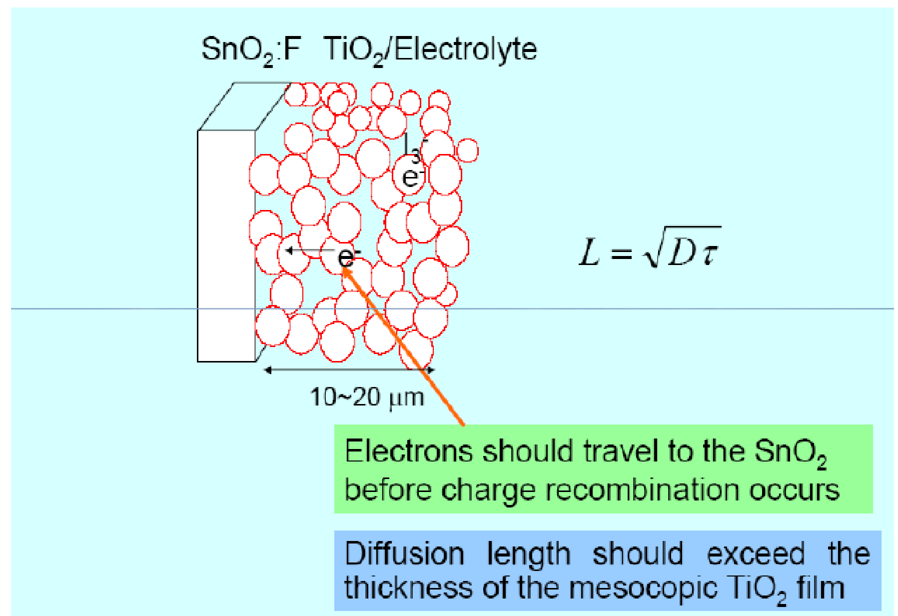
*k_3= μs- ms

*k_4= ns- μs

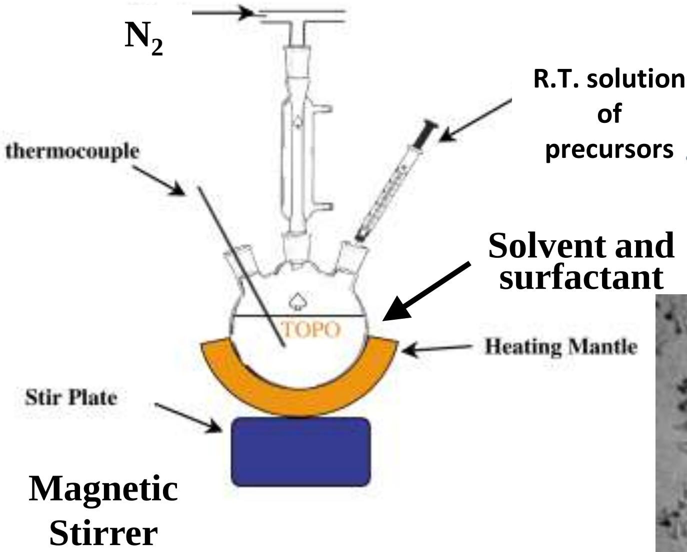
**k_5= ms- s

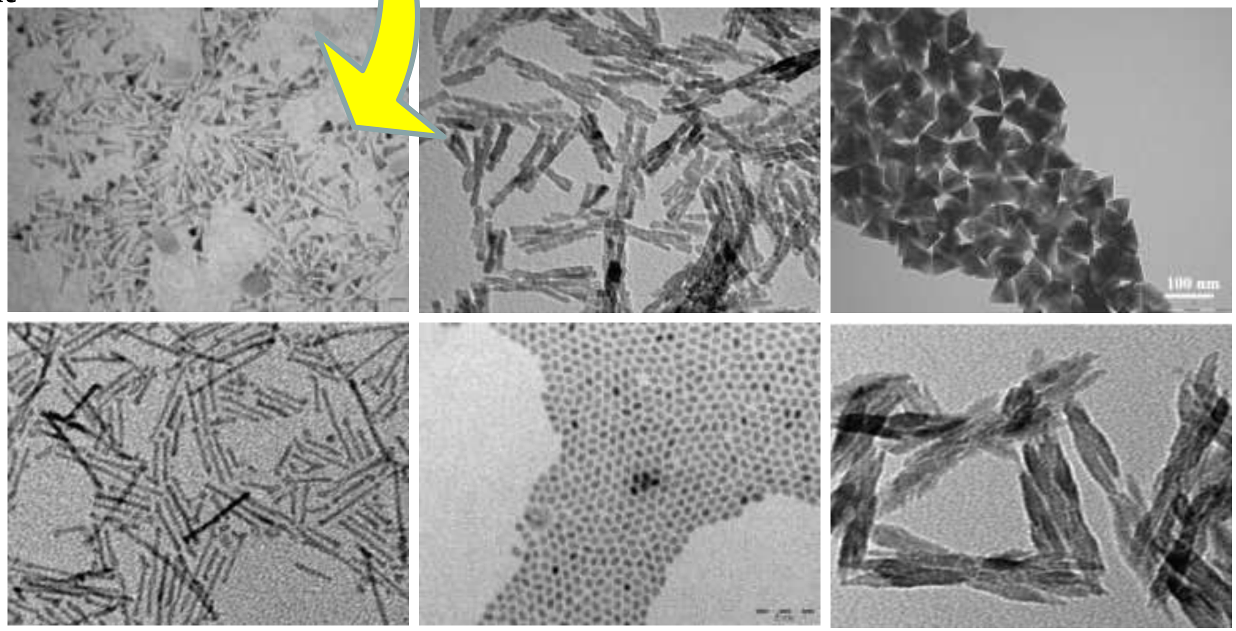
*k_6= μs- ms





DESIGN AND SYNTHESIS of ENGINEERED NANOCRYSTALS





Melcarne, G.; De Marco, L.; Carlino, E.; Martina, F.; Manca, M.; Cingolani, R.; Gigli, G.; Ciccarella, G.**;** **Journal of Materials Chemistry**, 2010, 20, 7248.

De Marco, L.; Manca, M.; Giannuzzi, R.; Malara, F.; Melcarne, G.; Ciccarella, G.; Zama, I.; Cingolani, R.; Gigli, G.; **Journal of Physical Chemistry C**, 2010, 114 (9), 4228.

Ciccarella, G.; Cingolani, R.; De Marco, L.; Gigli, G., Melcarne, G.; Martina, F.; Matteucci, F.; **World Patent N 2009/101640 A1**

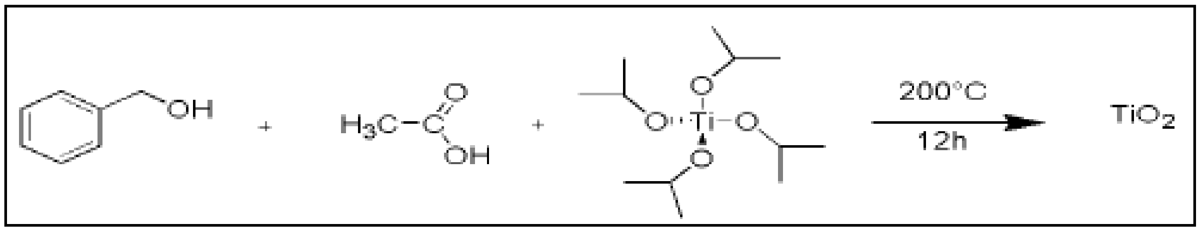
Cozzoli, P. D.; Kornowski, A.; Weller, H. ***J. Am. Chem. Soc.*** **2003**, 125 (47), 14539-1454

Buonsanti R., Grillo V., Carlino E., Giannini C., Kipp T., Cingolani R., Cozzoli, P. D. ***J. Am. Chem. Soci.*, 2008**, 130 (33), 11223-11233

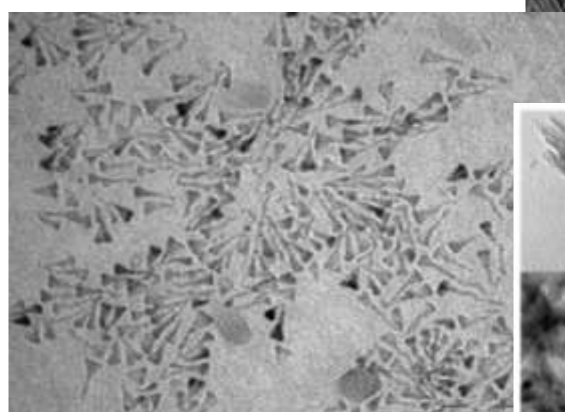
DEVELOPING HIGH EFFICIENT PHOTOELECTRODES

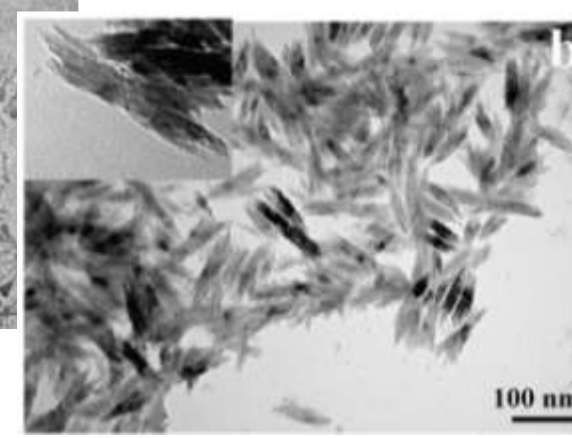
Synthesis of TiO2 nanorods through non hydrolytic approaches

- Besides to the physicochemical properties of titanium dioxide, costs and easy of processing are particularly key issues for industrial production
- It's practically and scientifically significant to explore new large-scale synthetic routes to fine-tuning the properties of nanotitania using simple one-step methods



- **Non hydrolytic route**
- **Surfactant-free synthesis**
- **Crystalline phase : anatase**
- **Low temperature**
- **High yield**





Melcarne G. et al. ***J. Mater. Chem.*, 2010**, 20, 7248

PATENT PCT/IT2008/000082 - ''PROCESS FOR THE PREPARATION OF TITANIUM DIOXIDE WITH NANOMETRIC DIMENSION AND CONTROLLED SHAPE''

Ciccarella G., Cingolani R., De Marco L., Gigli G., Melcarne G., Matteucci F., Spadavecchia J.

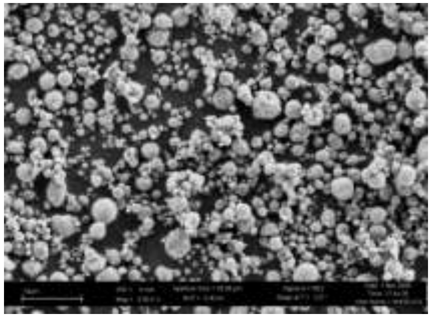
CNRNANO LECCE NNL

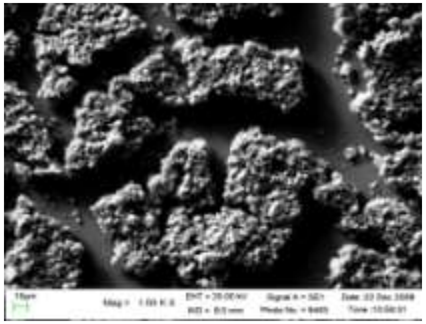
ORGANIC-CAPPED NCs: PASTE FORMULATION

1. calibrated proportion of the surfactant-stabilized hydrophobic NCs, ethyl cellulose and α-terpineol

2. incorporation of oleate-capped NCs in a **“wet” state** into organic template-binding matrix

highly homogeneous paste dispersions and no agglomeration prior to heating

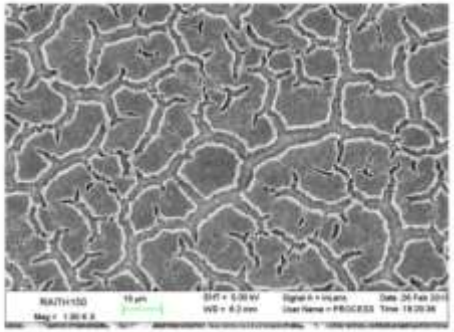


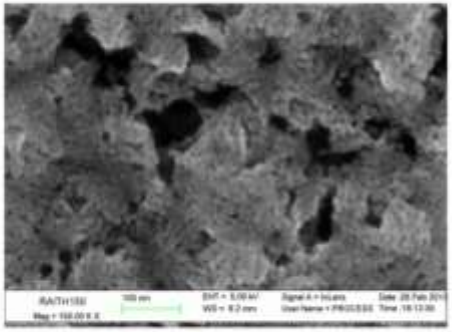


SPRAY DRIED NANOCRYSTALS

3. ethylcellulose dissolved in a **proper carrier solvent** (toluene) compatible with apolar NCs solution;

preparation processes carried out in polar solvents (ethanol) induce coalescence





4. final exchange of the solvent: addition of terpineol (high boiling solvent, more suitable for printable pastes) and removal of toluene by rotary evaporator.

CHEMICAL COMPOSITION:

TiO_2 nanonords 12% wt/wt; synthesis’ organic residuals 15%wt/wt; ethylcellulose 5% wt/wt; terpineol 68% wt/wt

De Marco, L. et al *“Novel preparation method of TiO2-nanorods-based photoelectrodes for dye-sensitized solar cells with improved light harvesting efficiency”*; **J. Phys. Chem. C**, 2010, 114 (9), 4228-4236

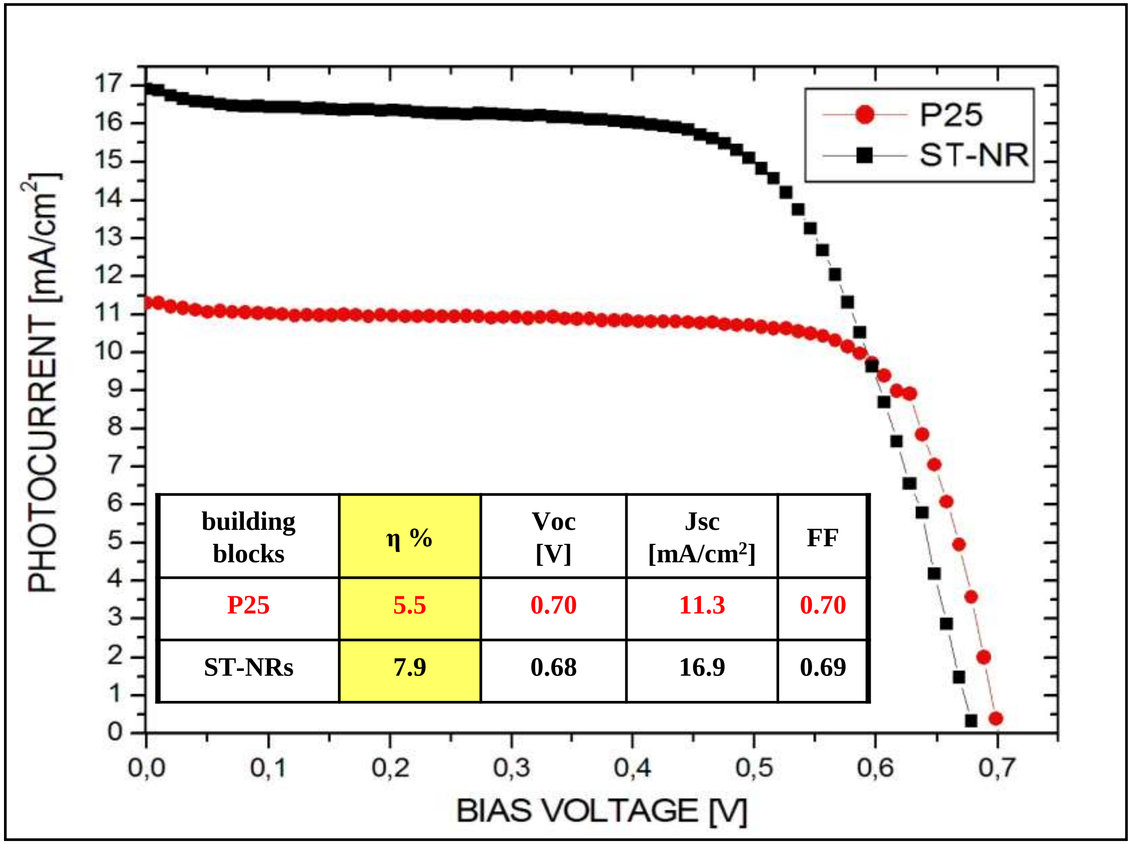
DEVELOPING HIGHLY EFFICIENT PHOTOELECTRODES

Preserving the original morphology of nanorods in the sintered photoelectrode

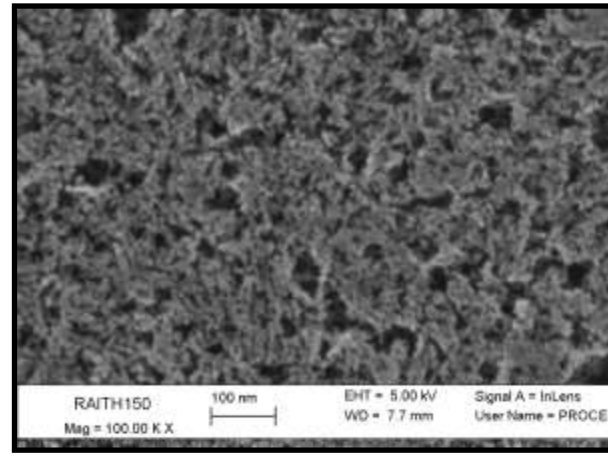
As result of the higher surface area, an higher number of dye molecules is adsorbed onto the TiO_2-nanorod-based photoelectrode:

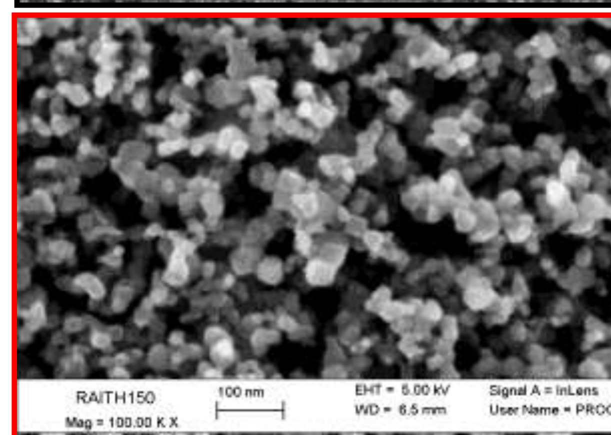
1.45×10^{-7} mol/cm^2 of N719 molecules adsorbed onto the SolvoThermal NanoRods-based film

0.55×10^{-7} mol/cm^2 of N719 molecules adsorbed onto the P25-based film



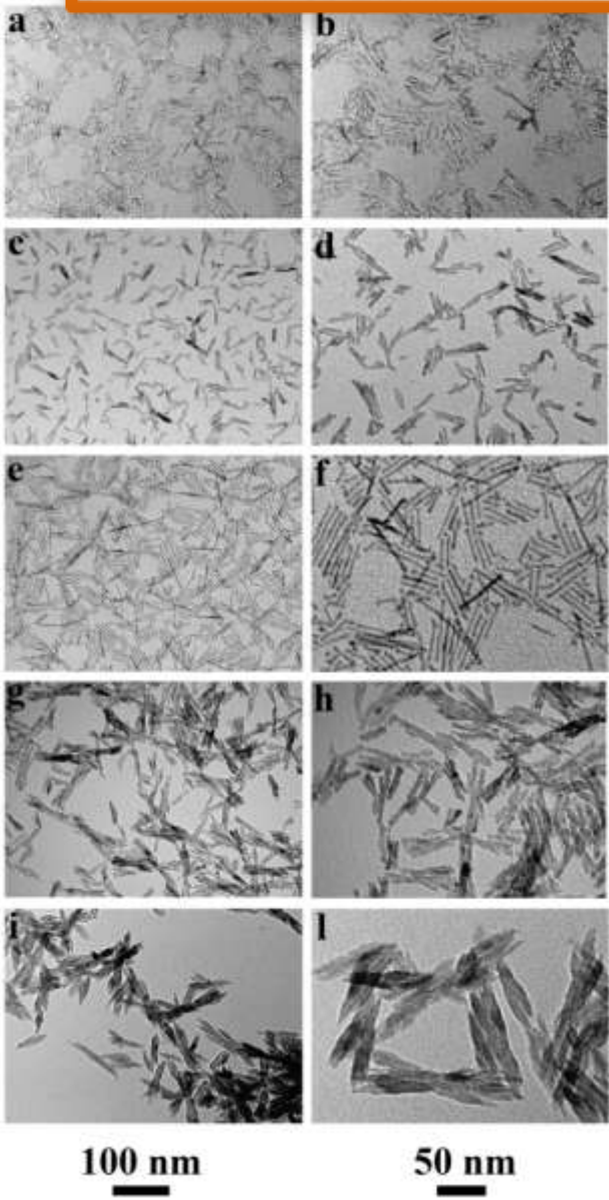
building blocks	η %	Voc [V]	Jsc [mA/cm²]	FF
P25	5.5	0.70	11.3	0.70
ST-NRs	7.9	0.68	16.9	0.69





De Marco L. et al "*Novel preparation method of TiO2-nanorods-based photoelectrodes for dye-sensitized solar cells with improved light harvesting efficiency*" **J. Phys. Chem. C**, 2010, 114 (9), 4228-4236

SYNTHESIS OF TiO_2 NANORODS



AR4: 3 x 12 nm (aspect ratio = 4)
hydrolytic reaction involving titanium tetraisopropoxide and nonanoic acid (100 C - 96 h)

AR8: 5 x 40 nm (aspect ratio = 8)
hydrolytic reaction involving titanium tetraisopropoxide and oleic acid (100 C - 96 h)

AR16: 3 x 50 nm (aspect ratio = 16)
non–hydrolitic approach involving titanium tetraisopropoxide and oleic acid (270 C - 2 h)

NB: 80-100 nm sized branched nanorods
aminolysis reaction involving titanium oleate complexes obtained from $TiCl_4$, oleyl amine and oleic acid (290 C - 1 h)

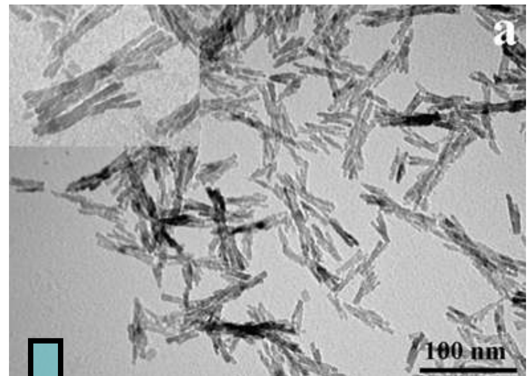
BB: 200 nm sized nano-bundles
obtained from NB nanocrystals by further dropwise alternating injections of $TiCl_4$ and oleic acid (290 C)

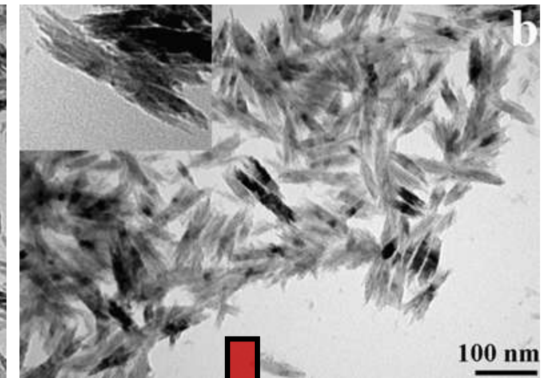
Buonsanti R. et al ***J. Am. Chem. Soc.***, **2008**, 130, 11223

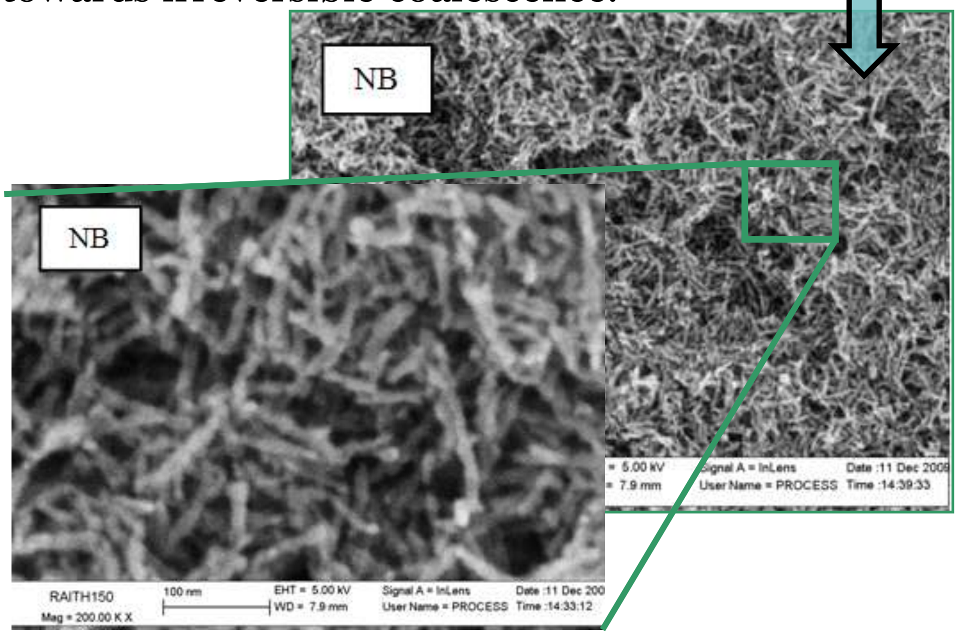
DEVELOPING HIGH EFFICIENT PHOTOELECTRODES

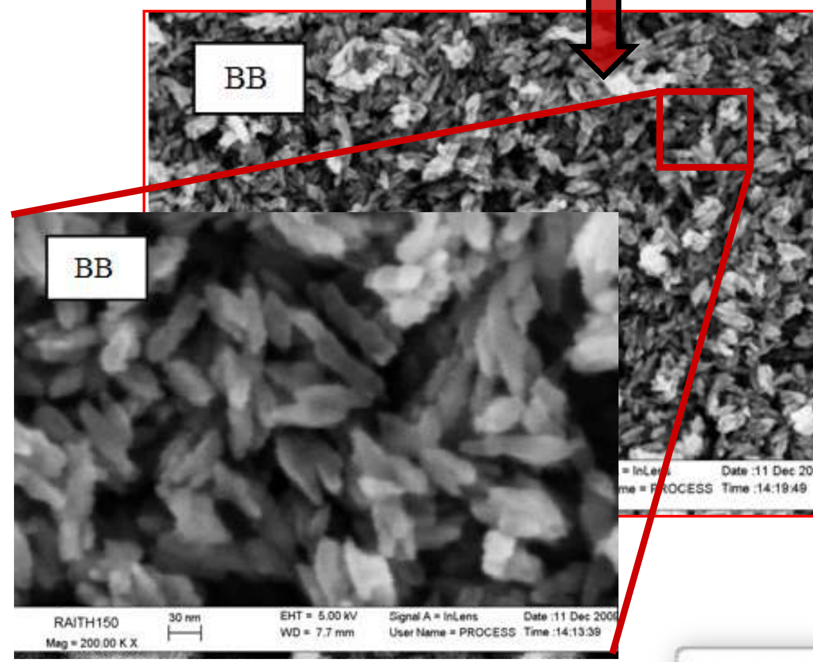
Branched nanocrystals having controlled shape and dimensions

The strong interaction of the organic capping ligands and ethylcellulose resulted in the build-up of a 'soft template' layer on the surface of the nanocrystals, which effectively allowed them to be kept well separated, preventing any tendency towards irreversible coalescence.









FROM TUNABLE SHAPED NCs to ENGINEERED PHOTOELECTRODES

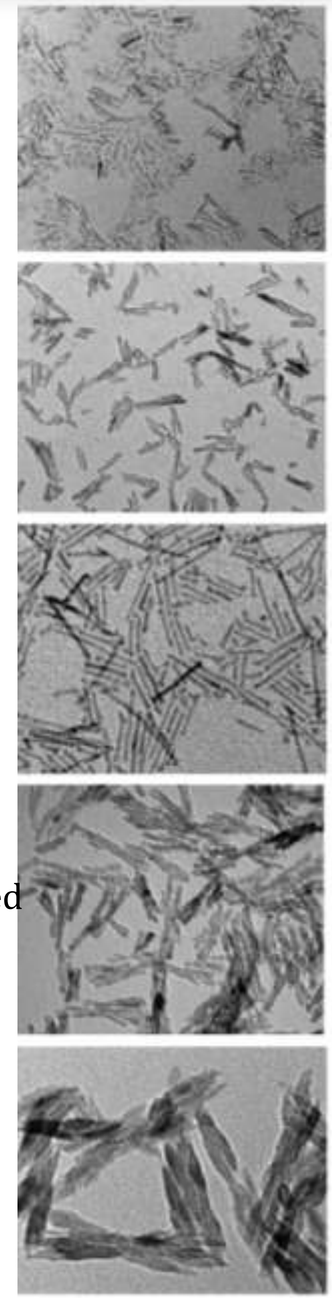
AR4: 3 x 12 nm
(aspect ratio = 4)

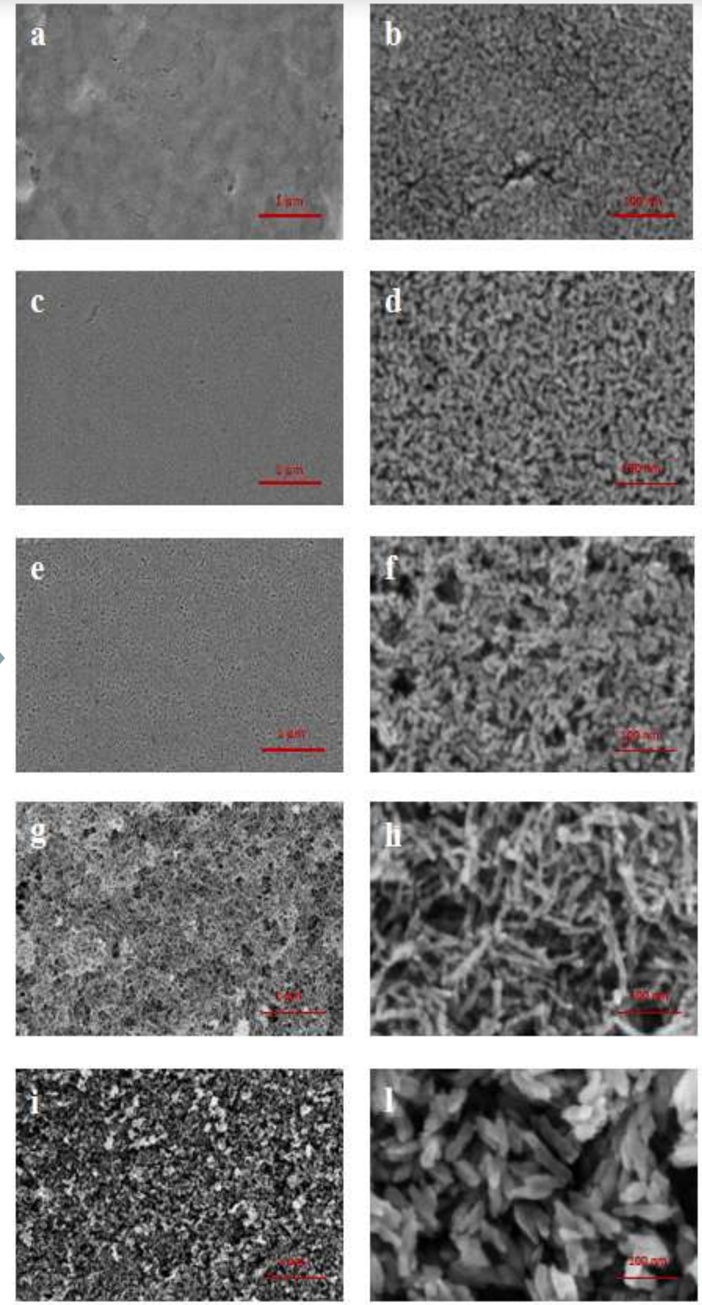
AR8: 5 x 40 nm
(aspect ratio = 8)

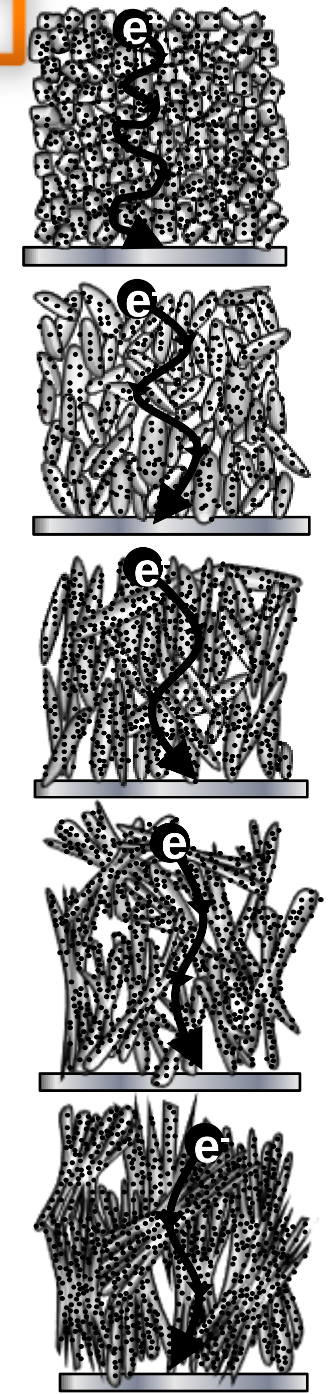
AR16: 3 x 50 nm
(aspect ratio = 16)

NB: 80-100 nm sized
branched nanorods

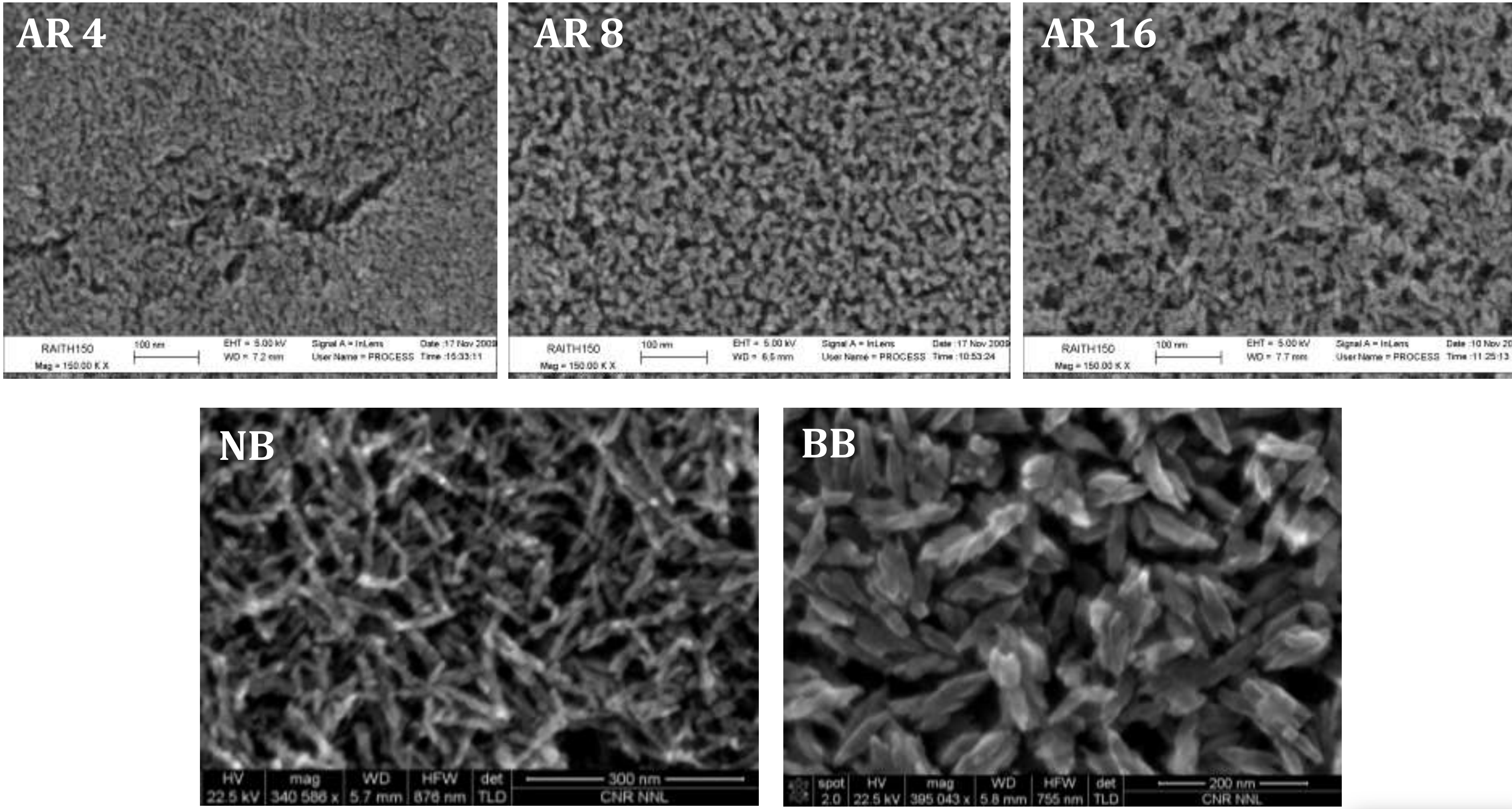
BB: 200 nm sized
nano-bundles





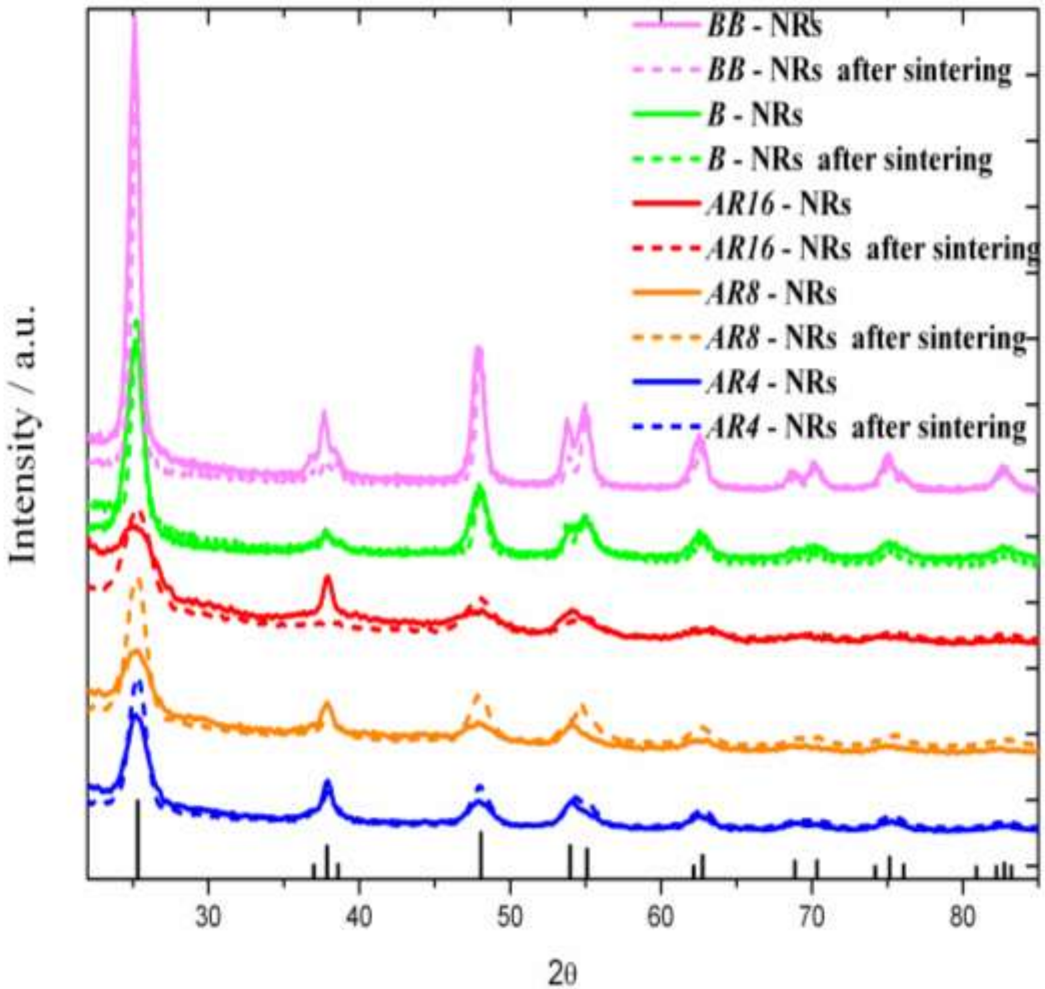


ENGINEERED PHOTOELECTRODES



De Marco L. et al. “*High quality photoelectrodes based on shape-tailored nanocrystals for DSSC*”- submitted to ***J. Mat. Chem***

XRD ANALYSIS



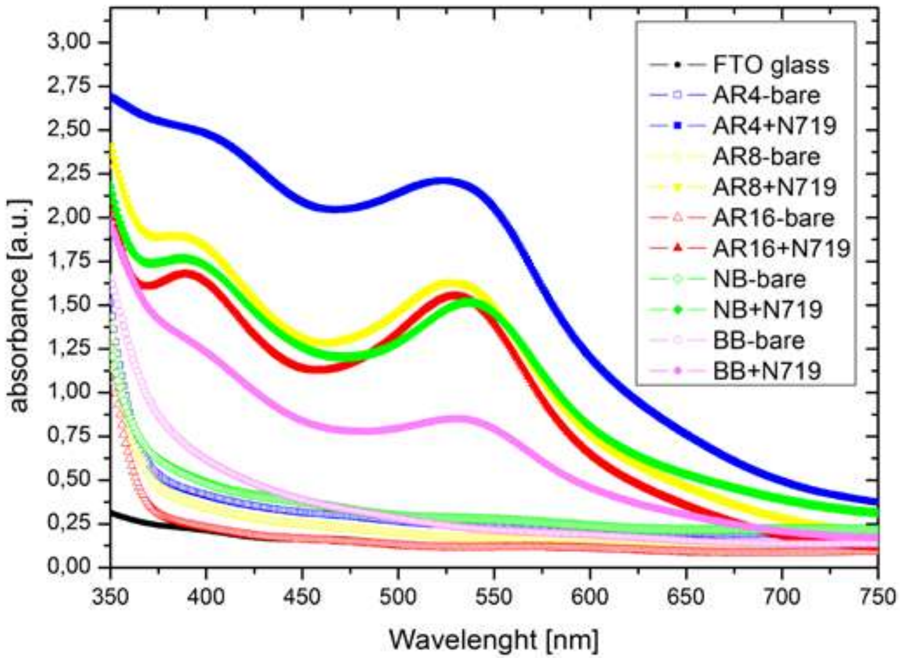
- no phase change occurs upon sintering: the **anatase structure** of the pristine TiO_2 nanocrystals is retained

- oleate-induced surface stabilization in the starting TiO_2 NCs retard their size/shape transformations upon thermal annealing, in contrast to what generally occurs for dry NC powders or uncapped NCs

- the minor narrowing of the reflection widths and small attenuation in the shape anisotropy signature, which emerge after the thermal treatment, arise from the combined effects of <u>slight domain growth</u> and <u>increased degree of crystallinity</u>

De Marco L. et al. "*High quality photoelectrodes based on shape-tailored nanocrystals for DSSC*"- submitted to ***J. Mat. Chem***

DYE-LOADING CAPABILITY



NRs	DYE LOADING (mol/cm^2)
AR4	2.16 x 10^{-7}
AR8	1.61 x 10^{-7}
AR16	1.47 x 10^{-7}
NB	1.46 x 10^{-7}
BB	0.96 x 10^{-7}

P25	0.66 x 10^{-7}
NPs	1.63 x 10^{-7}

✓Dye absorption decreases with the increasing of the nanocrystals mean size

✓Branched nanorods in spite of their bigger size maintained good light harvesting capability:

- 100 nm sized branched nanorods showed nearly the same dye loading of the 3 x 50 nm sized AR16 nanorods (NBs represent a pre-sintering assembly of smaller nanorods)

- 200 nm sized branched nanorods showed better dye loading capability in comparison to P25 (25-50 nm sized) conventional nanoparticles

De Marco L. et al. "*High quality photoelectrodes based on shape-tailored nanocrystals for DSSC*"- submitted to ***J. Mat. Chem***

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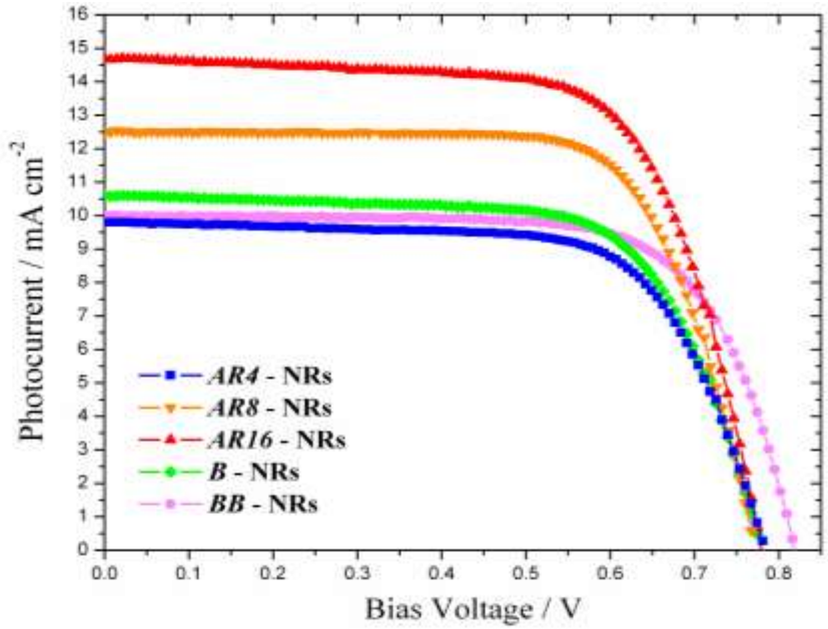
PHOTOVOLTAIC PERFORMANCES

Sample	η %	Voc [V]	Jsc [mA/cm^2]	FF
***AR4*-NRs**	**5.2**	0.77	9.8	0.69
***AR8*-NRs**	**6.7**	0.77	12.5	0.70
***AR16*-NRs**	**7.8**	0.78	14.7	0.68
***B*-NRs**	**5.8**	0.78	10.2	0.73
***BB*-NRs**	**5.7**	0.82	9.7	0.72
P25	**4.2**	0.71	8.5	0.70
***s*-NCs**	**5.1**	0.76	9.7	0.70



AR4, AR8, AR16: trend in photocurrent density is just opposite to the trend observed for dye absorption capability

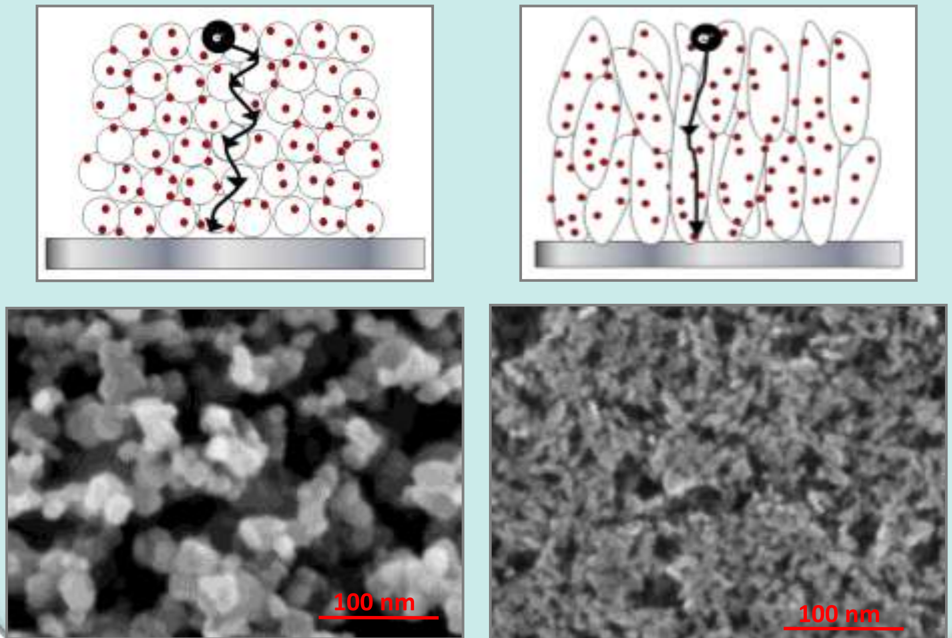
B: in spite they showed a good dye-loading capability furnished dramatically lower values of photocurrent density

BB: relatively high photocurrent density taking into account their reduced amount of adsorbed dye molecules; showed also the highest VOC value (reduced number of charge-recombination sites)

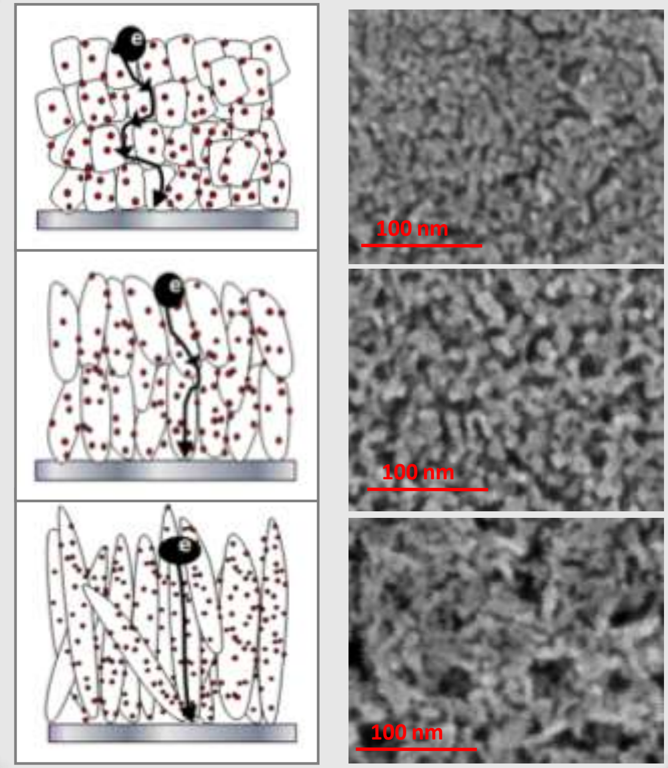
De Marco L. et al. "*High quality photoelectrodes based on shape-tailored nanocrystals for DSSC*"- submitted to ***J. Mat. Chem***

EXPLOITING DIFFERENT SHAPE TAILORED NANO-OXIDES

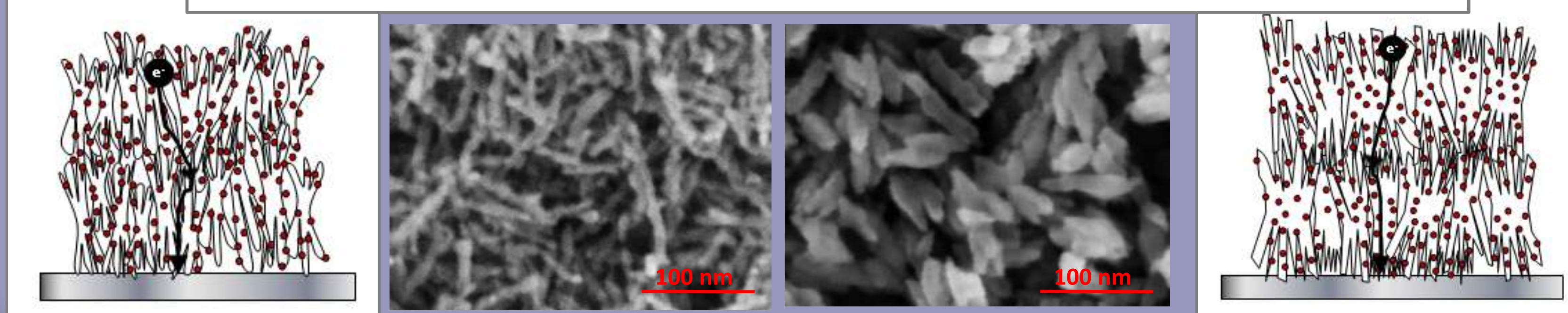
IMPROVING THE CHARGE COLLECTION EFFICIENCY



TUNING THE NANORODS ASPECT RATIO

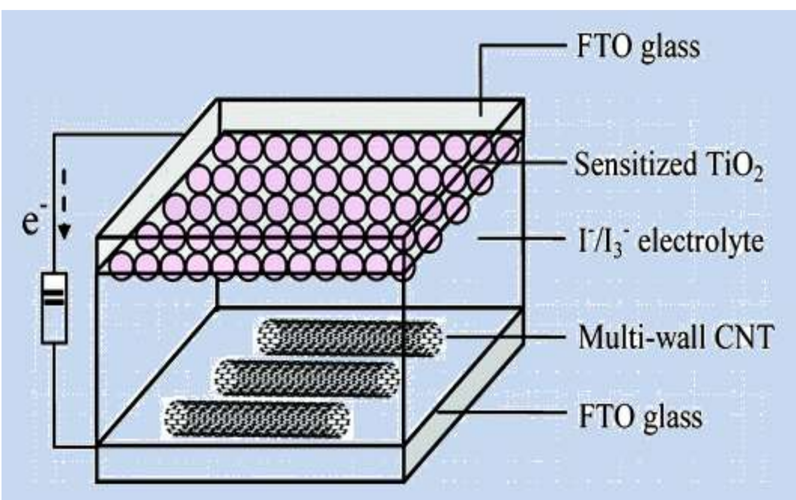


BALANCING LARGE SURFACE AREA & GOOD ELECTRON TRANSPORT

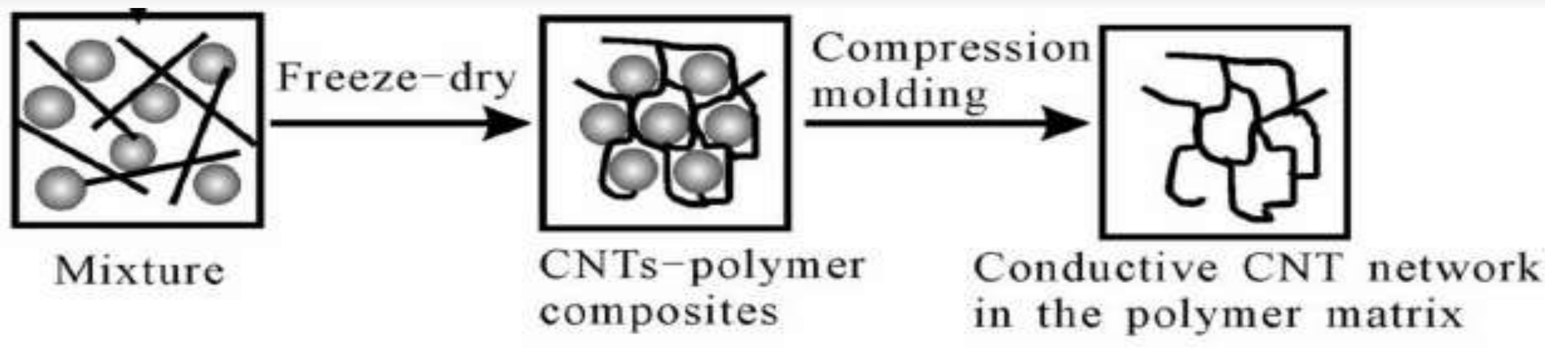


KEY COMPONENT #2 :COUNTER ELECTRODE

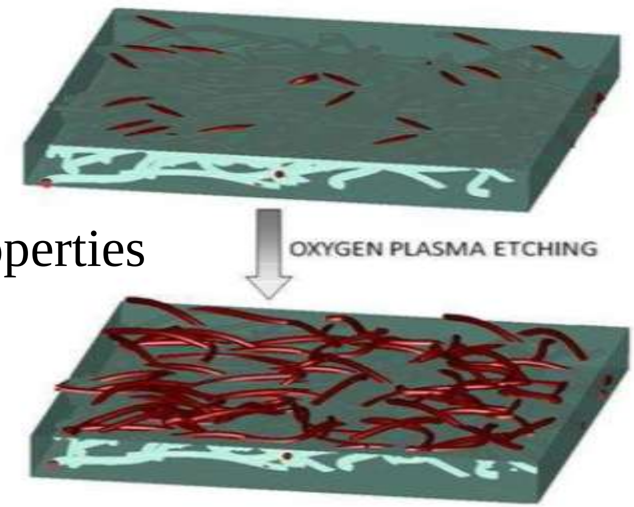
- Transparent Conductive Glass and Platinum represent to date more than 80% of the cost of a Dye Solar Cell
- Flexible DSCs are generally realized onto indium tin oxide (ITO)-coated polymeric plates (mainly PEN and PET). But ITO's rigid inorganic crystal structure develops hairline fractures upon bending, which are quite detrimental to the overall electrical performance
- We have thus been focusing on the development of carbon-nanotubes(CNTs)/polymeric composite materials to be used as effective electrocatalysts instead of Platinum.



CNTs-based flexible counterelectrodes

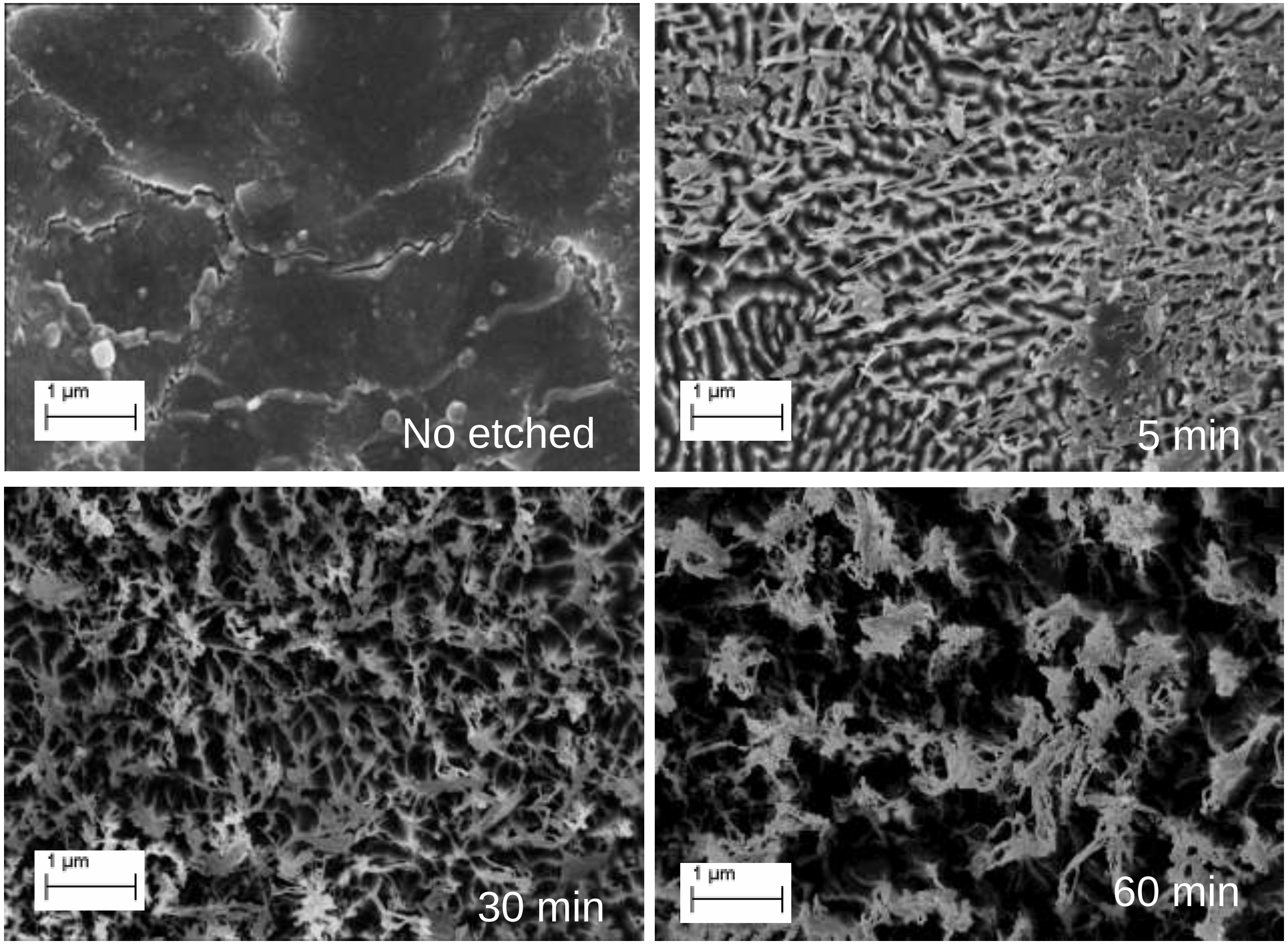


- development of CNTs-based nanocomposite materials:
  - mixing materials and additives in a proper solvent
  - casting and molding
- effect of CNTs concentration and dispersion
- tuning the mechanical and electrical properties
- surface treatments for the tuning of electrocatalitic properties



Malara et al. *"Flexible MWCNTs-based nanocomposite plates as efficient monolithic counter-electrodes for DSSCs"*- submitted to **Journal of Materials Chemistry**

CNTs-based flexible counterelectrodes



Top surface of the plates has been etched by oxygen plasma with the aim to remove the polymer capping layer and allows CNTs to partially merge from the matrix. Tuning of the morphological features was possible by adjusting the parameters affecting plasma treatment conditions.

Etching conditions:

- **Power : 150W**
- **Oxigen flow : 20 sccm**
- **Pressure : 30 mTorr**

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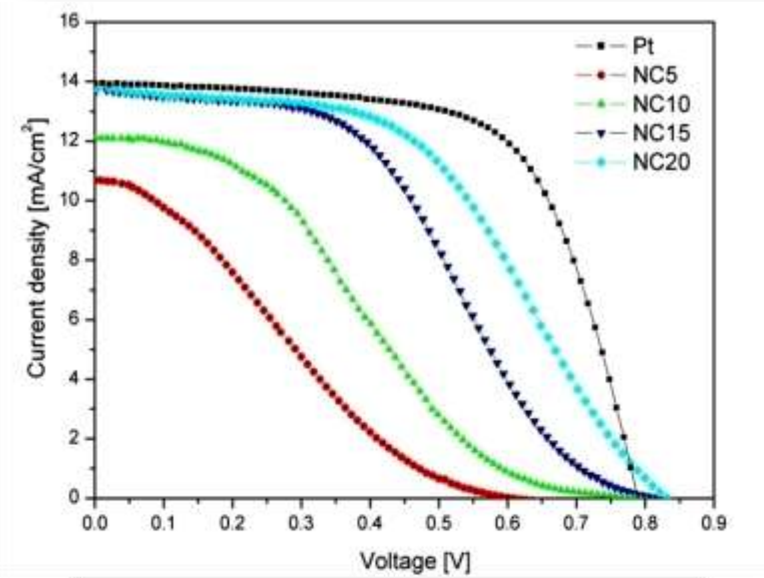
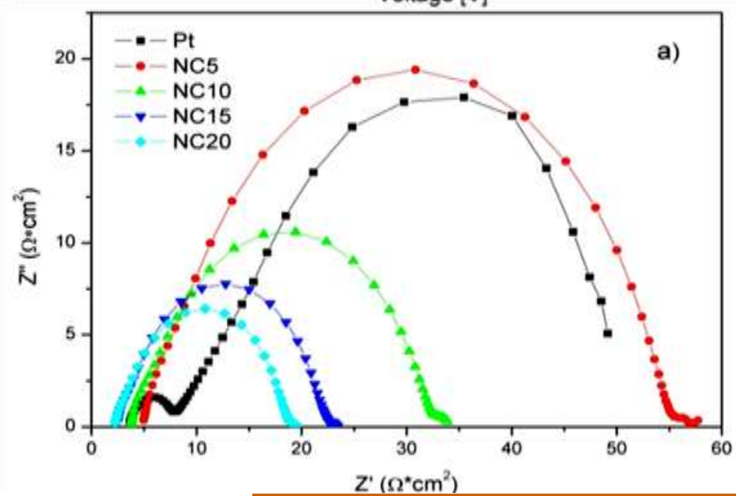
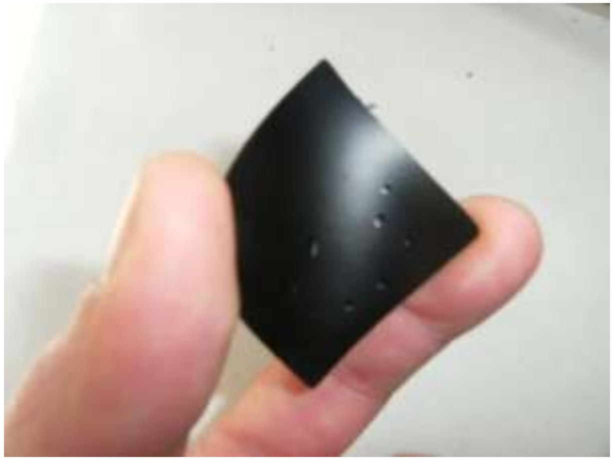
CNTs-based flexible counterelectrodes



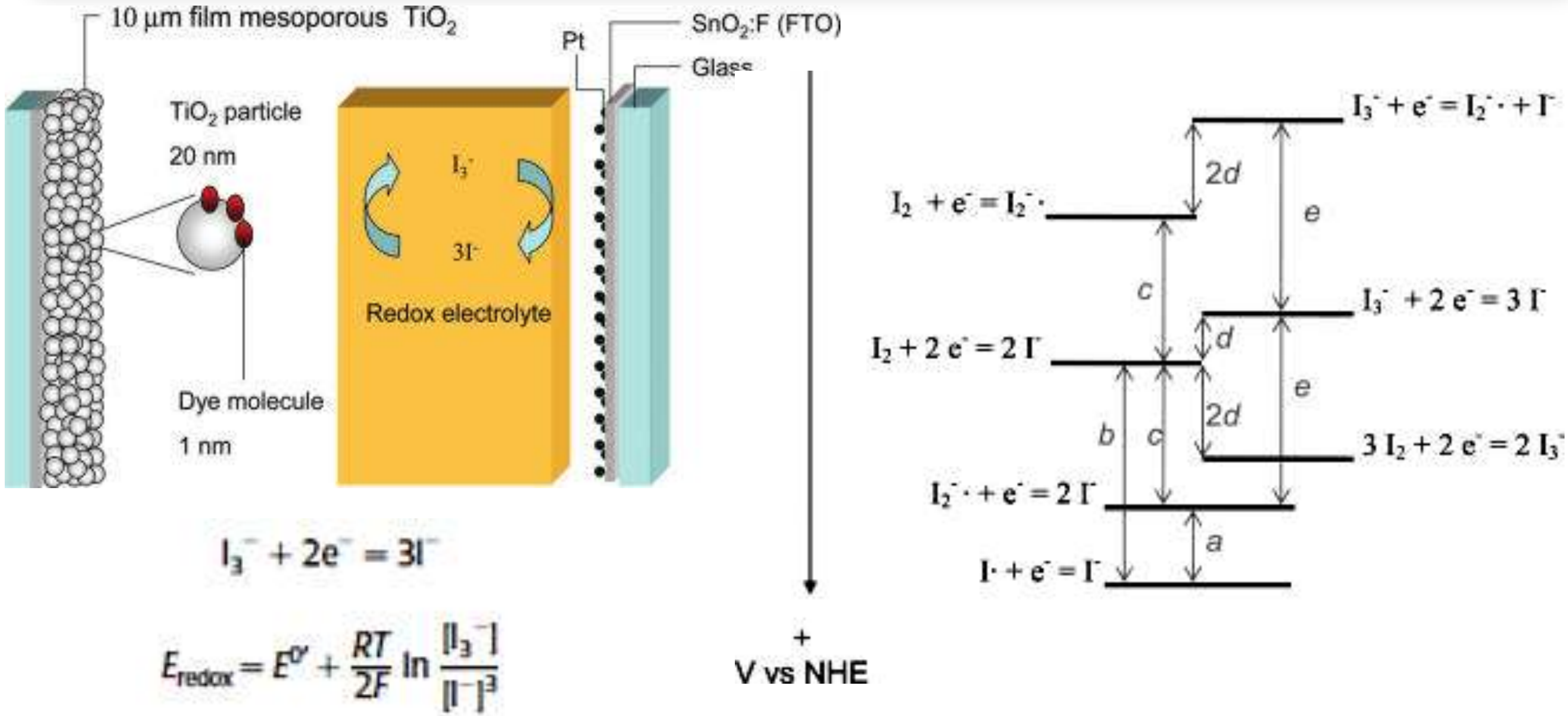
CE	FF	Voc [V]	Jsc [mA/cm^2]	η [%]
Pt reference	0.71	0.78	13.95	7.72
NC5	0.37	0.64	10.80	2.55
NC10	0.37	0.79	12.05	3.52
NC15	0.52	0.80	13.55	5.63
NC20	**0.59**	**0.82**	**13.80**	**6.67**





Malara et al. *"Flexible MWCNTs-based nanocomposite plates as efficient monolithic counter-electrodes for DSSCs"*- submitted to **Journal of Materials Chemistry**

KEY COMPONENT #3 : ELECTROLYTE



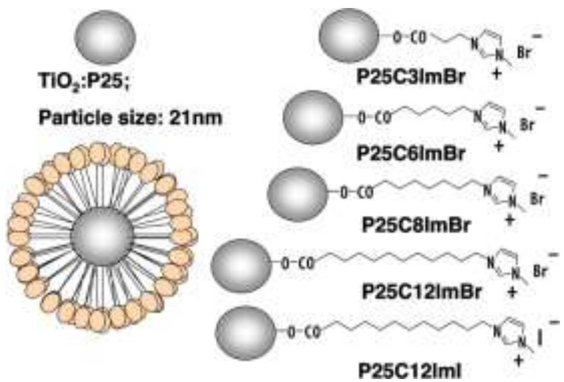
✓The reduced part of the couple regenerates the photo-oxidized dye.

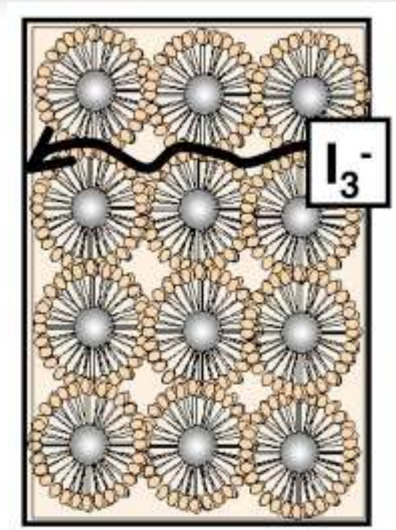
✓The formed oxidized species diffuses to the counter electrode, where it is reduced.

✓The photovoltage of the device depends on the redox couple because it sets the electrochemical potential at the counter electrode.

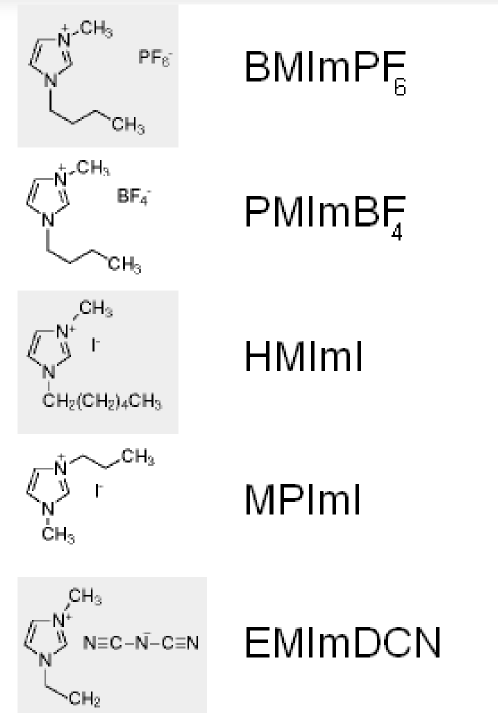
✓The redox couple also affects the electrochemical potential of the TiO2 electrode

QUASI-SOLID ELECTROLYTES

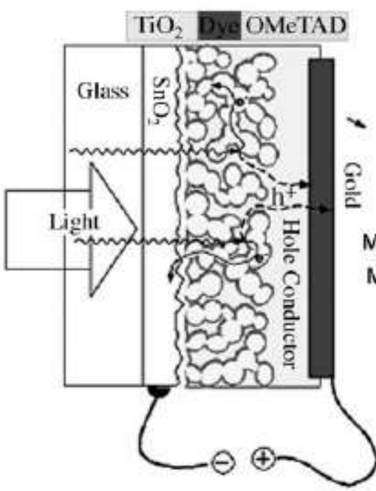


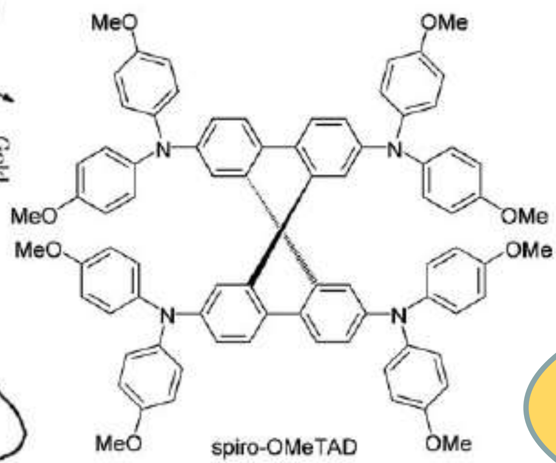


1) Functionalized NPs



2) Ionic Liquids



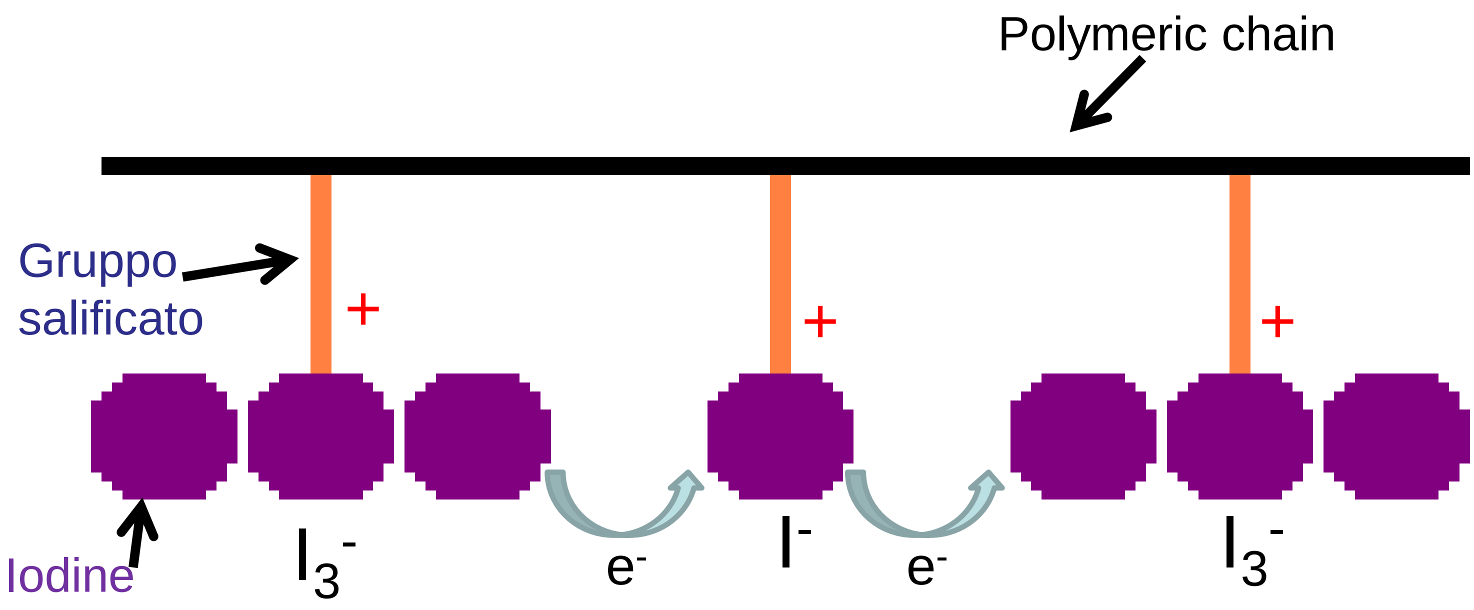


3) Molecular hole conducting layer

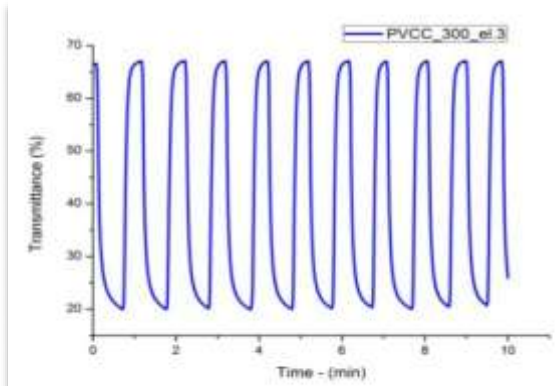
LONG TERM PERFORMANCES ARE STRONGLY AFFECTED BY SOLVENT VOLATILIZATION AND ELECTROLYTE LEAKAGE

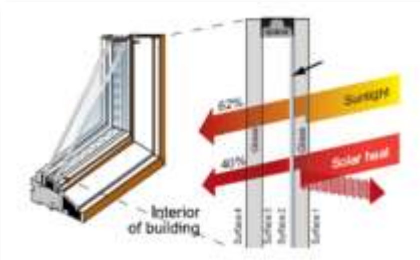
Poly(methacrylic)-based gel electrolytes

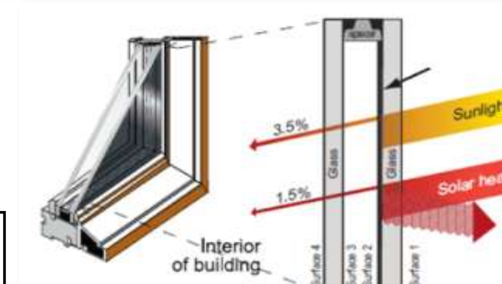
•Gelification of electrolyte increase the viscosity of the solution, lowering the performances.
•To came over this effect, quaternarizable nitrogen groups have been inserted in polymer chain to promote hopping (Grotthuss) charge transfer diffusion.

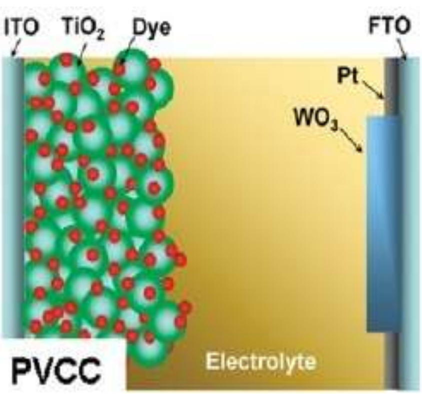


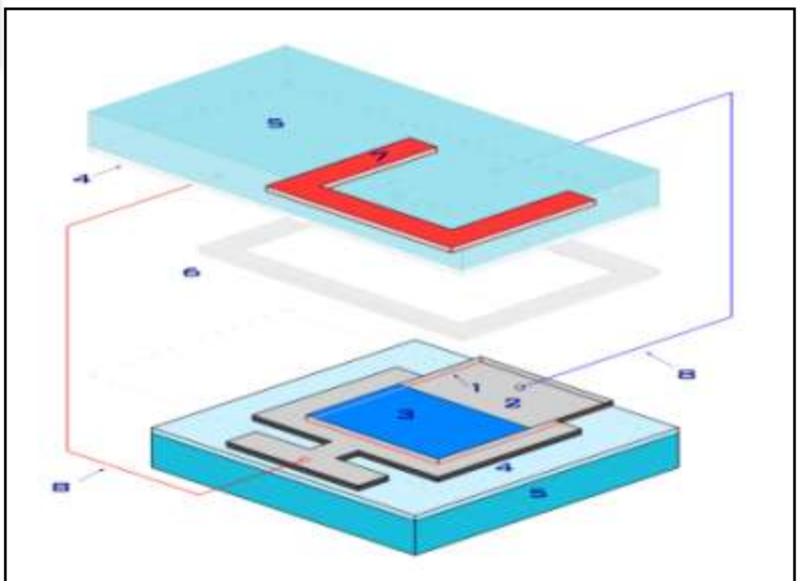
PHOTOVOLTACHROMIC DEVICES
towards smart multifunctional windows







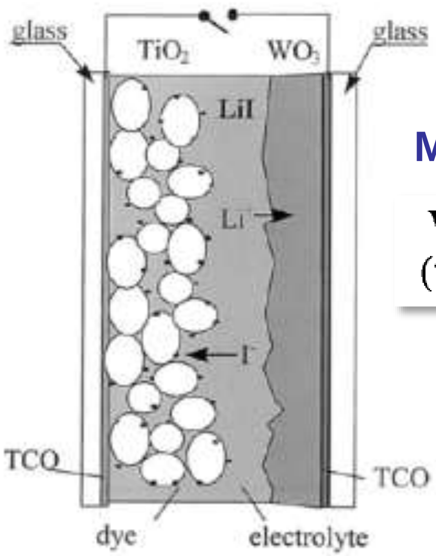




Photoelectrochromic cells (PECCs)

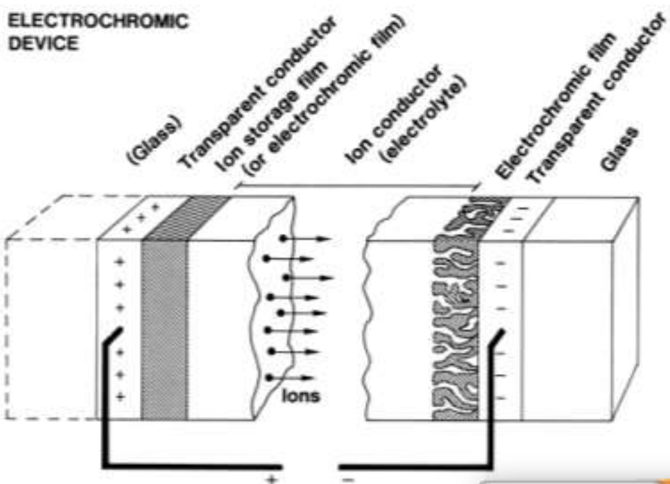
Photoelectrochromic cells (PEECs) are devices capable of a smart modulation of their optical transmittance depending on the available amount of daylighting.

- Don't require energy supply to operate, differently from common electrochromic devices
- Can be colored in short circuit condition if exposed to light
- Can be bleach in open circuit conditions or if short-circuited in dark
- Their architecture is very similar to that of DSCs but a layer of an electrochromic material is deposited on the counter electrode, typically tungsten oxide (WO_3)



Mechanisms of coloring/bleaching

$$\underset{\text{(transparent)}}{WO_3} + x(Li^+ + e^-) \rightarrow \underset{\text{(blue)}}{Li_xW^{VI}_{(1-x)}W^{V}_{x}O_3}$$



Photoelectrochromic windows and displays - Bechinger et al. ***Nature* 383, 608 - 610 (1996)**

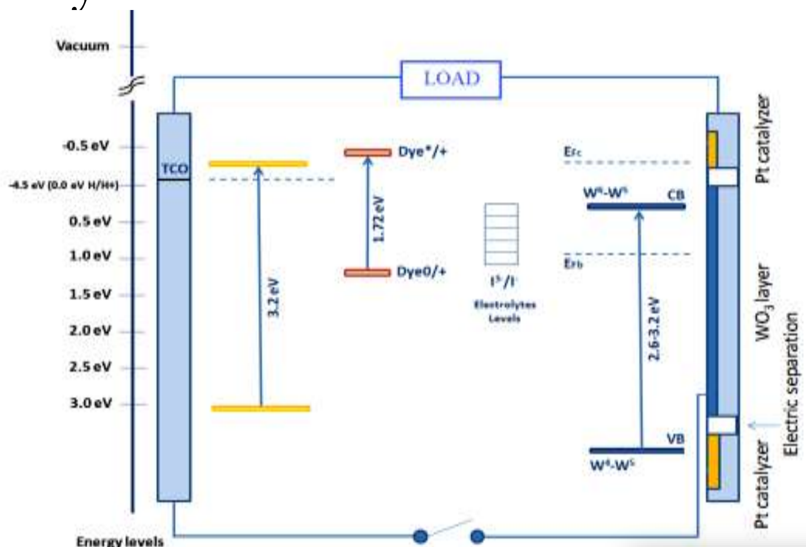
Novel smart architectures: photovoltachromic devices (PVCCs)

A specifically designed bifunctional counterelectrode has been realized by depositing a C-shaped platinum frame which bounds a square region occupied by a tungsten oxide (WO_3) film onto a transparent conductive substrate.

These two regions have been electrically separated to make possible distinct operations on one or both of the available circuits.

Such an unconventional counterelectrode made it possible to achieve a twofold outcome: a smart and fast-responsive control of the optical transparency and a relatively high photovoltaic conversion efficiency

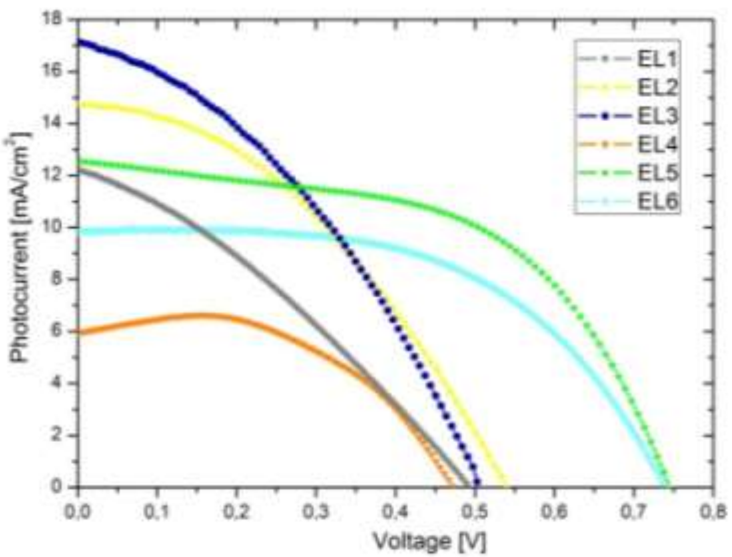
Electrolyte	LiI [M]	I_2 [M]	Solvent
El1	0.7	0.05	Acetonitrile
El2	0.7	0.025	Acetonitrile
El3	0.7	0.005	Acetonitrile
El4	0.7	0.0025	Acetonitrile
El5	0.7	0.005 + TBP	Acetonitrile
El6	0.7	0.005 + TBP + GNTC	Acetonitrile



Cannavale et al. *"Highly efficient smart photovoltachromic devices with tailored electrolyte composition"*- **Energy Environ. Sci.**, 2011, DOI: 10.1039/C1EE01231B

PVCCs performances

Electrolyte	$[I_2]$ M	[LiI] M	Additives M	Jsc [mA/cm²]	Voc [V]	FF	η [%]	WO_3 state Ble/Col
EL 1	0.05	0.7	-	12.1	0.49	0.55	**3.26**	Col
EL 2	0.025	0.7	-	14.8	0.54	0.60	**4.79**	Col
EL 3	0.005	0.7	-	17.2	0.51	0.58	**5.00**	Col
EL 4	0.0025	0.7	-	6.0	0.47	0.69	**1.94**	Col
EL 5	0.005	0.7	4-TBP / 0.5	12.3	0.74	0.72	**6.55**	Col
EL 6	0.005	0.7	4-TBP / 0.5 GNDT / 0.1	9.9	0.73	0.75	**5.42**	Col



Cannavale et al. *"Highly efficient smart photovoltachromic devices with tailored electrolyte composition"*- **Energy Environ. Sci.**, 2011, DOI: 10.1039/C1EE01231B

DYE SOLAR GROUP in LECCE

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Roberto Giannuzzi (electrical & electrochemical modeling)

Francesco Malara (alternative carbon-based counter electrodes)

Alessandro Cannavale (smart photovoltachromic devices)

Gianluca De Gregorio (synthesis of gel electrolytes)

Rita Agosta (novel device architectures)

Angela Scrascia (synthesis of organic dyes)

Giuseppe Ciccarella (molecular design)

Francesca Martina (technology transfer)

Prof. Giuseppe Gigli (scientific coordinator)

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