Tailoring the photoactivity of TiO_2-based materials by playing with morphology and electronic structure

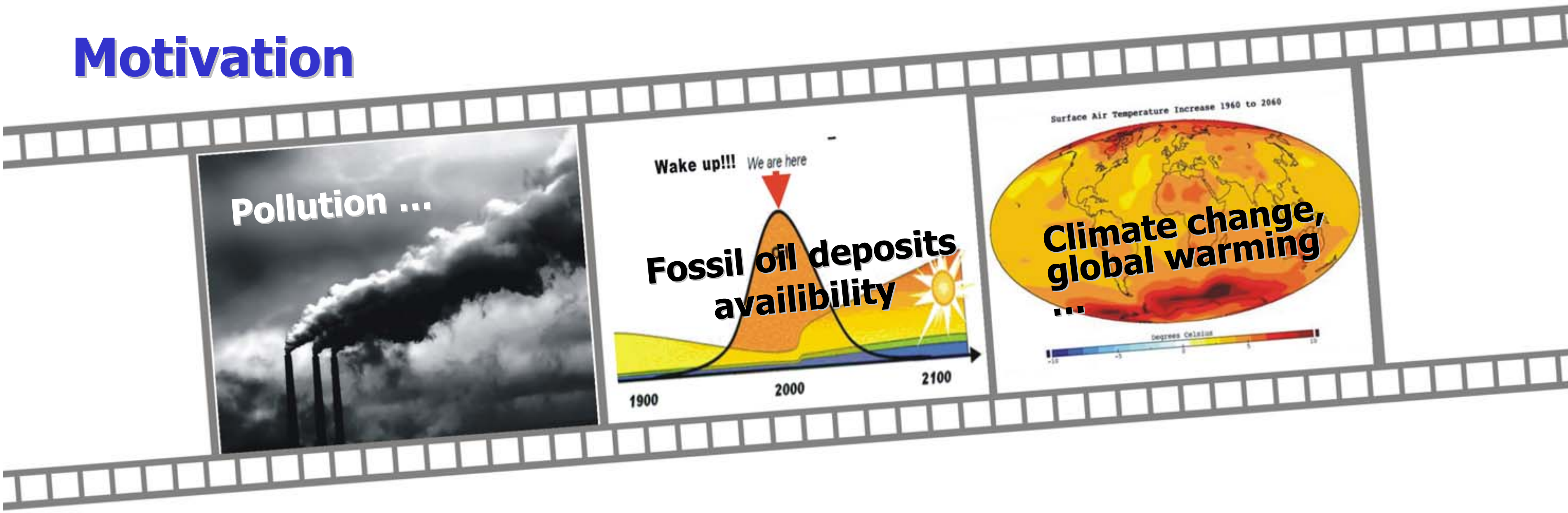
Federico Cesano

Dept. of Inorganic, Physical and Materials Chemistry IFM
NIS (Nanostructured Interfaces and Surfaces) Centre of Excellence,
University of Torino

23 June, 2008

Classical and new approaches to thin film photovoltaics- NIS Colloquium

Motivation



Among possible strategies to limit these drawbacks:
use of semiconductor TiO_2 materials

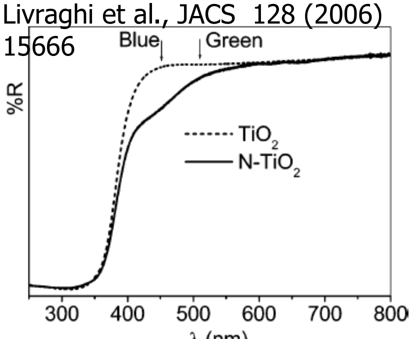
Photocatalysis

high surface area materials, doping,
dyes encapsulation, ...

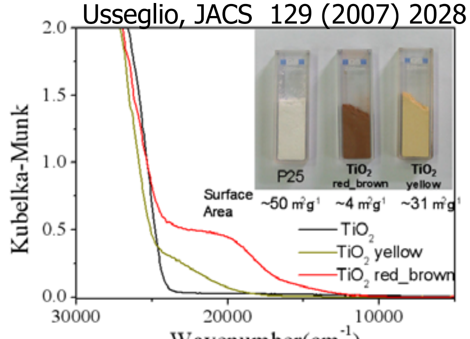
Green energy production, H_2 economy (DSSCs, water splitting)

nanoarchitectures ...

Livraghi et al., JACS 128 (2006) 15666



Usseglio, JACS 129 (2007) 2028

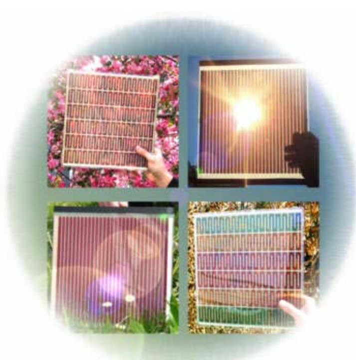


✓ Large-scale use of photovoltaic devices for electricity generation:

> **"0.1% of the heart's surface, if coated with solar cells with efficiency ~10%, would satisfy our present energy requirements"** **M. Gratzel**

This technology needs:

-cost reduction,
-increase of the solar-cells efficiency



Costs:	DSSCs	<<<<	Si	<<<	GaAs
Energy Conversion Efficiencies:	DSSCs	<	Si	<<	GaAs
	~8-10%		8-15%		~20%

DSSCs are working also in low-light conditions, they can be used indoor and in a very claudy sky

DSSCs: what they are

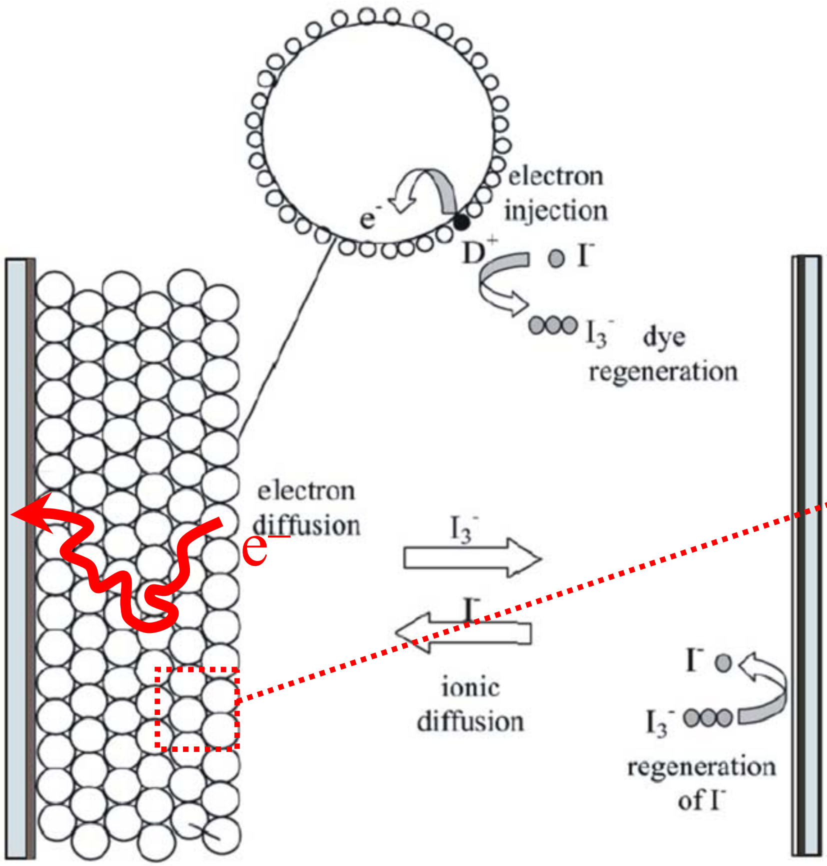


Fig. 3 Summary of the processes taking place during the regenerative cycle in the dye-sensitized cell.

PCCP 9 (2007) 2630

M. Gratzel, Nature 2001

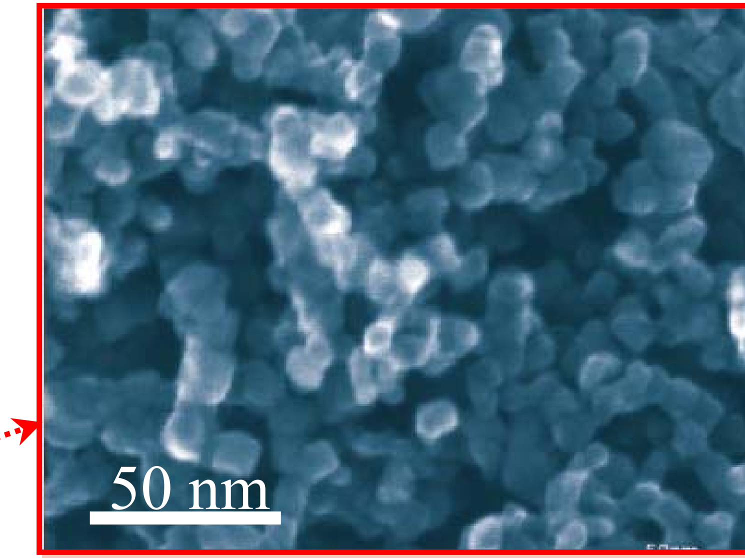


Figure 4 Scanning electron micrograph of the surface of a mesoporous anatase film prepared from a hydrothermally processed TiO_2 colloid. The exposed surface planes have mainly {101} orientation.

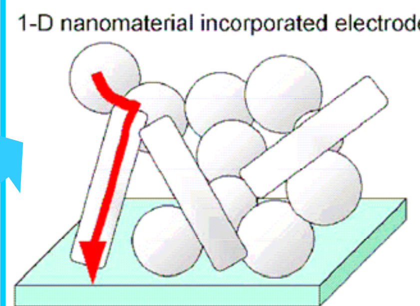
Working life: 10^8 turnover cycles (20 years)

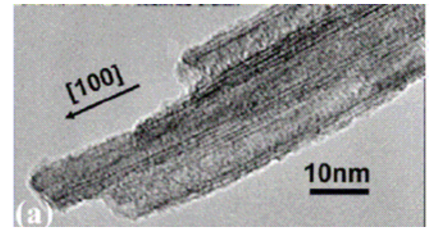
$\eta_{max.} \sim$ 10-11% (AM1.5 illumination = 1000 W/m^2 *

*(equator mean solar irradiance)

Charge collection is considered a limiting factor in performance!

New strategies to increase the efficiency: TiO_2 nanotubes and pillars

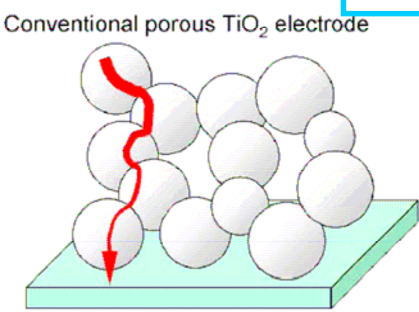




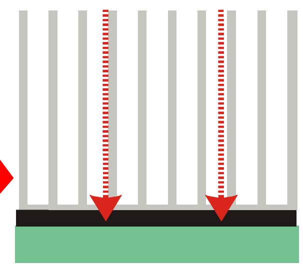
Rolling –up of TiO_2 sheet is promoted

Hydrothermal methods

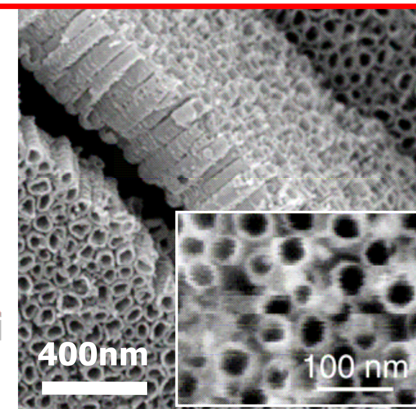
Zhang Appl. Phys Lett 82 (2003) 281



Suzuki, Centr. Eur. J. Chem. 4(3) 2006 476



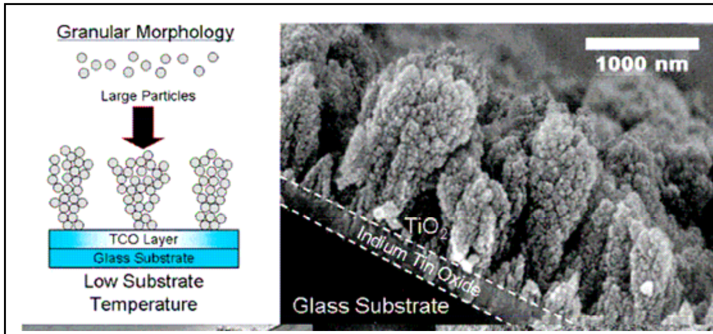
Anodization of Ti films or foils



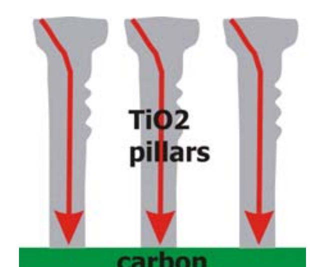
Gopal, Nano Letters 6 (2006) 215

Zhu, Nano Letters 7 (2007) 69

Columnar TiO_2 structures protruding from a conductive support



Thimsen, J. Phys. Chem. C 112, (2008) 4134



Outline

Bundles of TiO_2 elongated Nanoarchitectures

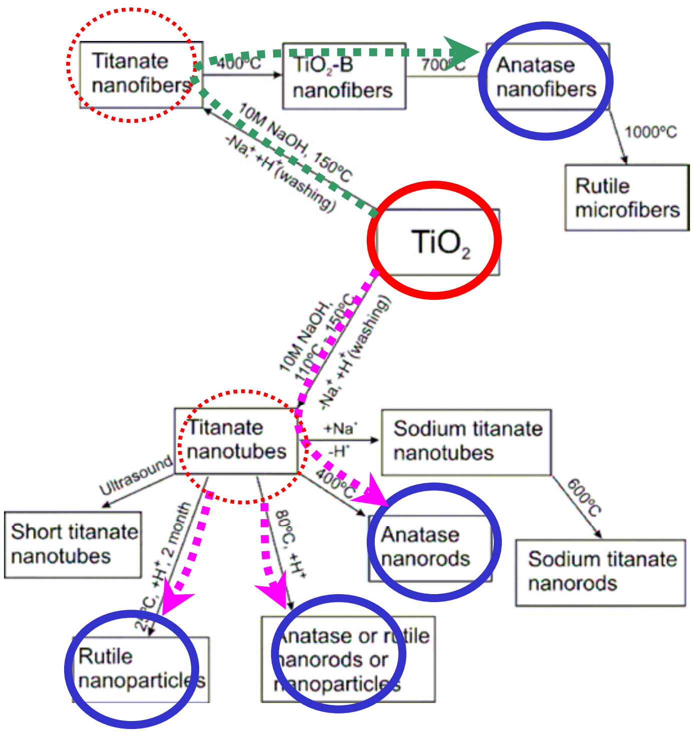
- TiO_2-nanostructures by means of hydrothermal methods via-titanate conversion;

Ordered arrays of TiO_2 nanotubes, rods and pillars

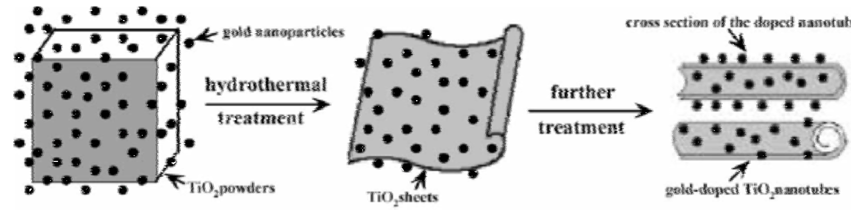
- TiO_2 nanotubes by means of anodization of Ti films and foils,
- TiO_2 granular/columnar arrays via flame aerosol synthesis,
- TiO_2 pillars via a controlled oxidation of carbon-based composites

Hydrothermal synthesis

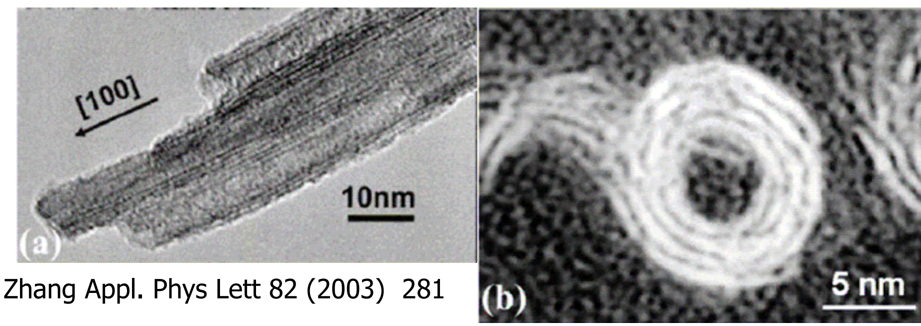
TiO_2-based nanostructures from TiO_2 and NaOH at ~110-180°C



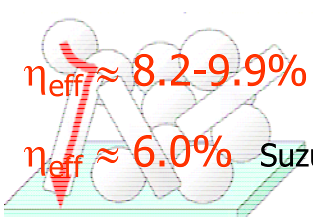
Bavykin et al. Adv. Mater. 18 (2006) 2807



Zhu et al. Mat. Res. Bull. 41 (2006) 1097



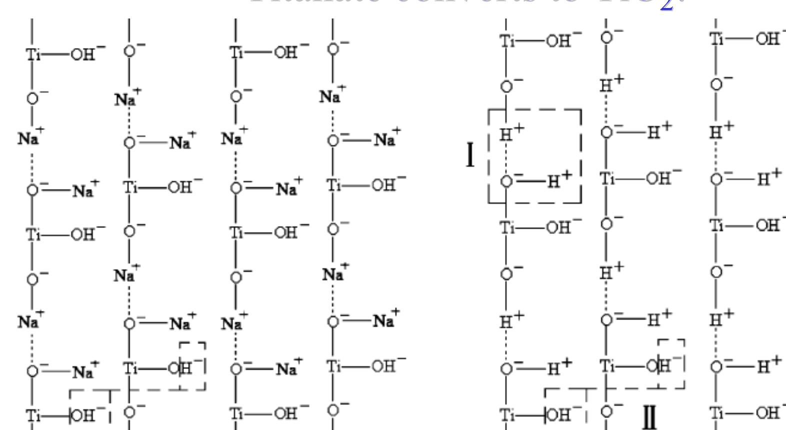
Zhang Appl. Phys Lett 82 (2003) 281



$\eta_{eff} \approx$ 8.2-9.9% Hsiao, J Photochem. Photob. A 188 (2007) 19

$\eta_{eff} \approx$ 6.0% Suzuki, Cent. Eur. J. Chem. 4 (2006) 476

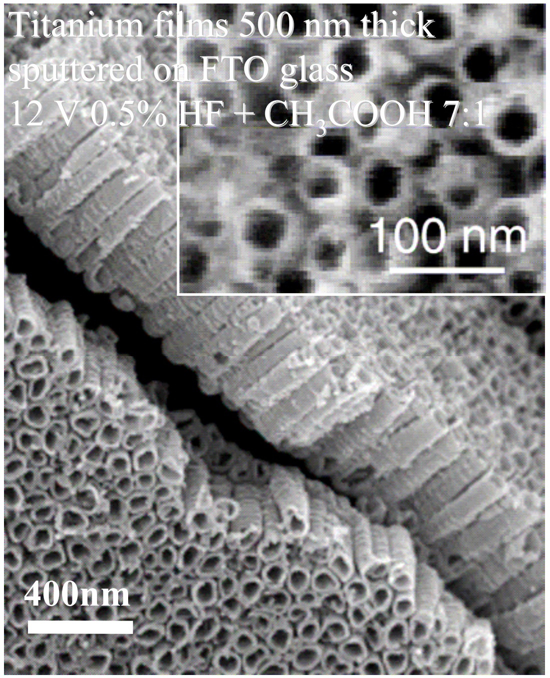
Titanate converts to TiO_2:



Zhang et al., J. Mol. Cat. A: Chem. 217 (2004) 203

Anodization of Ti films/foils

Ti film

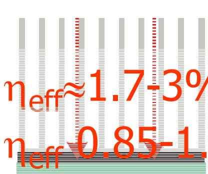


Gopal, Nano Letters 6 (2006) 215

Zhu, Nano Letters 7 (2007) 69

The as obtained TiO_2 oxide film is amorphous

and should be thermal treated to increase the cristallinity

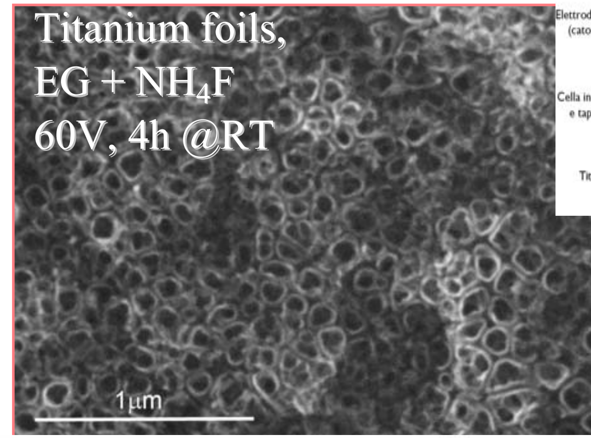


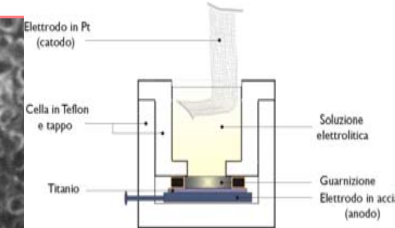
$\eta_{eff} \approx 1.7\text{-}3\%$ Zhu, Nano Letters 7 (2007) 69

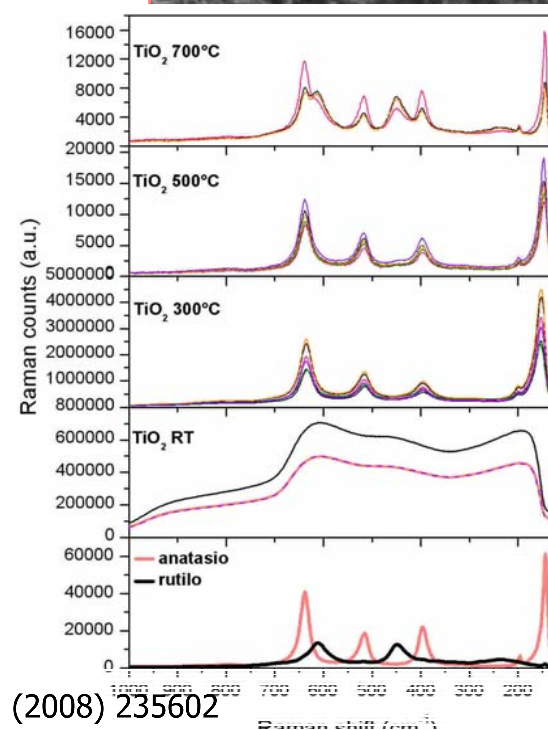
η_{eff} 0.85-1.65% Stergiopoulos, Nanotechnology 19 (2008) 235602

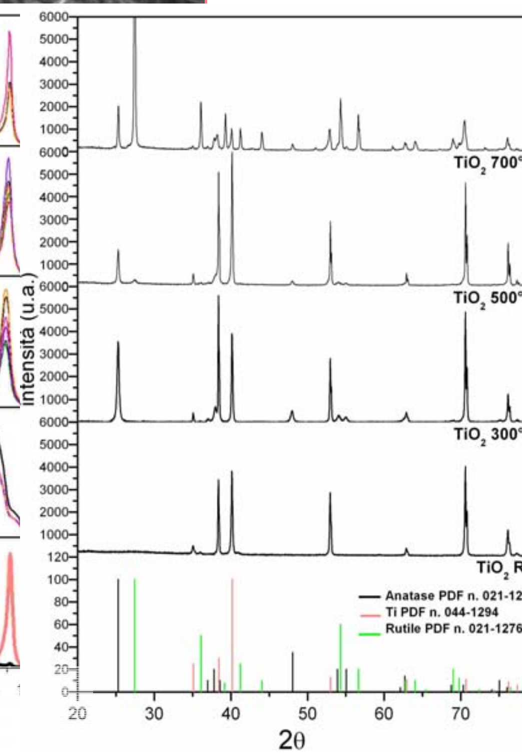
Ti foil

By courtesy of Centro Ricerche Fiat and of Dr. E. Bortolotti

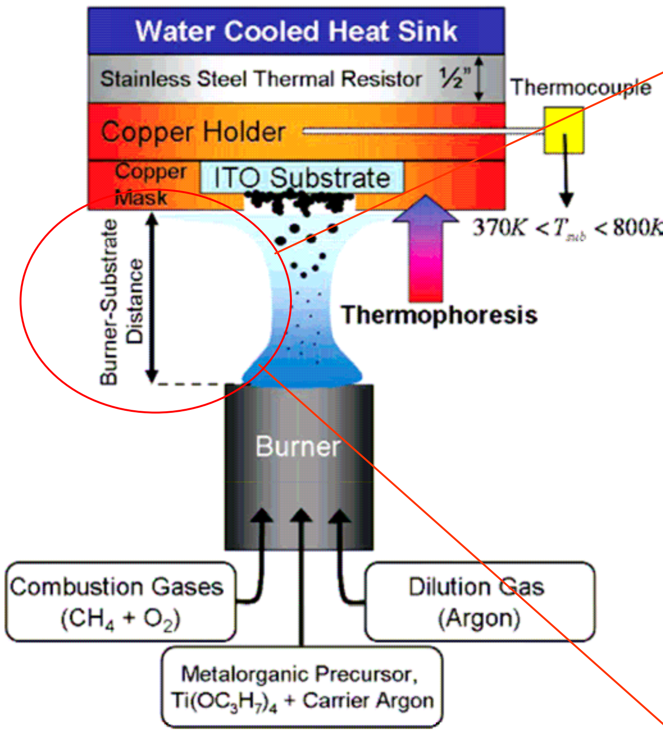








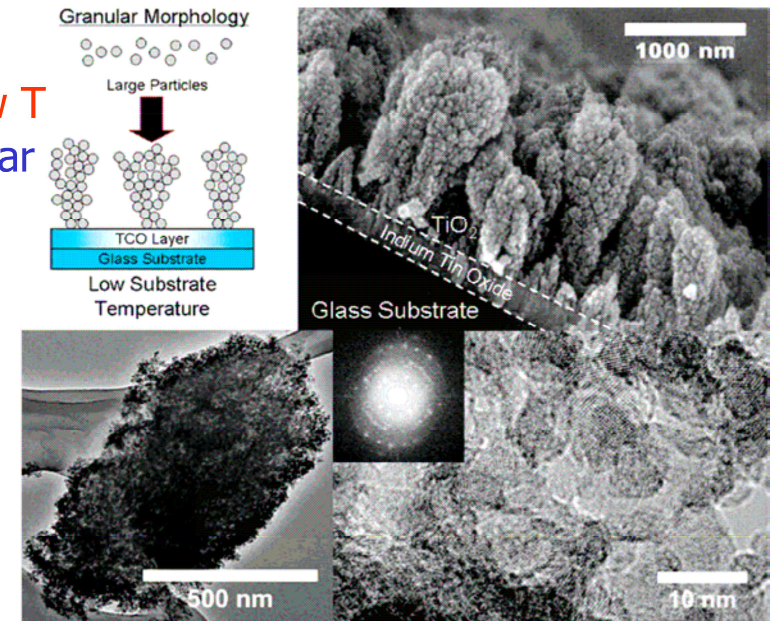
Columnar TiO_2 via flame aerosol synthesis



~5cm low T

TiO_2 granular growth

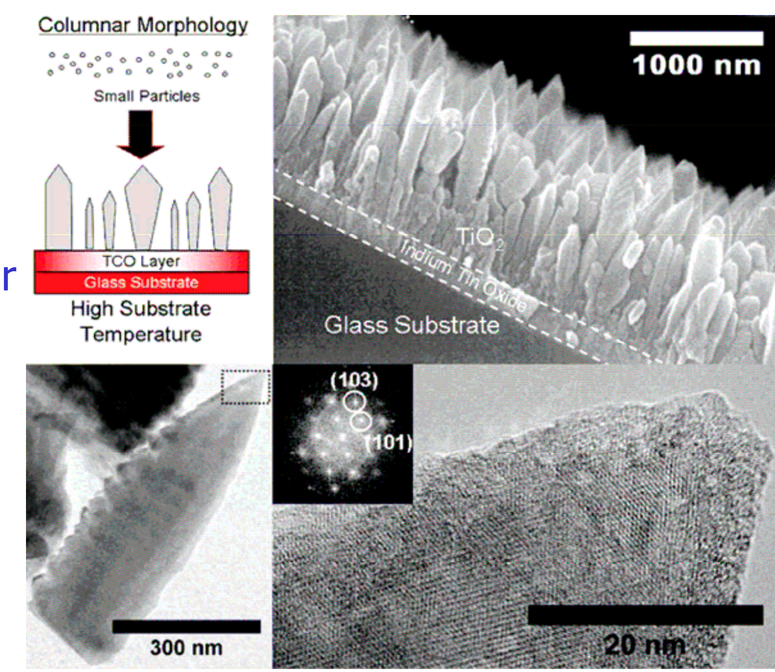
$\eta_{eff} \approx 2\%$



~2cm high T

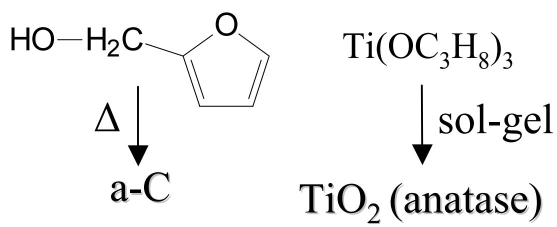
TiO_2 Columnar growth

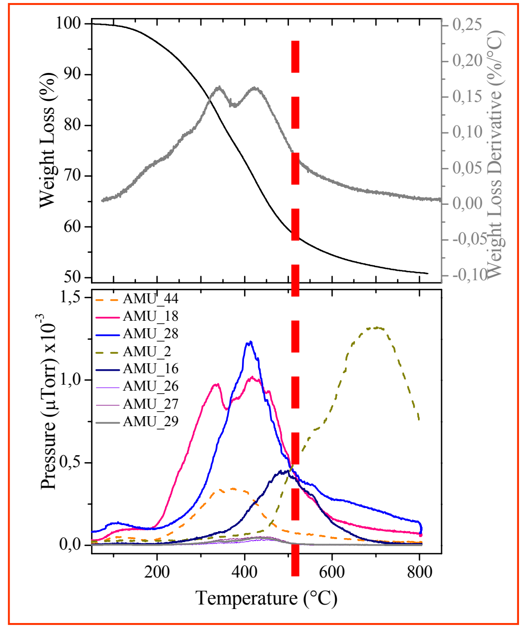
$\eta_{eff} \approx 6\%$

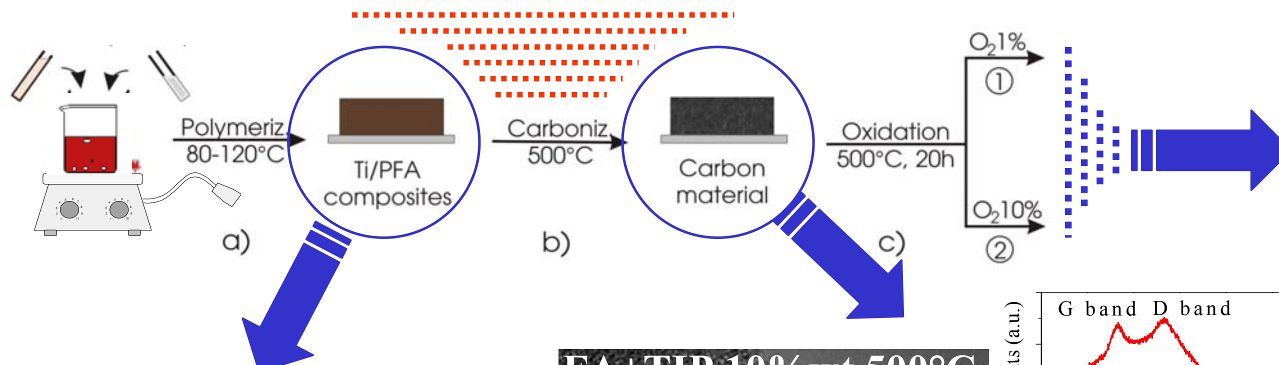


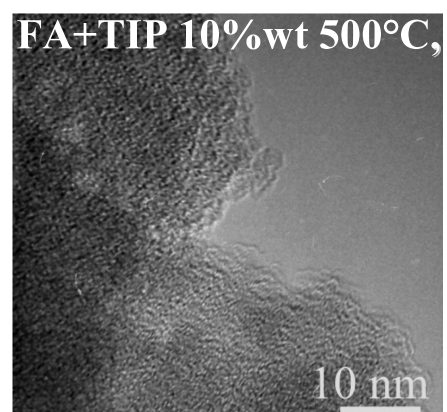
Thimsen, J. Phys. Chem. C 112, (2008) 4134

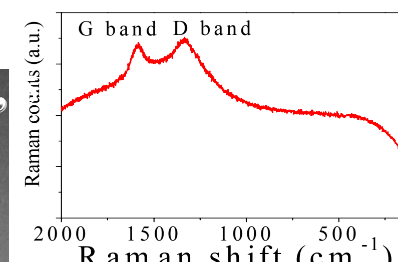
Nanostructured TiO_2 pillar arrays

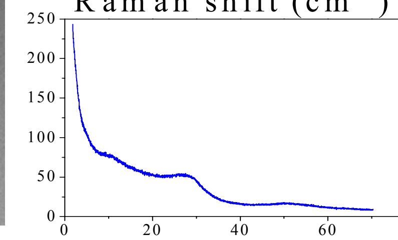






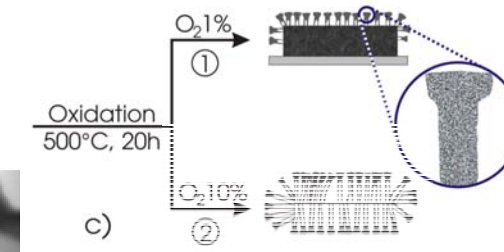


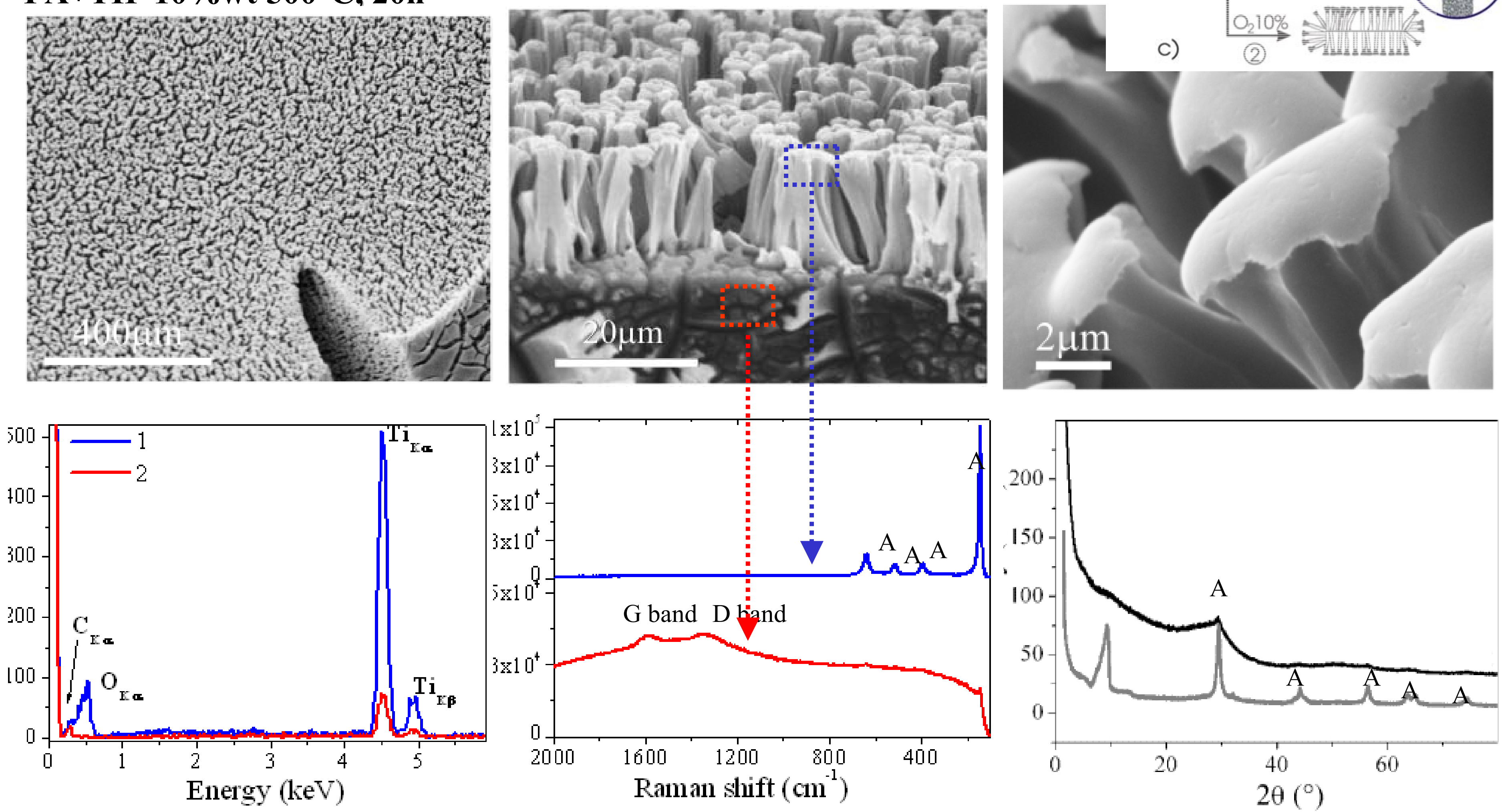




Route 1: Mild oxidation (O_2 1%)

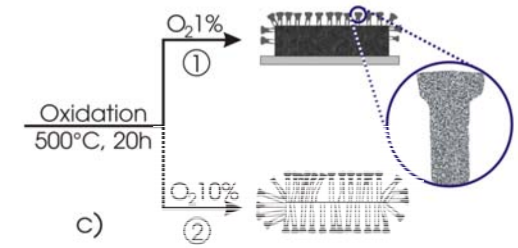
FA+TIP 10%wt 500°C, 20h

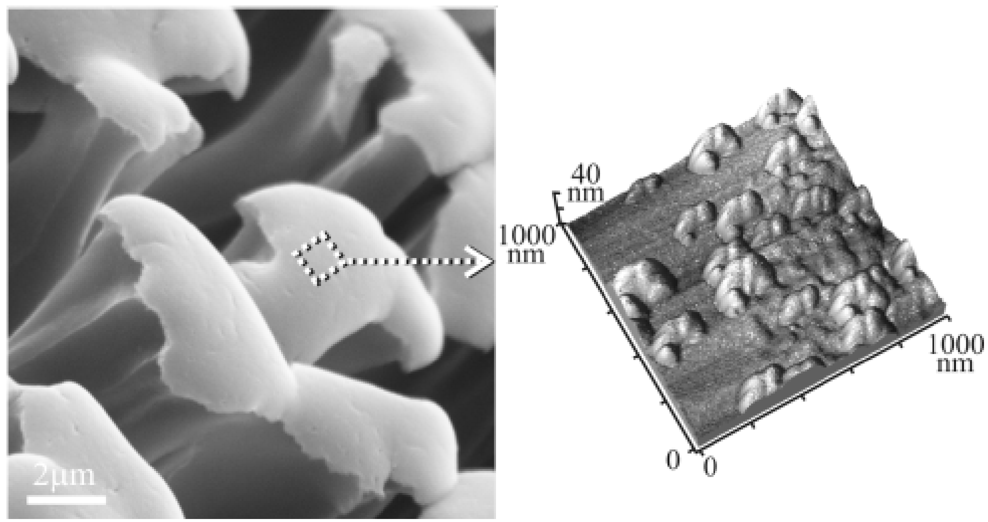


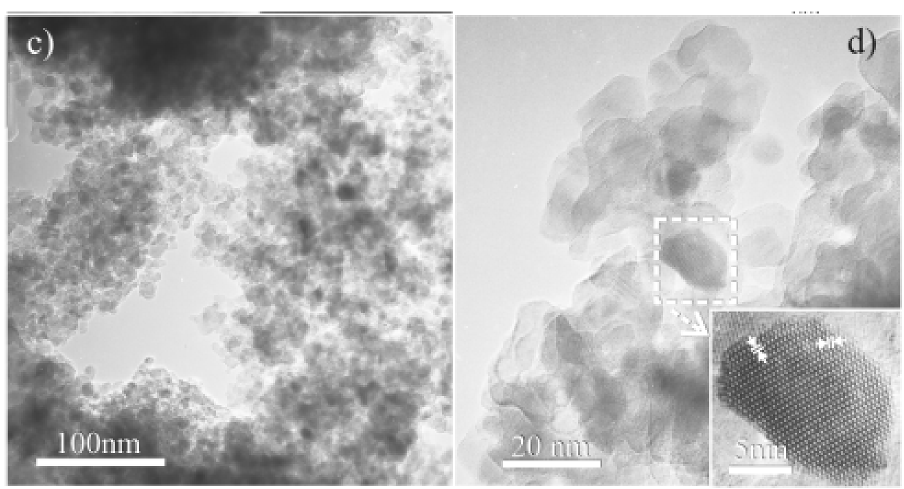


TiO_2 pillar array/C composites

Route 1: Mild oxidation (O_2 1%)



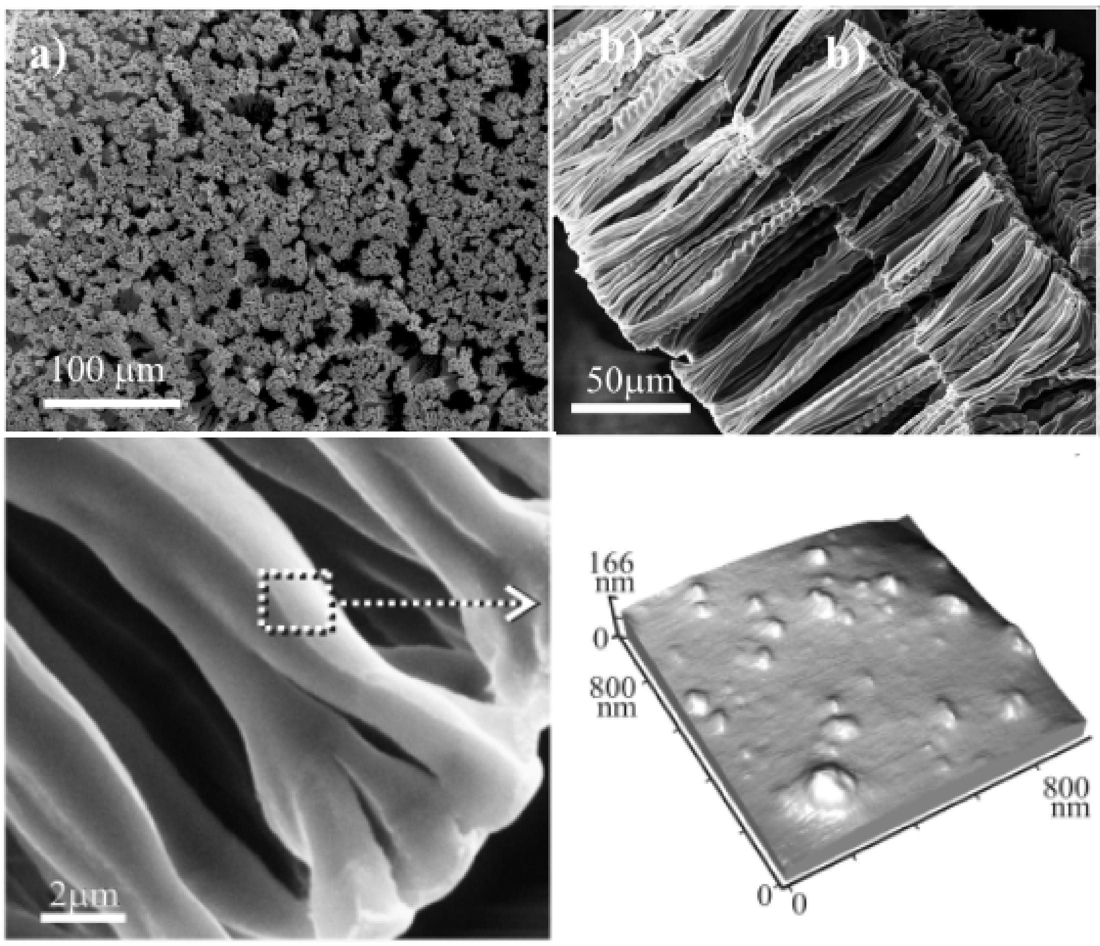


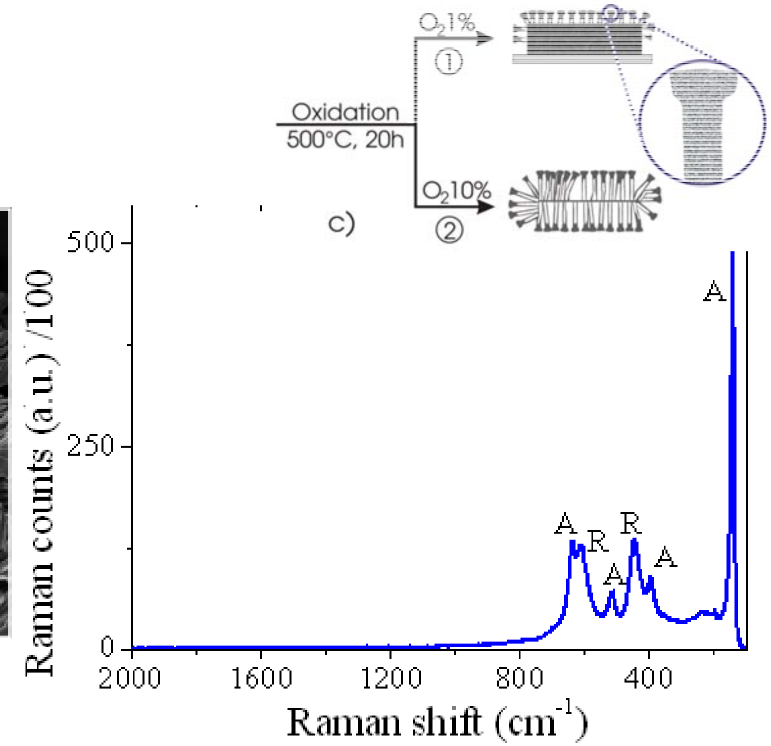


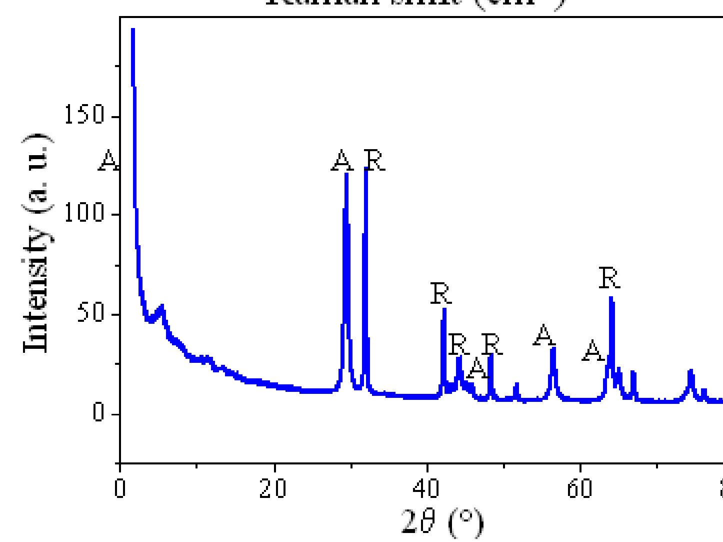
Cemented anatase nanoparticles of 10-20 nm size range

Route 2: Stronger oxidation (O_2 10%)

FA+TIP 10%wt 500°C, 20h

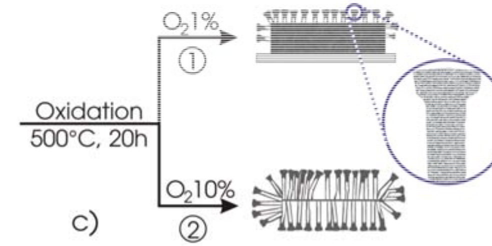


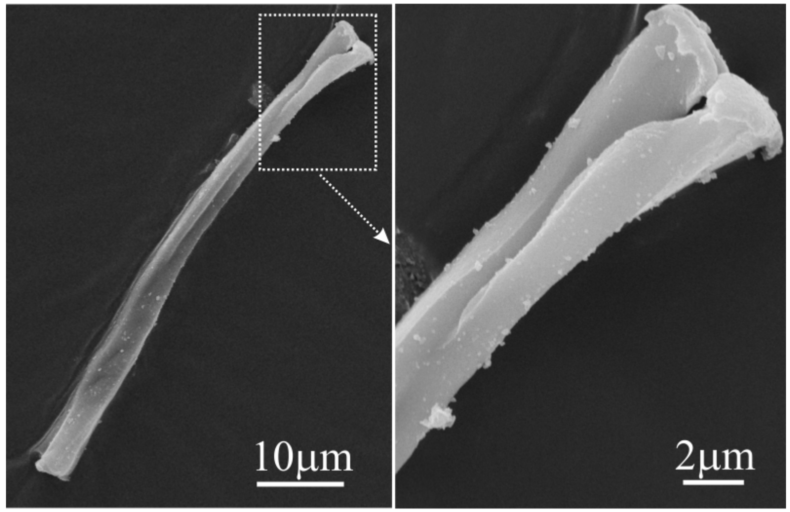


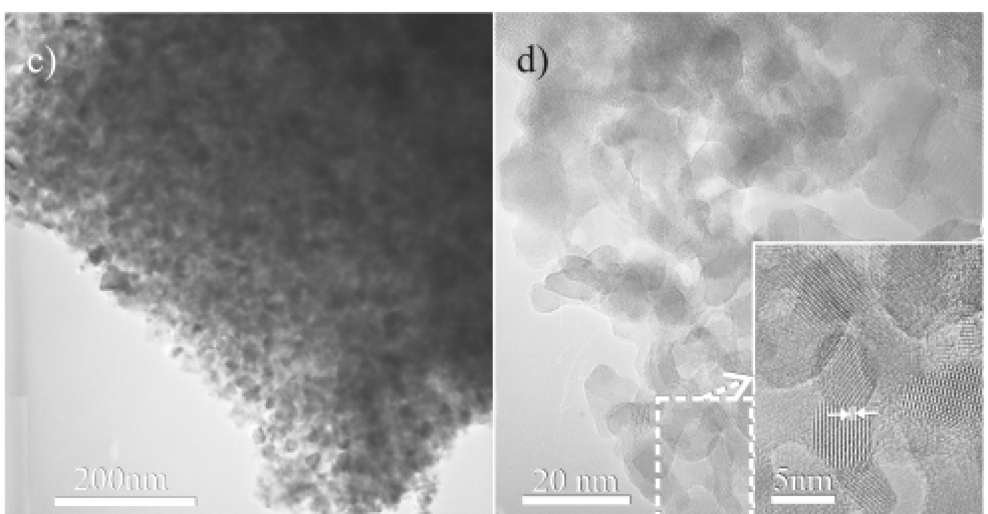


Complete oxidation: pure TiO_2 pillar arrays

TiO_2 pillars (after mechanical stress)





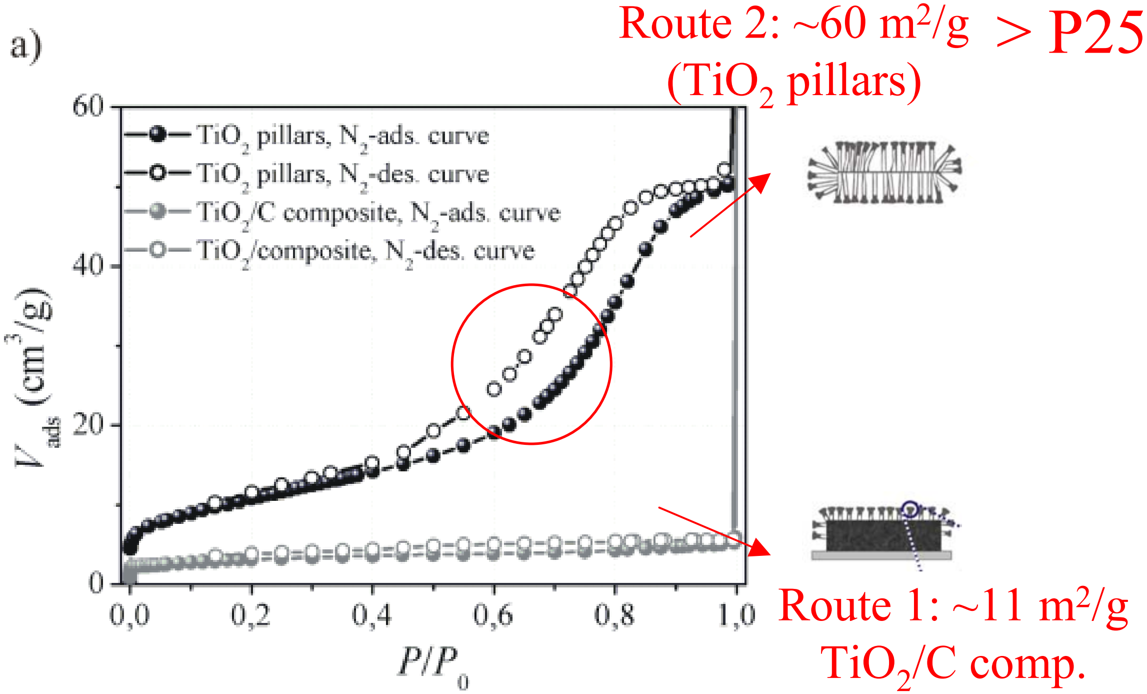


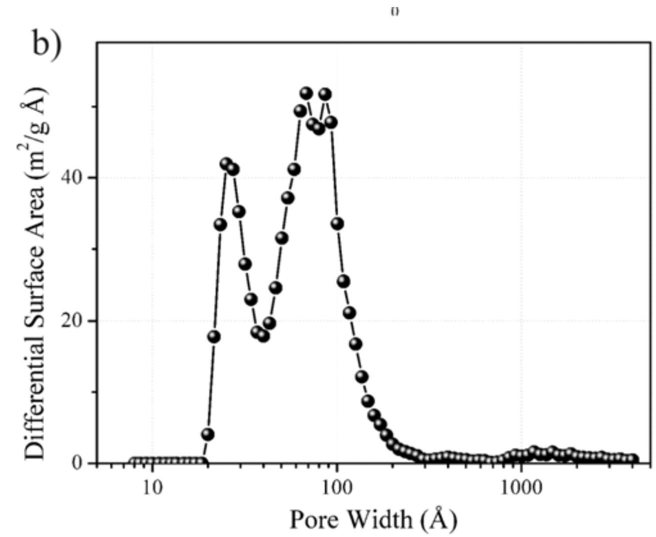
- **Anatase and rutile nanoparticles of 10-20 and ~50 nm**

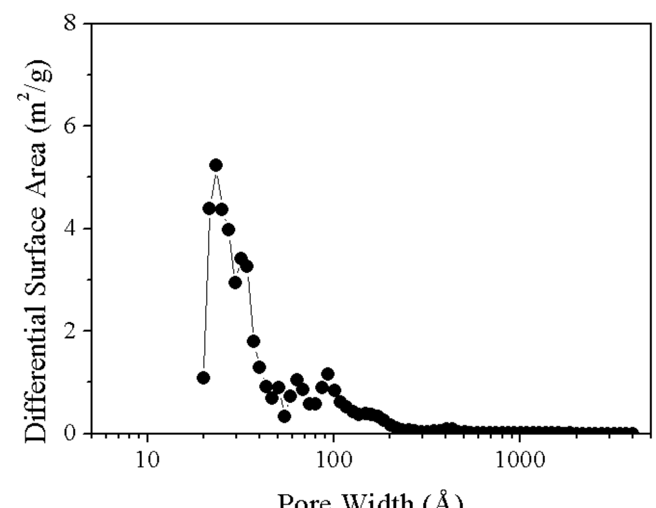
- **Good Cristallinity and interparticle contact (they are "cemented")**

Very robust character

Surface area and porosity





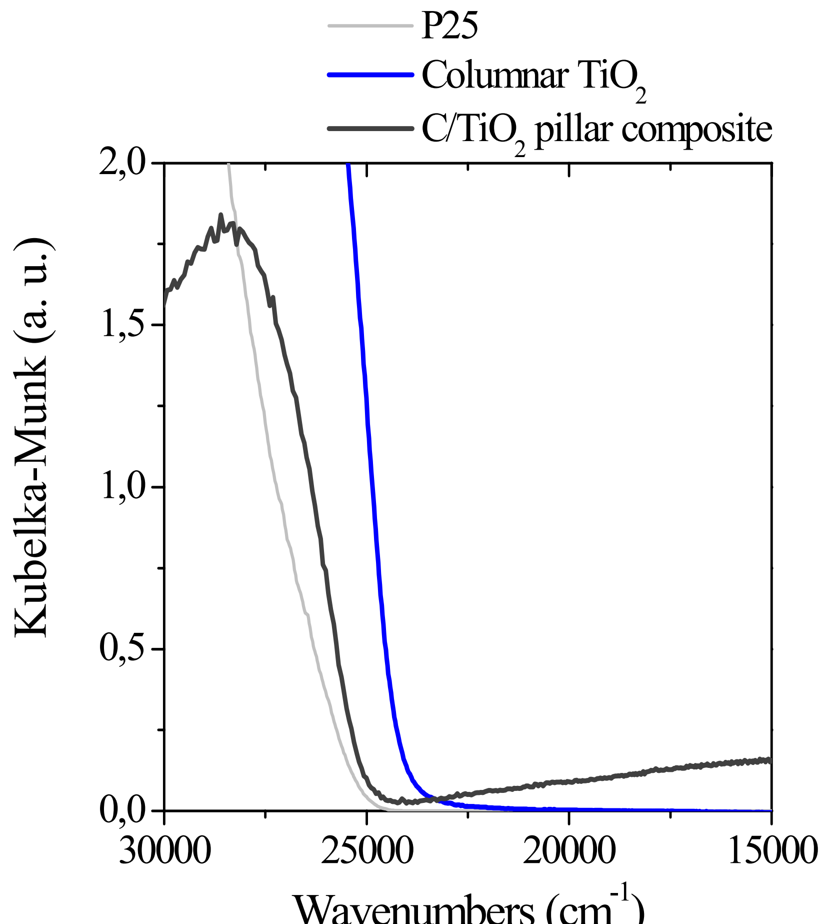


	S_{BET} (m²/g)	S_{micro}[a] (m²/g)	S_{meso}[a] (m²/g)	S_{meso}[b] (m²/g)	V_{pore}[c] (cm³/g)
1%	11	9	n.a.	6	0.008
10%	60	0	37	57	0.104

[a]Estimated using the t-plot method (Harkins and Jura thickness curve).

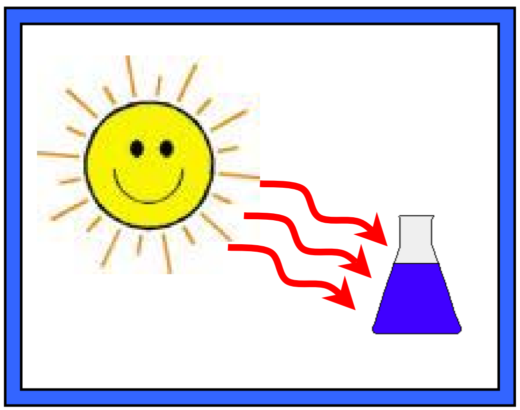
Optical properties

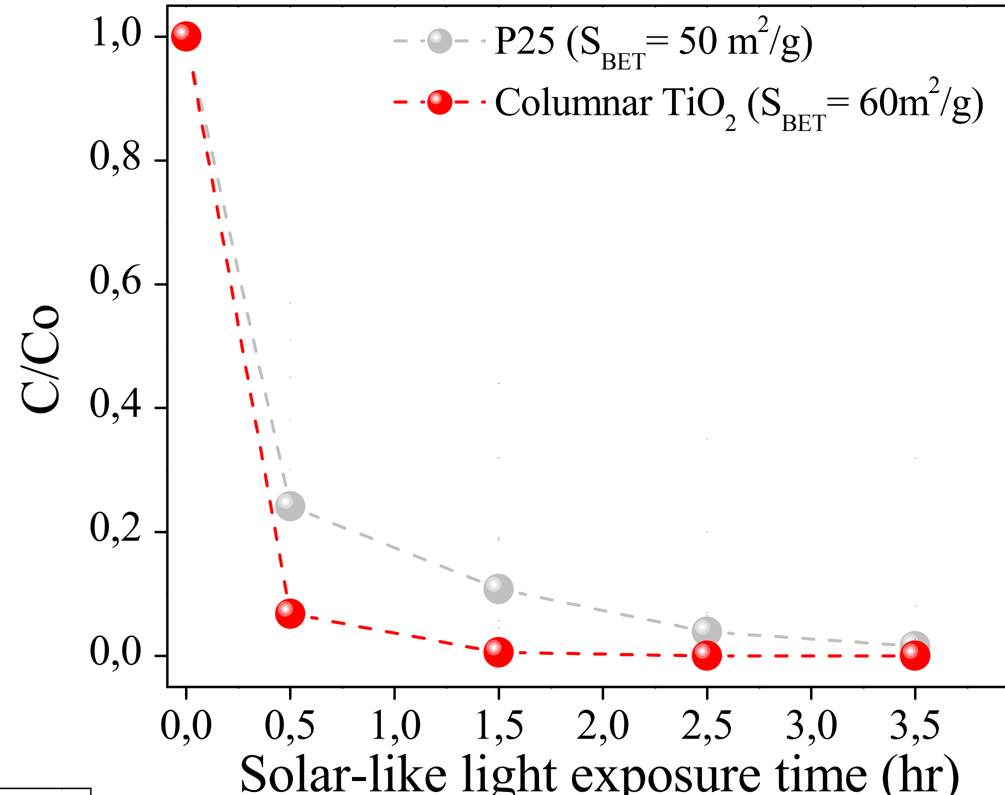
UV-Vis

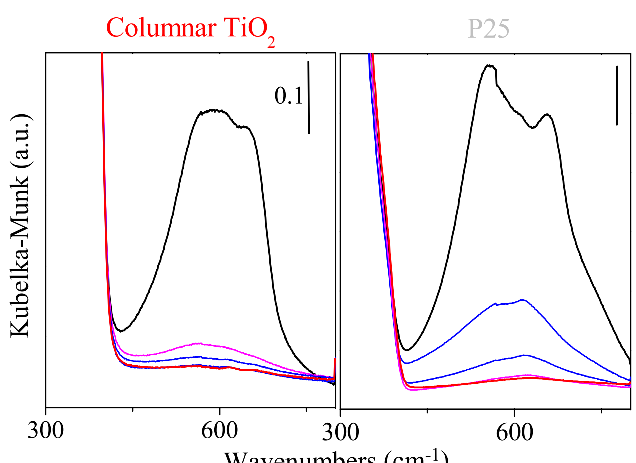


Columnar TiO_2 material: two steps towards photocatalytic applications

MB photodegradation







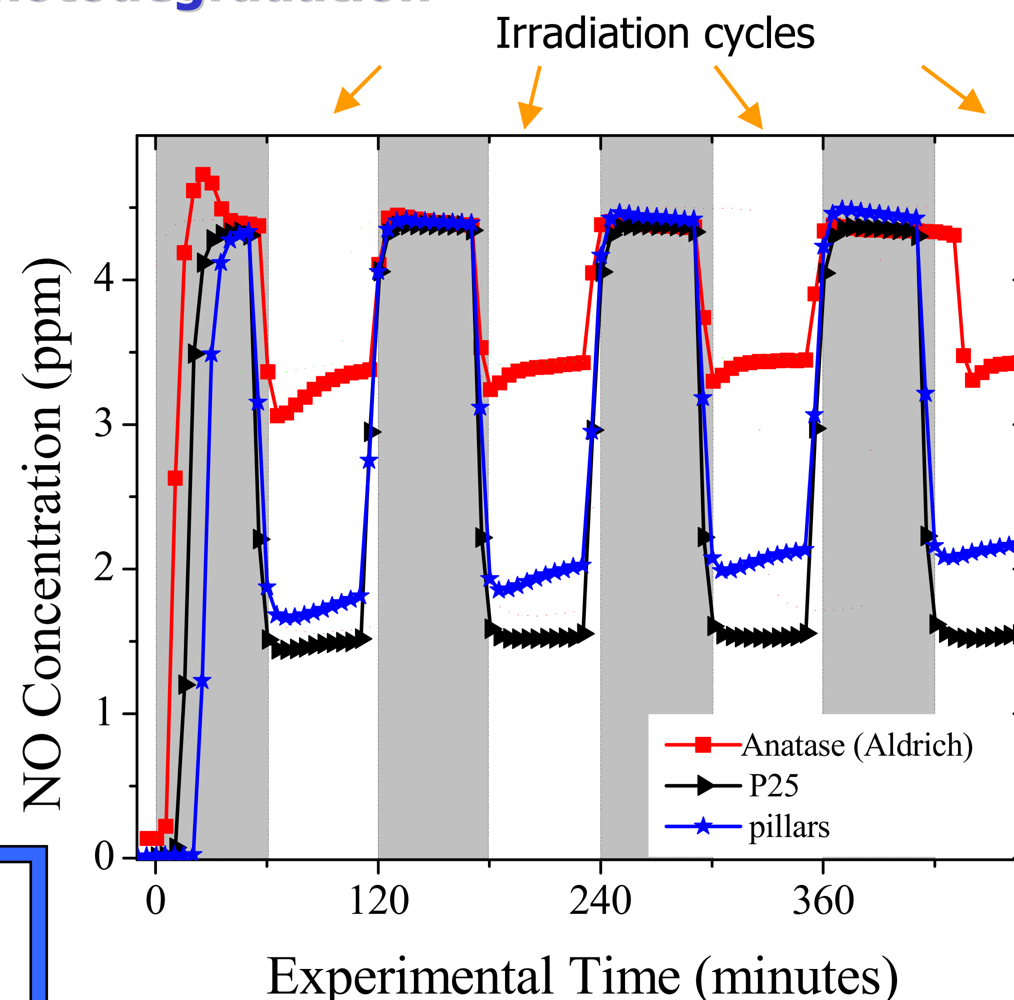
TiO_2 pillars show a high photoactivity if compared to P25

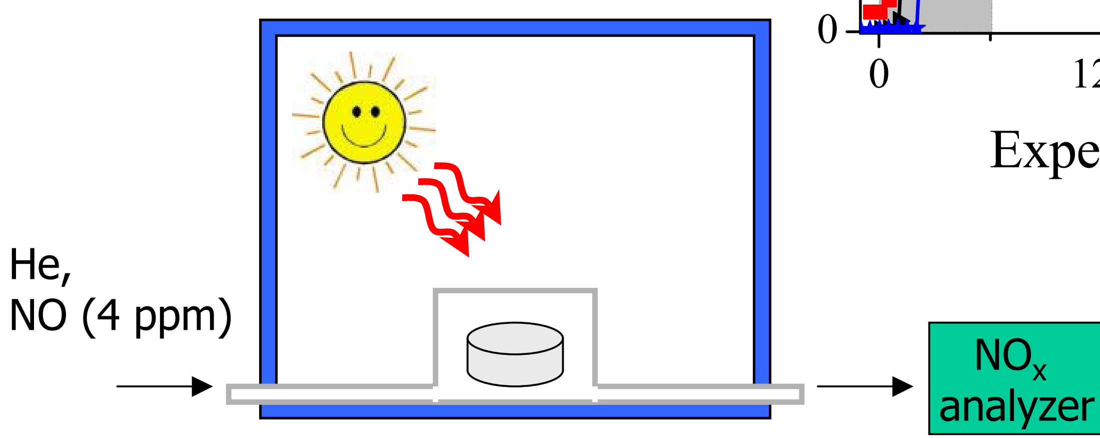
NO Photodegradation

SOLARBOX 3000 with a Xenon lamp (2500W) which reproduces the solar light (295-3000 nm).

Experimenal conditions: 250W/m^2, 50% humidity

NO_x gas analyzer





Pillar material Conclusions

Nanostructured micropillar TiO_2 array either pure or implanted on a carbon matrix, have been prepared via a controlled oxidation of hybrid systems coming from TIP and FA homogeneous solutions:

✓Mild oxidation treatments (O_2 1%, 500°C) lead to form parallely oriented elongated pillars emerging from a compact a-C phase based on cemented anatase nanoparticles;

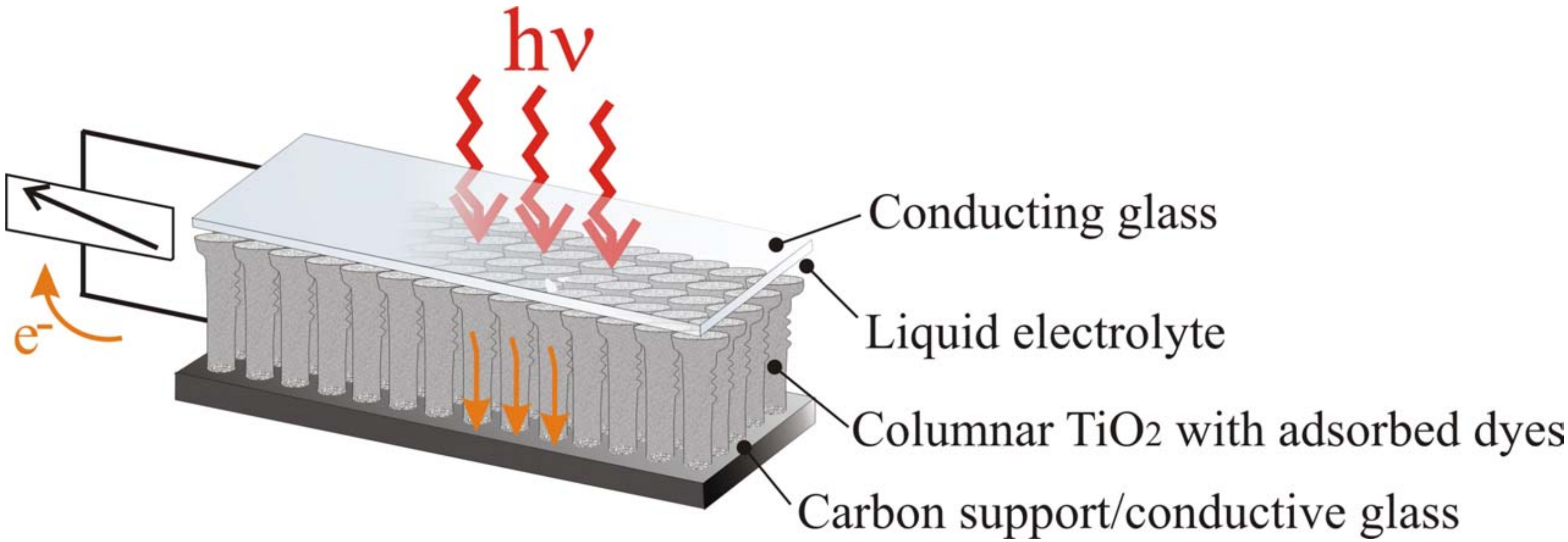
✓Strong oxidation treatments (O_2 10%, 500°C) lead to form pure TiO_2 pillars, where anatase and rutile nanoparticles are coesisting in an intimate contact;

✓TiO_2 pillar phase shows a higher photoactivity than P25 under solar-like irradiation

✓The NO photodegradation efficiency is close to that one of P25, if compared to TiO_2 pure anatase

ADVANCED MATERIALS In press

Perspectives: Dye-sensitized solar cells



... Work in progress ...

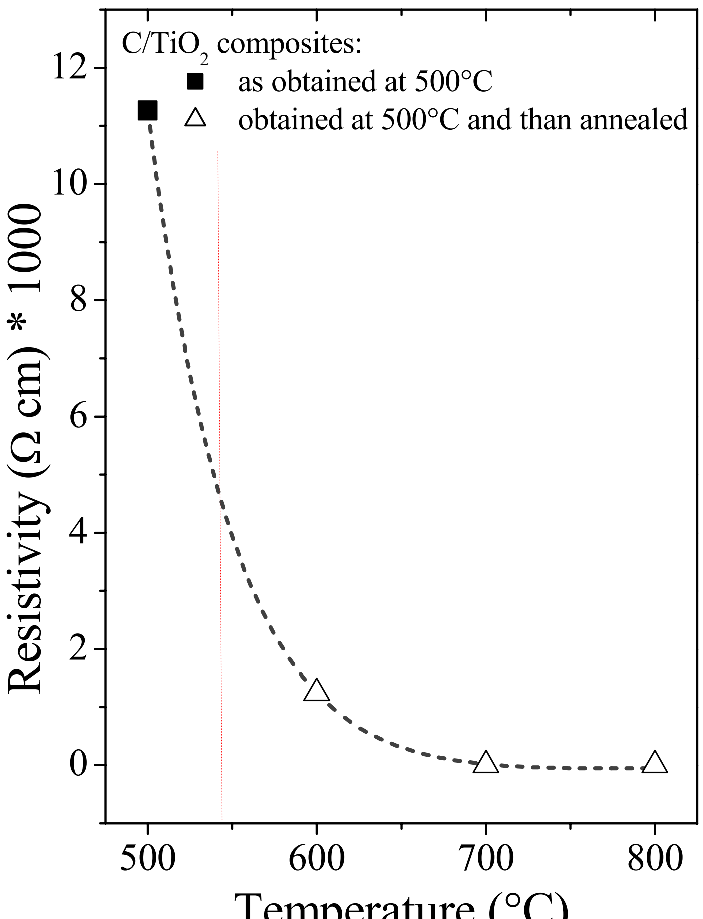
-surface homogeneity and regularity

-reduction of the adhesion problems (between TiO_2 pillar on different supports)

-electric conductivity of the carbon support …

TiO_2/C composite: electric properties of the C-phase

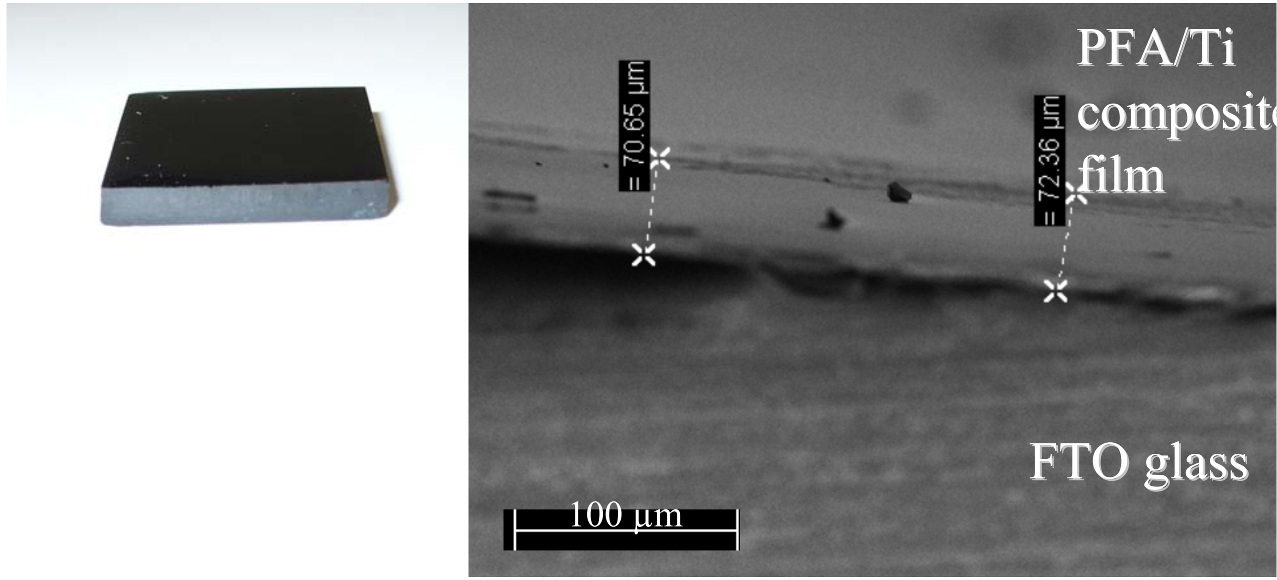
The conductivity of the carbon strongly depends on treatment temperature, because electric resistivity is affected by the presence of impurities, crystallinity degree of the material



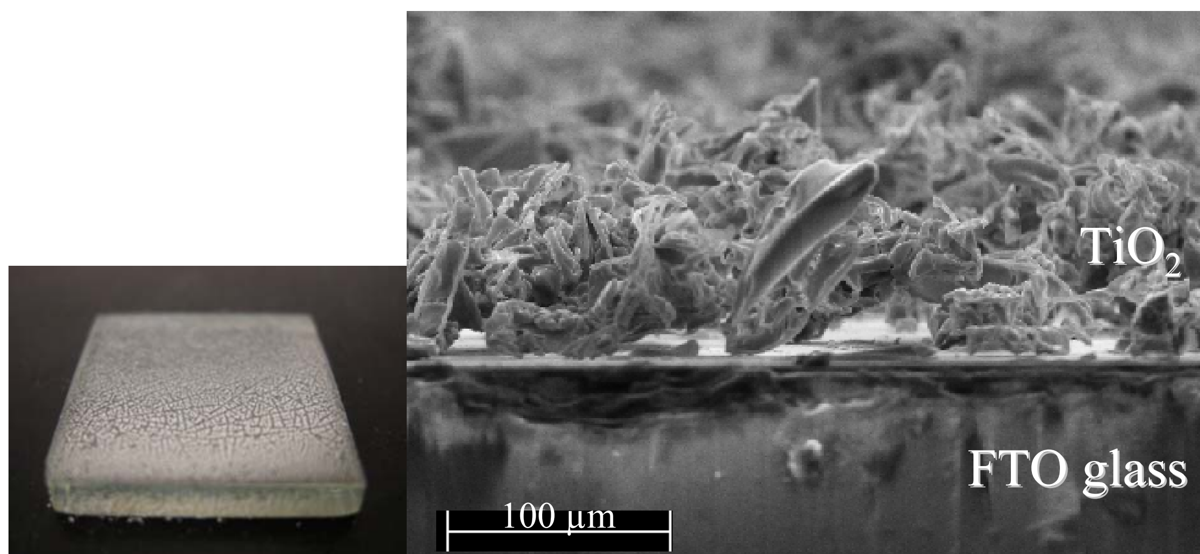
Treatment temperature:	Electric resistivity (@RT):
As obtained at 500°C	**~11000 Ω·cm (0.1-100 µA)**
-Annealed at 800°C	**2.8 Ω·cm**

TiO_2 pillar-covered FTO electrode

As deposited PFA/Ti composite film:



After thermal treatment at 500°C 15h:



- **Problems of TiO_2 film homogeneity**
- **Electric conductivity after the preparation is satisfactory**

General conclusions:

-Data reported in literature are so far too low and from them it is not possible to compare conversion efficiencies of materials, because of the wide range of possible combinations of components (TiO_2, sensitizer, electrolyte) and film thickness; neverthless

- it has been shown that electron transport in elongated TiO_2 nanostructures is promoted

… a particular thank to Prof.

A. Zecchina

D. Scarano

S. Bertarione

G. Spoto

G. Agostini

S. Bordiga

J. Vitillo

C. Lamberti

D. Pellerej

G. Ricchiardi

J. Uddin

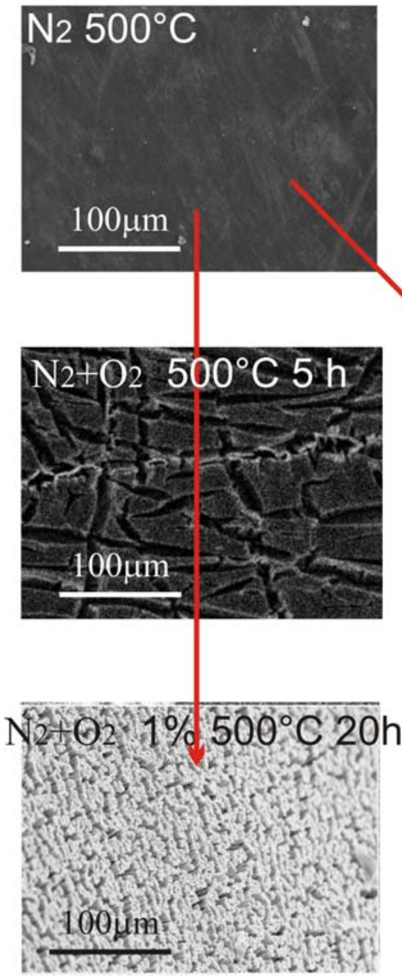
A. Damin

G. Viscardi

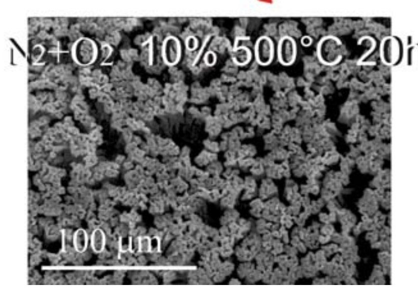
A. Castellino

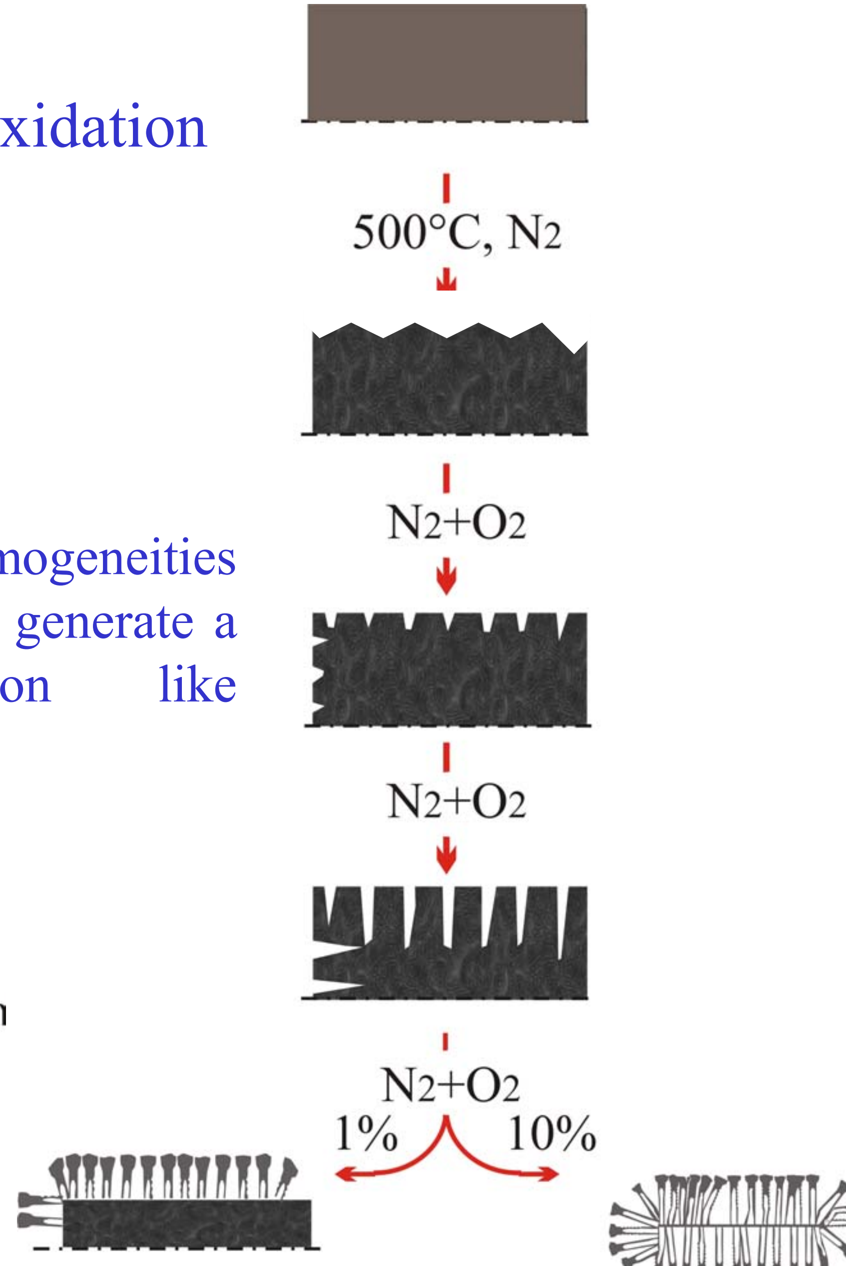
… and …
all of you!

Scheme of pillars formation under oxidation



presence of disomogeneities at the surface can generate a localized oxidation like pitting on metals





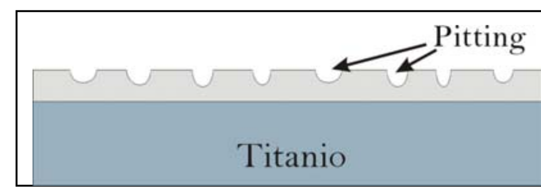
Scheme of pores formation under electro-oxidation of Ti

Steps of growth of the oxide:

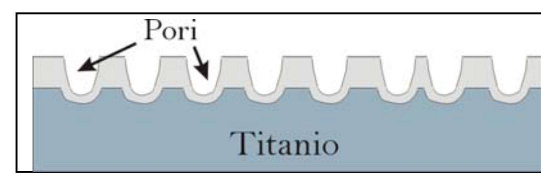
The surface of the metal is homoneously covered by a thin layer of TiO_2

A localized oxidation of the TiO_2 film (pitting) is promoted by the F^-:

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O$$



Pores formation



Growth of the pores and anodization of the metal among pores