IFA-CEA (C1-07) : TiO_2-based nanoparticles for applications in photovoltaic cells or bactericide elements (NanoPhoB)

→ photocatalysis

Roadmap of the project

Year one :
synthesis of « X-doped » nanoparticles by laser pyrolysis

Year two :
Synthesis of new generation of nanoparticles

Selection of nanoparticles from year one
Elaboration of (SDSSC) solid state Dye Sensitized Solar Cells

Partners implied in the project:
- National Institute for Lasers, Plasma and Radiation Physics (NILPRP), Laboratory of Laser Photochemistry, Bucharest, Romania; Ion Morjan – Director of the Project
-Edifices Nanométriques, CEA - IRAMIS/SPAM, Saclay, France, Nathalie Herlin Boime - Director of the Project
- XLIM institute, Limoges, France, Johann Bouclé

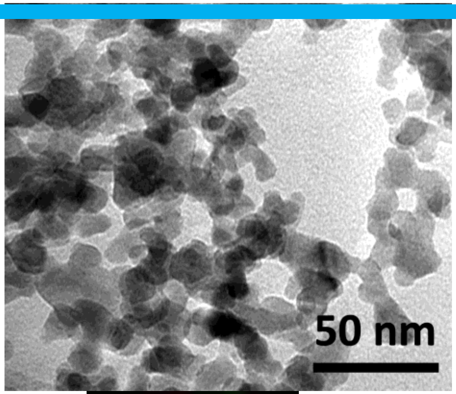
NanoPhoB

1- Introduction : The Nanophob project

- > objectives of the project

-> The laser pyrolysis technique

-> synthesis and characterization of TIO_2 based nanoparticles



2 - TiO_2 based devices

DSSC device performances

N-doping effect :

- > Numerical simulations : isolated TiO_2 clusters

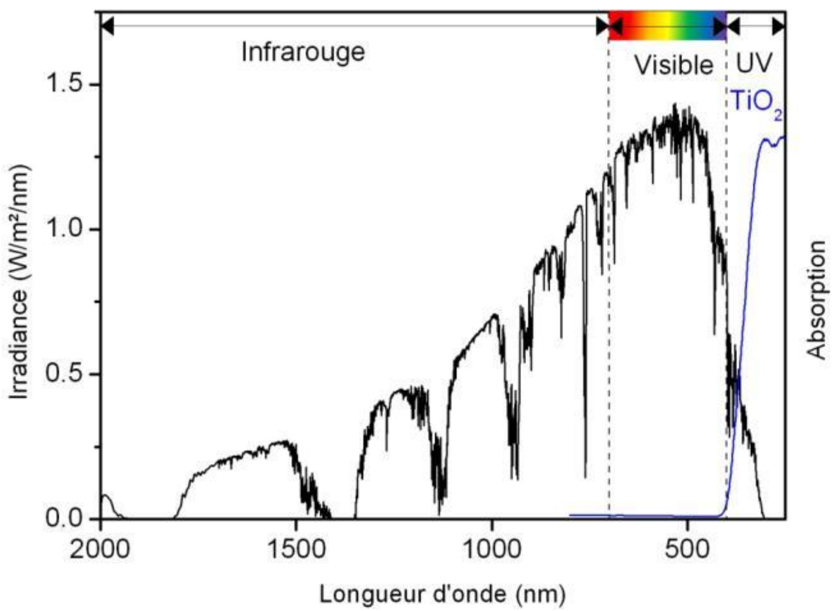
- > EPR characterization

3 – TiO_2 for photocatalysis

degradation of salicilic acid

1- Laser pyrolysis

Absorption of TiO_2 *vs*
Solar emission



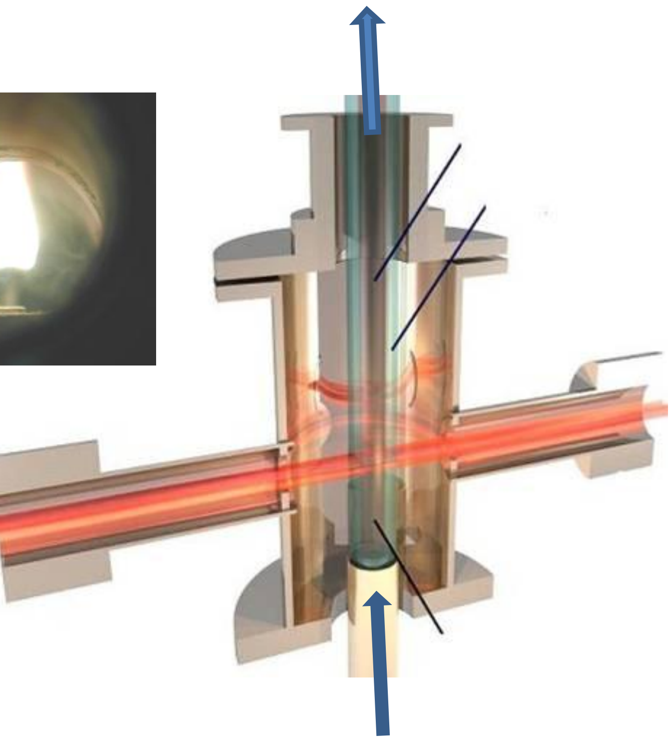
Rutile : Eg = 3,0 eV – 411 nm

Anatase : Eg = 3,2 eV – 384 nm

UV = 5 % of solar energy

Shift the optical gap toward the visible range
- > Introduction of hetero-elements (C, N, S)

TiO_2
X-TiO_2, (X= S,N, C)



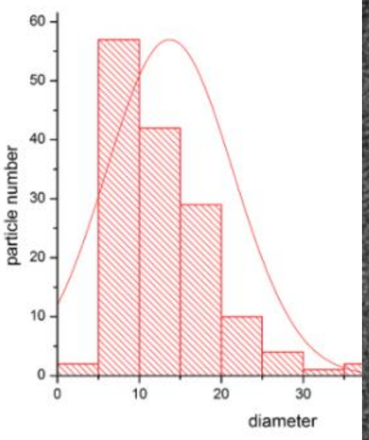
Ti/O precursors

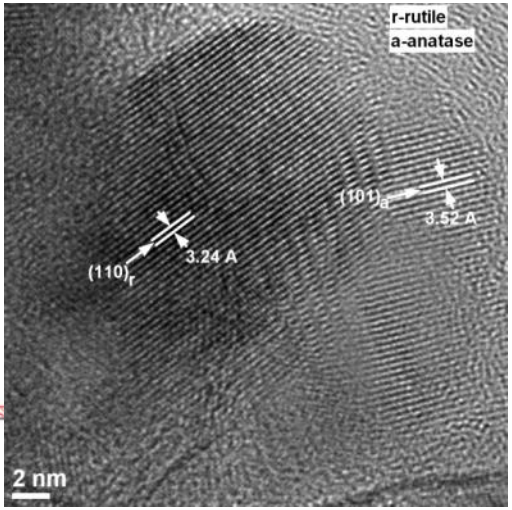
TTIP (Titanium tetraisopropoxid)
or $TiCl_4$ + air

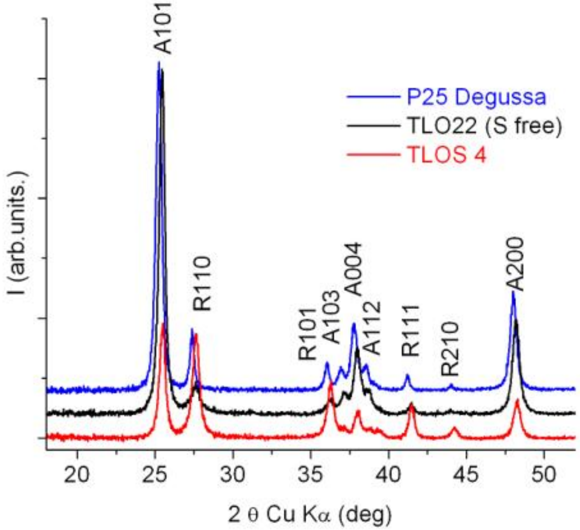
Precursors of N, S and C

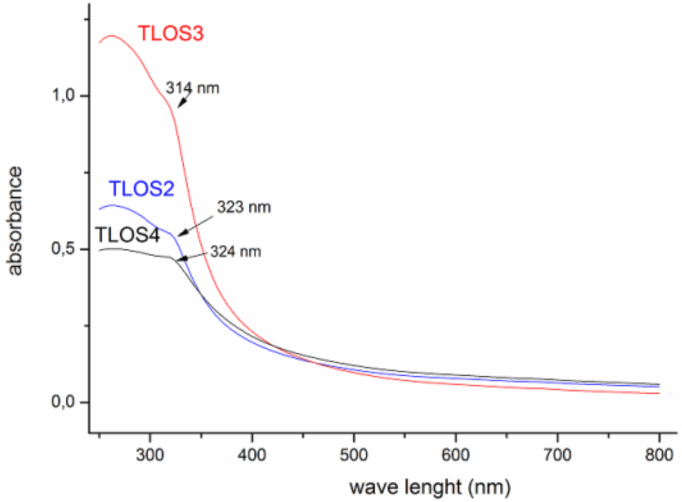
1- S-doped nanoparticles

$TiCl_4$ and different sulfur precursors
SF_6 or dimethyl disulfide





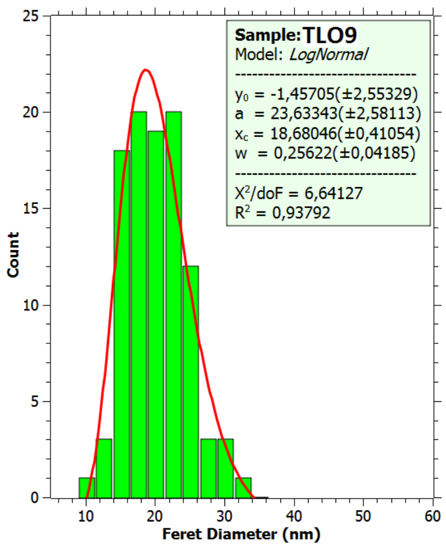


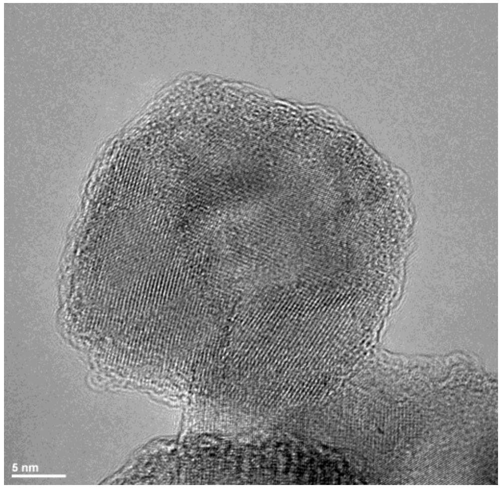


Nanoparticles with :
- diameter in the range 10-20 nm
- S content up to 4 %
- variable anatase to rutile ratio
- **red-shift of the gap (compared to TiO_2)**

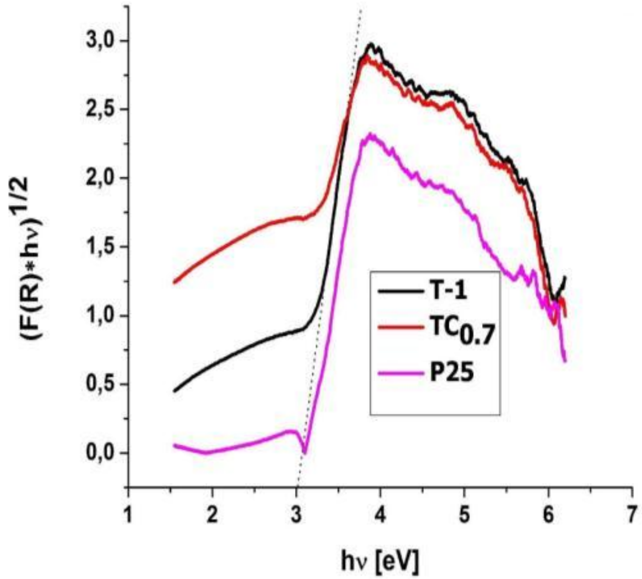
1- C- "doped" nanoparticles

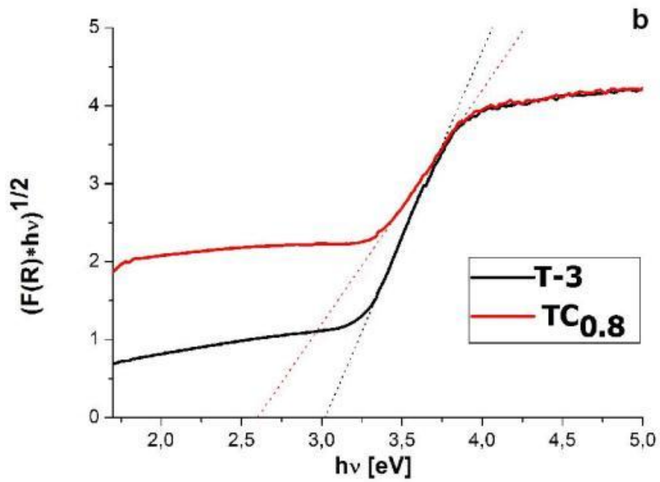
Synthesis from $TiCl_4 + C_2H_4$





Core-shell structure



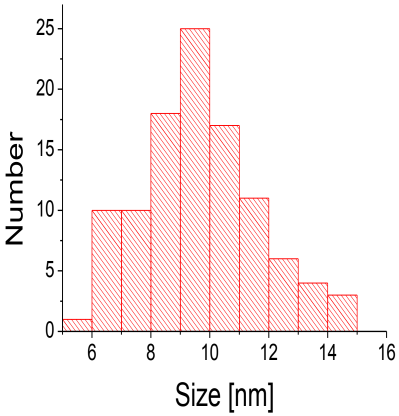


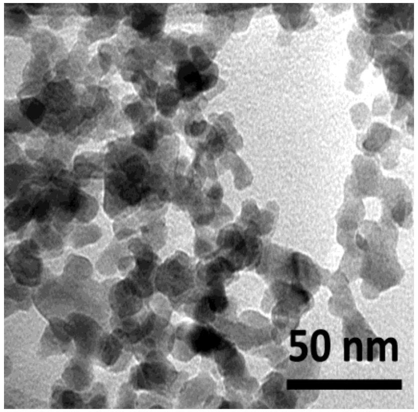
Nanoparticles with :

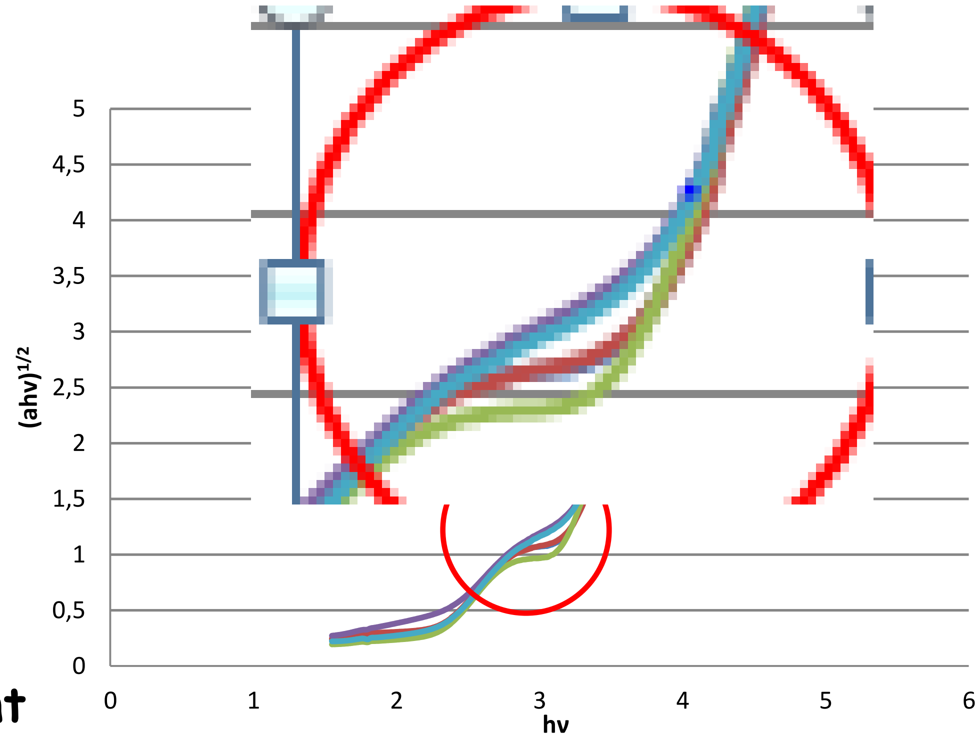
- diameter in the range 10-30 nm
- core shell structure
- C content in the range 15 to 21 %
  (correlated to C_2H_4 flow rate)
- **gap between 2.6 and 3.2 eV**

1- N-doped nanoparticles

Synthesis from TTIP + NH_3







Nanoparticles with :

- diameter in the range 8-12 nm
- N content in the range 0.2 to 2 % (correlated to NH3 flow rate)
- more than 90 % anatase
- **a second gap in the visible intensity correlated to N content**

Outline

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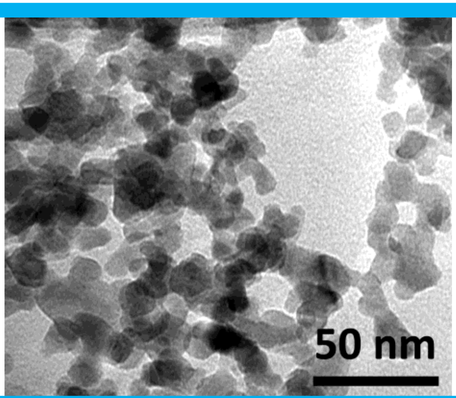


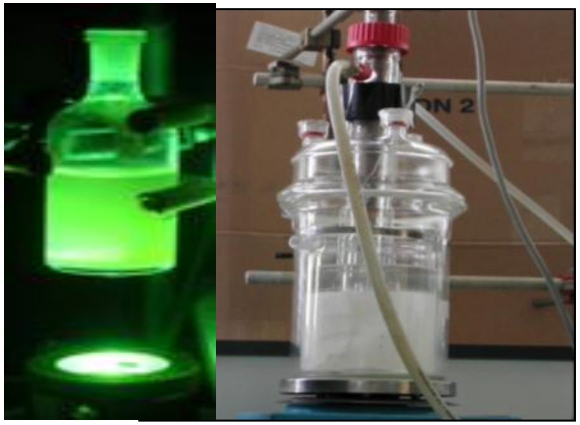
2 - TiO_2 based devices

DSSC device performances

N-doping effect :

- > Numerical simulations : isolated TiO_2 clusters

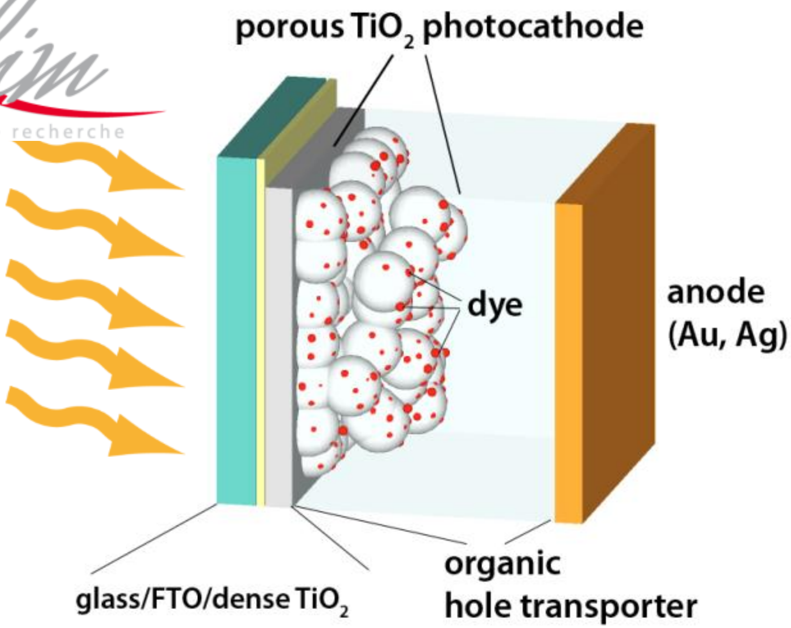
- > EPR characterization



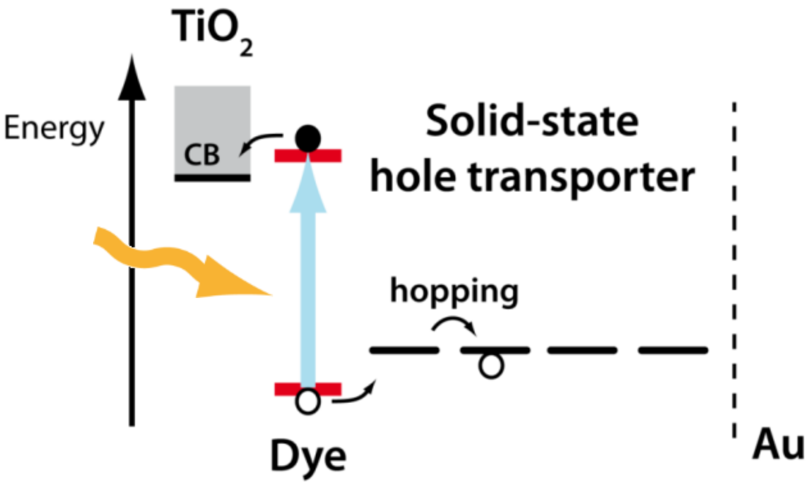
3 – TiO_2 for photocatalysis

degradation of salicilic acid

2 - Solid-State Dye-Sensitized Solar Cells (SSDSC)

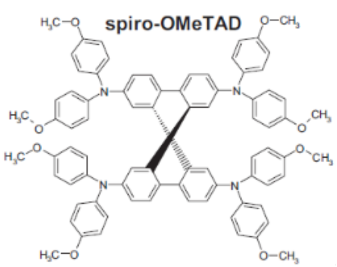


U. Bach, M. Grätzel et al. *Nature* **395** (1998)
B.E. Hardin et al. *Nat Photon* **6** (2012) 162-1(



Spiro-OMeTAD

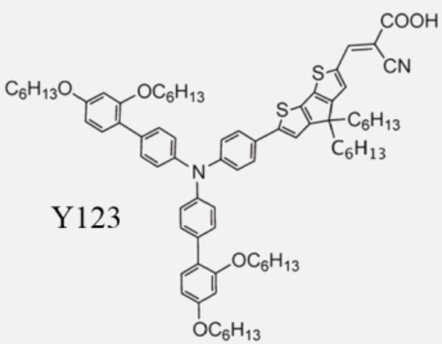
HOMO ~ 5 eV
T_g = 121°C
$\mu_h = 10^{-3} - 10^{-4}$ $cm^2.V^{-1}.s^{-1}$



✓Allows efficient dye regeneration
✓Suitable TiO_2 pore filling up to several µm

J. Krüger et al., *Appl. Phys. Lett.* **79** (2001) 2085
I.-K. Ding et al., *Adv. Funct. Mater.* **19** (2009) 2431

State of the art



η = 7%

J. Burschka et al., *J. Am. Chem. Soc.* **133** (2011) 18042-18045

Fabrication of porous TiO_2 photoanodes and solid DSSC

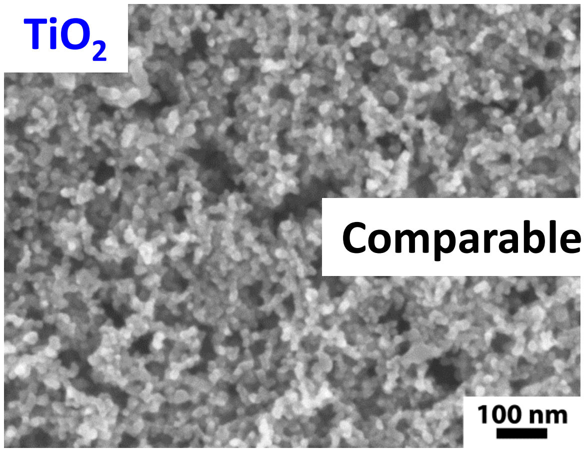
- Nanocrystals (15 wt.%)
- Ethanol
- Ethyl cellulose (EC)

TiO_2:EC = 3:2 (wt.)

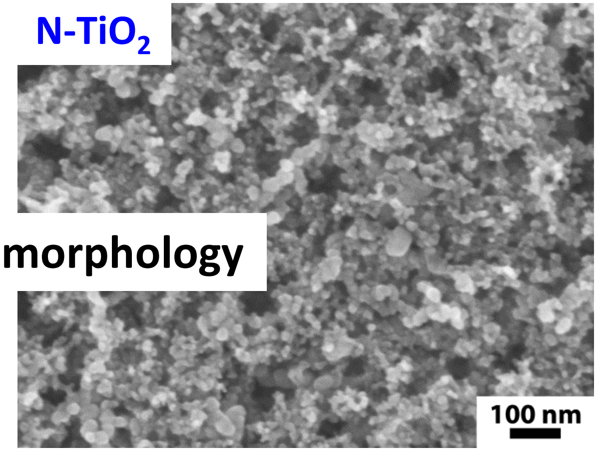
→ Sonication → Spin-Coating → Sintering + $TiCl_4$ treatment → **2 µm thick porous film**

H. Melhem at al., *Adv. Energy Mater.* **1** (2011) 908

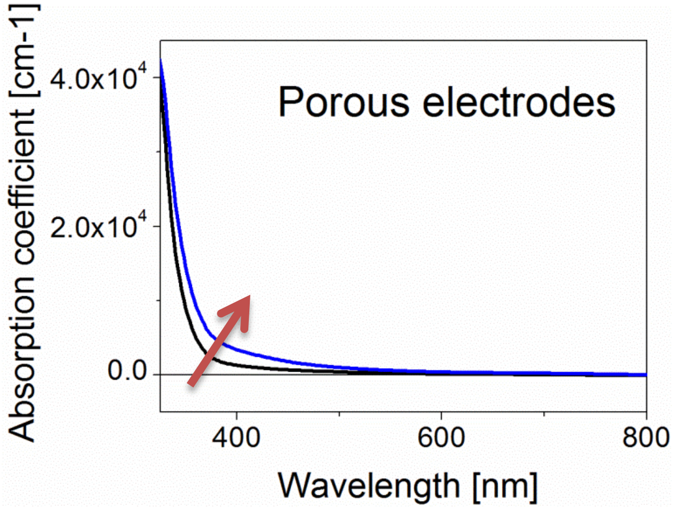
TiO_2



N-TiO_2

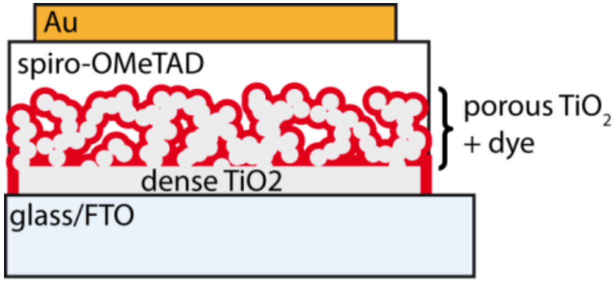


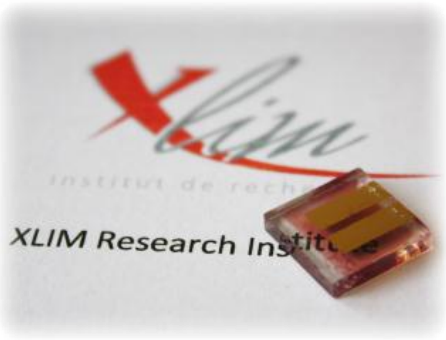
Comparable morphology



Solar cell processing

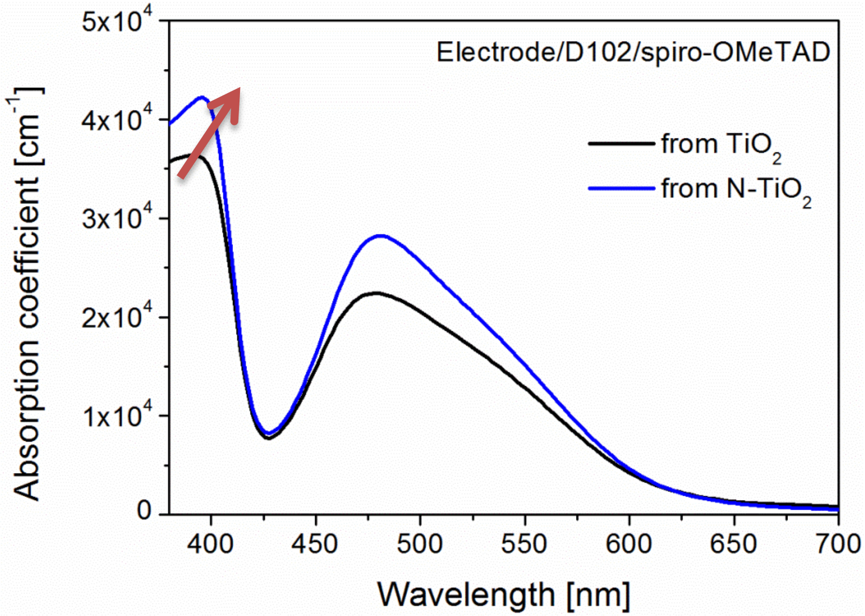
Organic Dye **D102**
Spiro-OMeTAD (Li-TFSI, t-BP)
Active area = 0.18 cm²





2 - SSDSC : Device performance

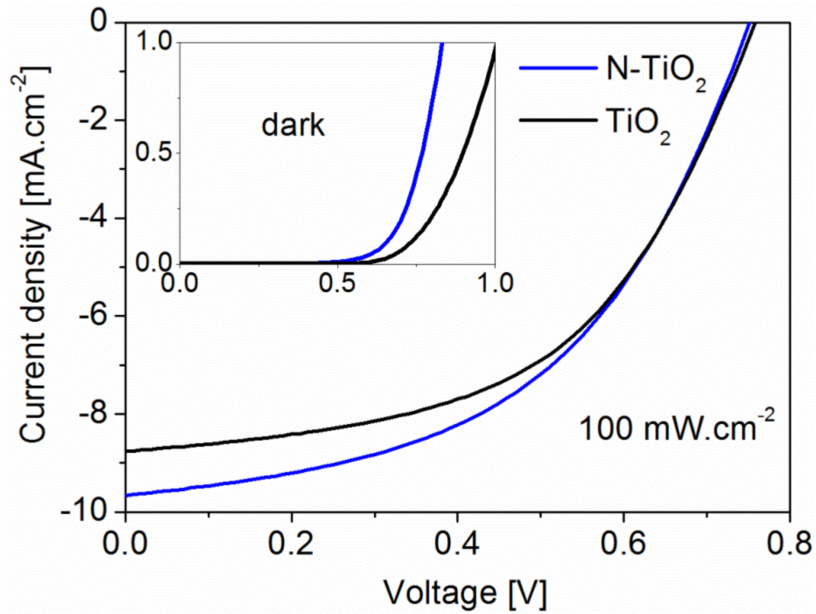
Absorption of the dye-sensitized electrodes



- ✓ **Clear contribution from the N-doping** around 400 nm
- ✓ Improved dye adsoprtion with doping

Photovoltaic performances under 1 su

100 mW.cm-2, AM1.5G (Spectral mismatch correcte



	J_{sc} (mA.cm^{-2})	V_{oc} (mV)	FF	η (%)
TiO_2	8.7	760	0.52	3.4
N-TiO_2	**9.7**	**750**	**0.49**	**3.6**

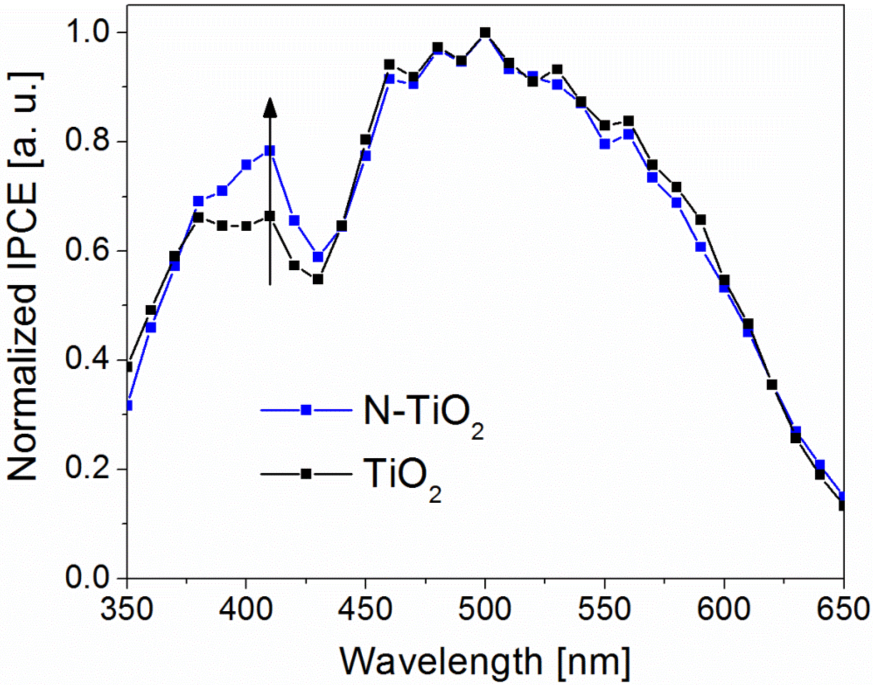
⇒ Improved photocurrent with doping

No modification of Voc : no drastic change in the CB of TiO_2

H. Melhem at al., *under publication solar Energy Materlals* (2012)

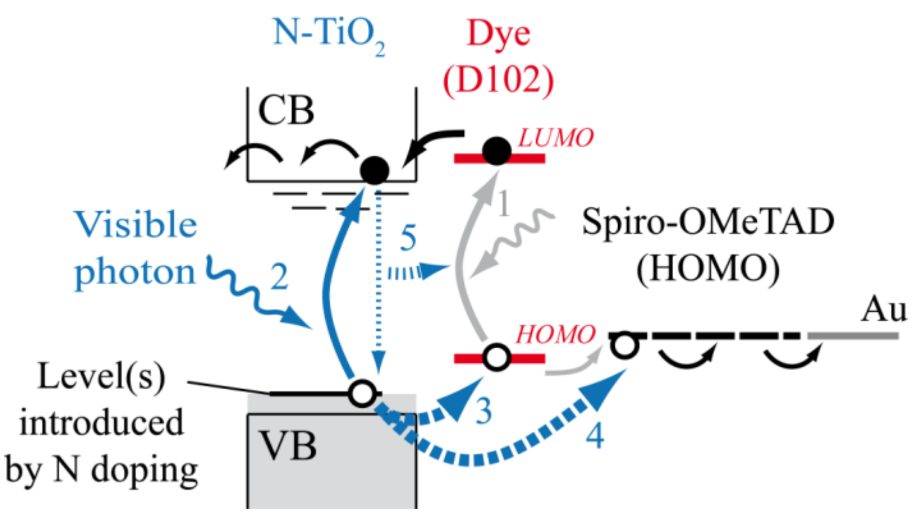
2 – SSDSC : Device performance

Incident photon to current efficiency spectra



Direct **contribution of N-TiO$_2$ to current generation**

⇒ ***Towards additional charge generation paths***



H. Melhem at al., *under publication* (2012)

Underlying mechanisms ?

investigation by EPR shows an increased mobility of charges attributed to N atoms in substitution

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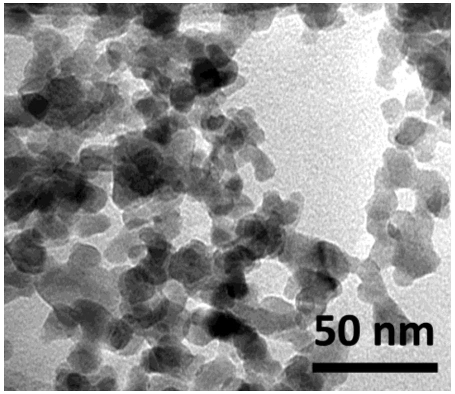

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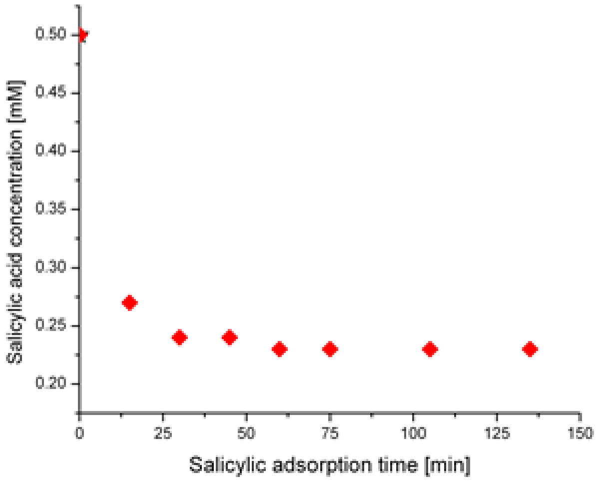
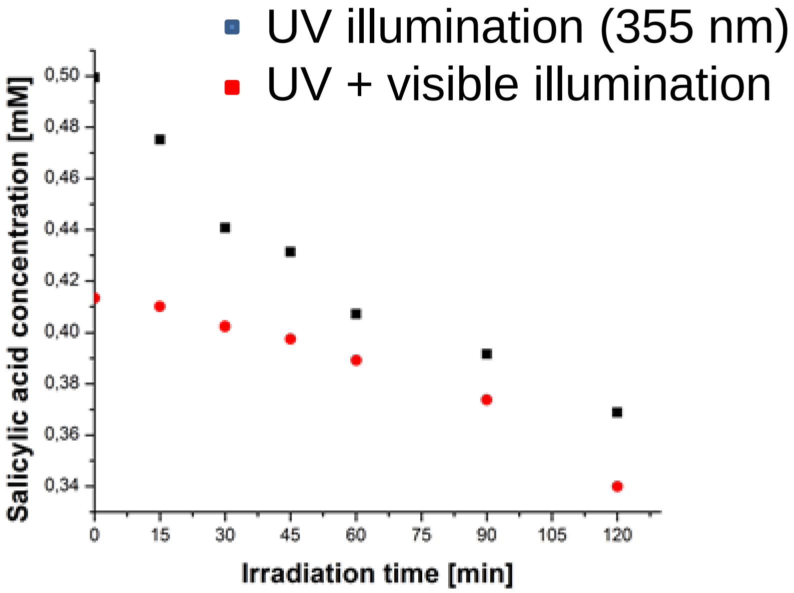
Photocatalysis : degradation of salicylic acid

C-TiO_2 sample





Adsorption in the dark
stability after 25 minuts
-> photocatalysis

Efficiency under UV illumination
Improvement under UV + visible

Promising preliminary results : to be continued

Conclusion and perspectives

- ✓ various X-TiO_2 nanoparticles
- ✓ Demonstration of efficient Solid-State DSSC based on N-doped TiO_2 nanocrystals, Influence of N-doping on device performance

⇒ *Improved photocurrent*

⇒ *Direct conversion of photons into electrons from the doped metal oxide*

- ✓ promising photocatalytic results

- ✓ Insights in the characterization of synthesized particles (HRTEM, XPS,…)
- ✓ Synthesis of novel TiO_2-based polymeric composites and characterization (structural and photocatalytic properties)
- ✓ Insights in the mechanisms of charge transfer in PV cells (-> improvement of efficiency) PhD Jin Wang
- ✓ Complementary photocatalytic measurements

Common proposal to the international call of ANR ?

Dissemination

scientific production :

- E. Popovici *et al*, **Development of systems for the laser synthesis of nanoparticles starting from liquid precursors**, Applied Surface Science (Elsevier) Volume 258, Issue 23, 15 September 2012, Pages 9326–9332,
- M. Scarisoreanu *et al*, **Structural evolution and optical properties of *C-doped TiO2 nanoparticles* prepared by laser pyrolysis**, Applied Surface Science (Elsevier) , 2012, submitted
- R. Alexandrescu, *et al*, **Development of TiO2 and TiO2/Fe-based polymeric nanocomposites by single-step laser pyrolysis**, Applied Sueface Science (Elsevier) , 2012, submitted
- H. Melhem *et al*, **Direct photocurrent generation from nitrogen doped TiO_2 electrodes in solid-state dye-sensitized solar cells: towards optically-active metal oxides for photovoltaic applications.** accepted solar energy materials and solar cells, 2012

b) Communication at International Conferences

-M. Scarisoreanu et al, Structural evolution and optical properties of C -doped TiO2 nanoparticles prepared by laser pyrolysis E-MRS 2012 Spring Meeting, Strasbourg, May 14-18, 2012

-R. Alexandrescu, et al. Development of TiO2 and Ti/Fe-based polymeric nanocomposites by single-step laser pyrolysis, E-MRS 2012 Spring Meeting, Strasbourg, May 14-18, 2012

-INVITED: R. Alexandrescu, et al. , Fe-based / methyl methacrylate polymeric nanocomposite prepared by laser pyrolysis: structural and thermal properties, 1st Annual World Congress of Advanced Materials Conference (WCAM-2012), June 6-8, 2012 Beijing, China

-INVITED: N. Herlin-Boime et al, **Laser pyrolysis, a gas phase process for synthesis of original nanoparticles suitable for development of photovoltaic applications, NANO2012, August 27-30, Rodos (Greece)**

Mobilities 2012

Dr. Nathalie Herlin-Boime : working visit in Bucharest 2326.01. 2012

Post doc Mc
(France): 05

Dr Rodica A
the period 1!

In progress : Jin Wang, PhD student, working visit in Bucharest