# Nanomaterials, Nanotechnology and Engineering of Materials



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Materials Science Department, New University of Lisbon, Portugal Members of Exec. Committee of E-MRS

# **Topics**

- What is Nanotechnology
- What are Nanomaterials
- How this implies changes in Engineering
- Examples of Applications
- A study case of products design
- Nanotech Products
- The Promise of Tomorrow
- Toxicity
- Disadvantages



# What is Nanotechnology?

### Nanotechnology is about:

- Making small objects
- Manipulating small objects
- Creating new materials by varying the size of the objects with outstanding performances, where the effects of quantum physics become more prominent
- Building structures from small objects





## What is Nanotechnology?, Continued

Nanotechnology provides mankind the ability to make things the way nature has been doing it for eons; atom by atom from the bottom up.

For example, nature takes brittle materials, but forms them together to be very strong, e.g., clam shells.







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# Nanotechnology

### **TECHNOLOGIES**

Nanomaterials Nanofabrication Scanning Probe Microscopy Self-Assembly

### **APPLICATIONS**

Super strong materials Super Slippery Materials Tissue Engineering Drug Delivery Super fast/small computers Sensors





# Is Nanotechnology really new?



During the middle ages, the Muslims who fought crusaders with swords of Damascus steel had a high-tech edge carbon nanotubes and nanowires in their sabres. Damascus sabres were forged from Indian steel called wootz. It is likely that the sophisticated process of forging and annealing the steel formed the nanotubes and the nanowires, and could explain the amazing mechanical properties of the swords.

TEM image of cementite nanowires





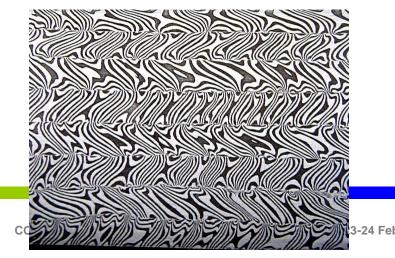
## **Damascus Steel**



50 microns

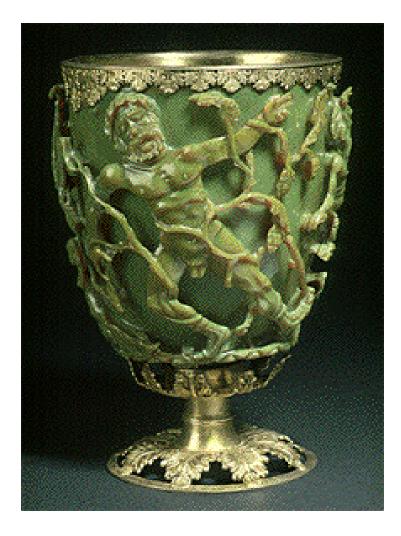
Damascus blade showing the Damascene surface pattern containing a combined Mohammed ladder and rose pattern

http://www.tms.org/pubs/journals/JOM/9809/Verhoeven-9809.html Cementite bands



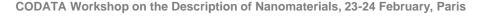


# Is Nanotechnology really new?



- Lycurgus cup,4<sup>th</sup> century AD (now at the British Museum, London).
- Depicts King Lycurgus of Thrace being dragged to the underworld
- When illuminated from outside, it appears green. However, when illuminated from within the cup, it glows red.





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# Is Nanotechnology really new?





Suspensions of spherical gold particles with various diameters (150, 100, 80, 60, 40, 20 nm from left to right) in water. The difference in colors is due to different scattering and absorption behaviour of small and large gold particles.



# How did it started in 20<sup>th</sup> century? There's Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics



Richard Feynman Cal Tech, 1959

"People tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction. *Why cannot we write the entire 24 volumes of the Encyclopedia Brittanica on the head of a pin?*"

### This goal requires patterning at the 10 nanometer scale.





# Why is Small a Big Deal?

What are some advantages of making things **smaller**?

- Some extraordinary properties can be achieved (structural, electrical, etc.)
- Economic benefits cost, quantity
- Technologic benefits speed, power, integration, practical.



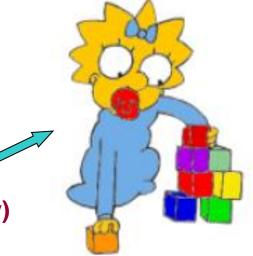


### Building Complex Structures with Small Objects



Top-down (i.e. Lithography)

#### Bottom-up (i.e. Self-assembly)

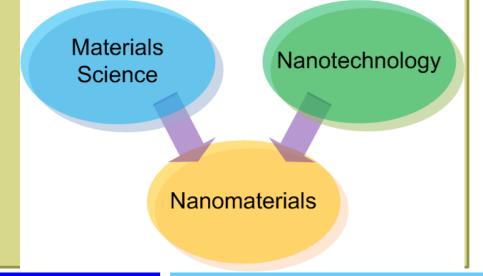






### What are nanomaterials?

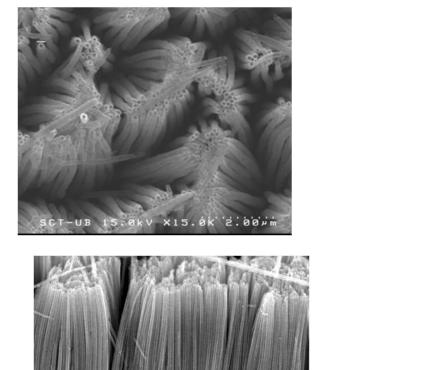
European Commission definition, 2011: "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%."

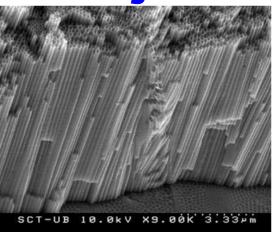


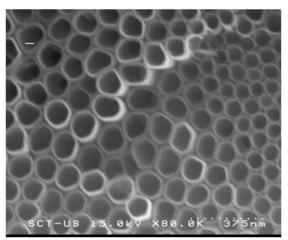




## What are Nanomaterials?: The small reference objects







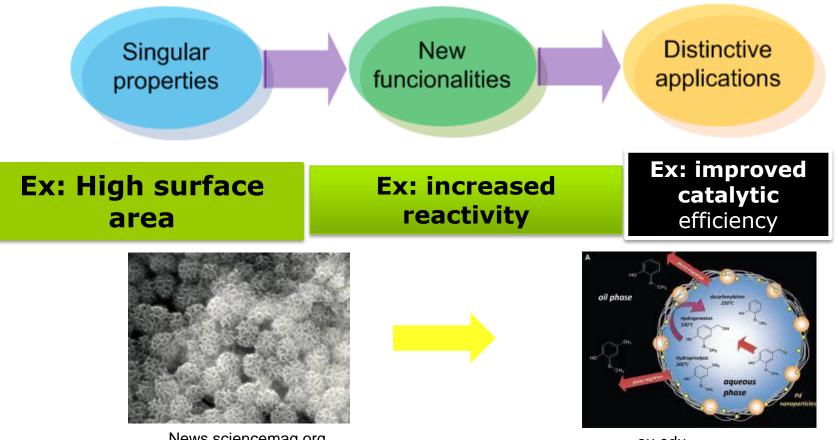
Anodic oxidation of Ti foil. Excellent electrical contact with the titanium

base electrode.





### What are the relevancy of Nanomaterials?



News.sciencemag.org

ou.edu

Nanomaterials properties controlled by surface effects such as Van der Waals forces, hydrogen bonds, covalent bonds, hydrophobicity, ionic conduction or quantum mechanical tunneling

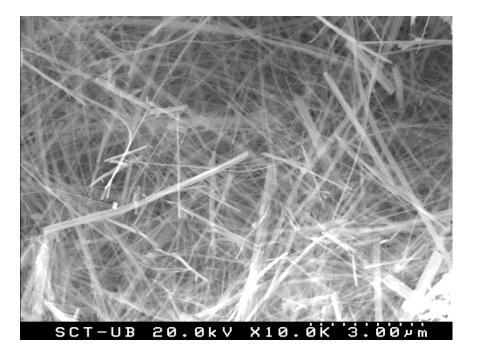


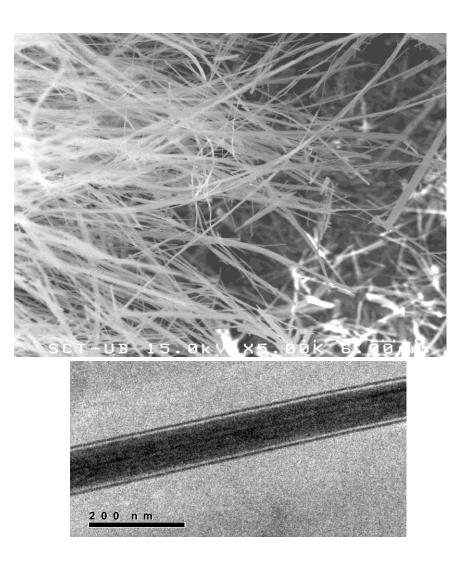


### What we can do with Nanomaterials?

### **INCREMENT OF SURFACE AREA**

Hydrothermal treatment with 10M NaOH







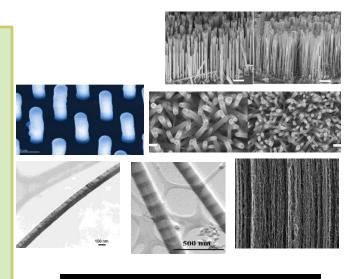


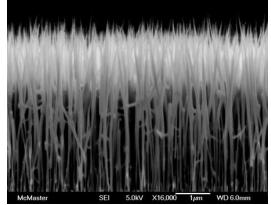
## What we can do with Nanomaterials?

### **Nanowires and Nanotubes**

**Lateral dimension:** 1 – 100 nm

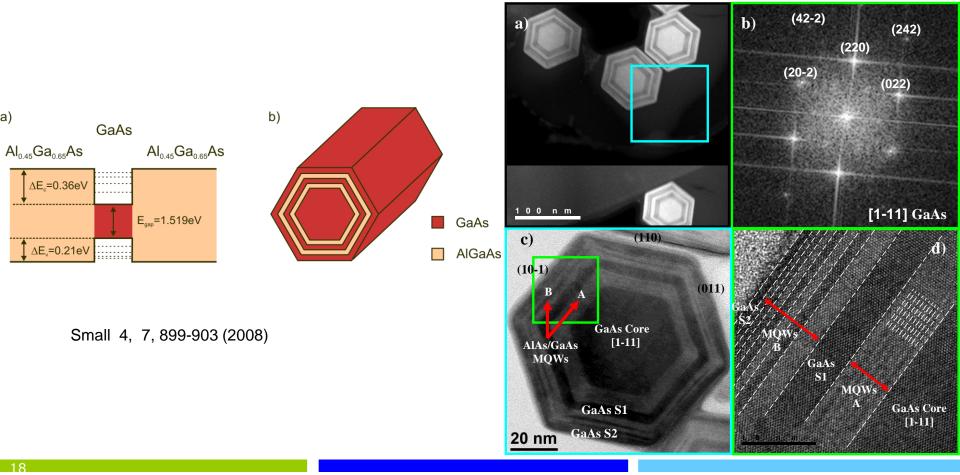
- Nanowires and nanotubes exhibit novel physical, electronic and optical properties due to
  - Two dimensional quantum confinement
  - Structural one dimensionality
  - High surface to volume ratio
- Potential application in wide range of nanodevices and systems
  - Nanoscale sensors and actuators
  - Photovoltaic devices solar cells
  - Transistors, diodes and LASERs





Nanowire Solar Cell: The nanowires create a surface that is able to absorb more sunlight

## Nanomaterials: Nanowires with coaxial quantum wells



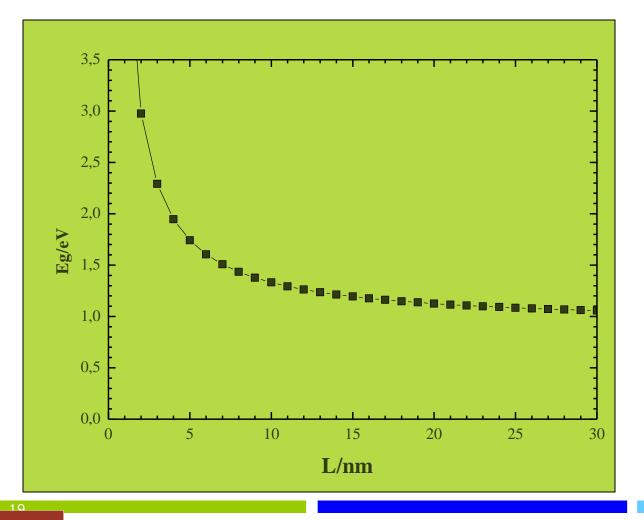


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CSU

### What we can do with Nanomaterials?

### Play with "colour": Band gap engineering



ZH Hu, et al. J. Non Cryst. Solids Vol.: 352 Issue: 9-20 Pages: 1900-1903, 2006

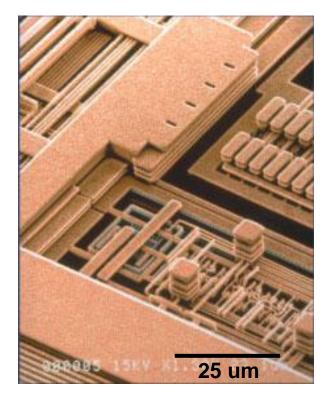
Y. Xu et al, J. Non
Cryst. Solids, Vol.:
352 Issue: 9-20
Pages: 19721975, 2006



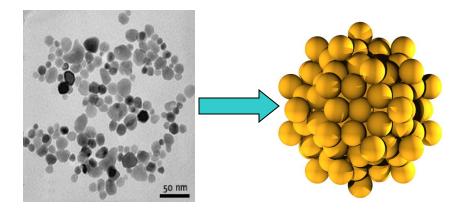


i3N

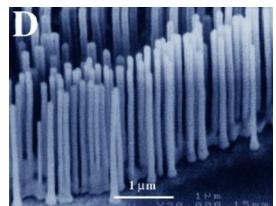
## **Engineering: making small objects**



Optical lithography Electron beam lithography **Top-down approach** 



Self-assembly of nanoparticles, individual atoms, molecules **Bottom-up approach** 



Chemical deposition Bottom-up approach

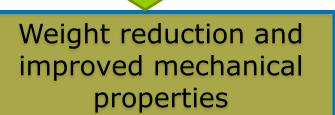




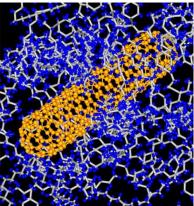
# **Carbon Nanotubes in Engineering**

### Composites

Polymer, ceramic or metal composites with CNT



#### **Polymer-CNT composite simuation**



#### nasa.gov



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#### **Polymer-CNT composites examples**



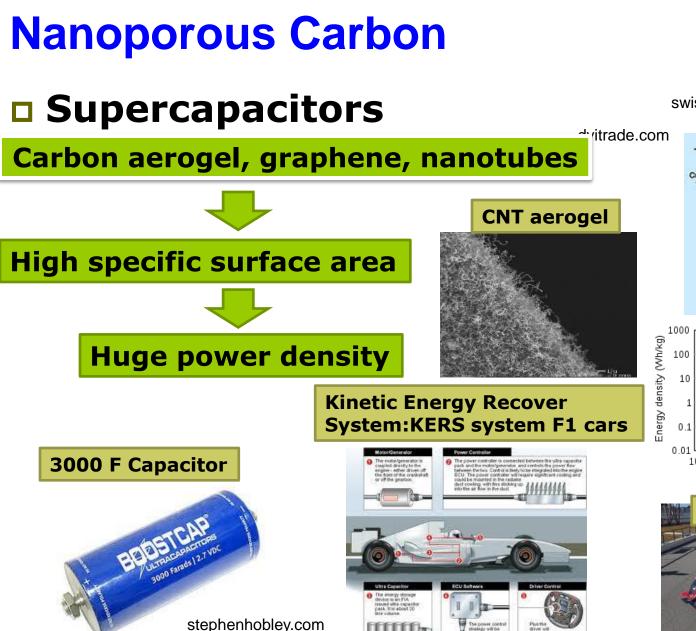
justmeans.com

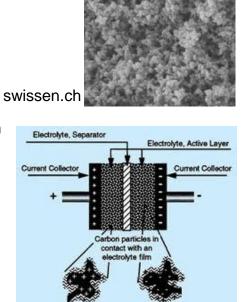
Zyvex Technologies vessel "Piranha"

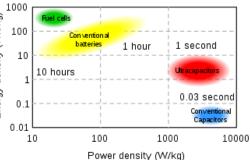


Carbon fiber infused with CNT Tensile strength 60 Gpa (60 x higher than steel)





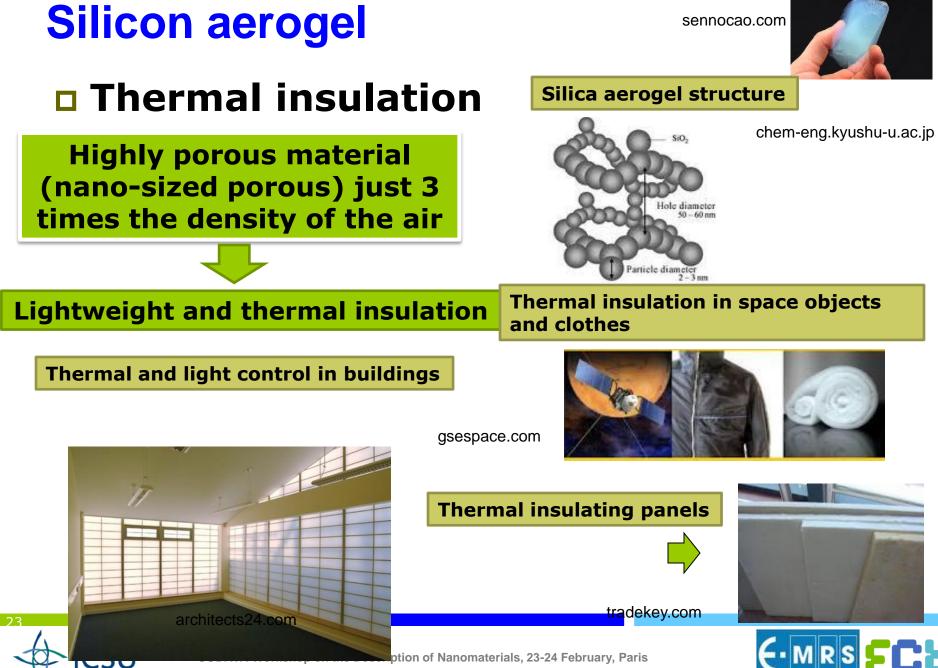








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## **Platinum nanostructures**

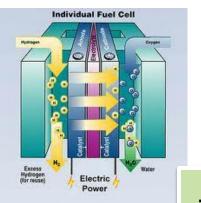
### Fuel Cells

### **Increased electrode effective area**

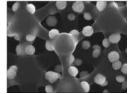


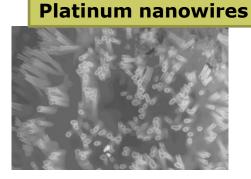
#### optics.rochester.edu

**Reduce Pt amount and/or cell size** 



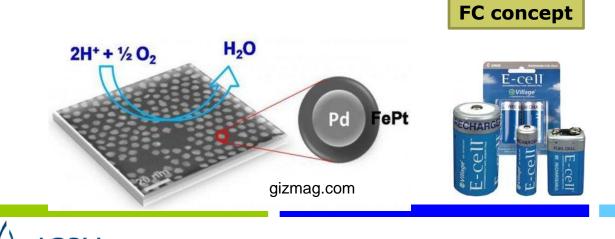
ne.ucsd.edu





Pt nanowires can increase the area and mass specific activities of 0.77 mA/cm<sup>2</sup> and

1.83 A/mg<sub>Pt</sub>, respectively.



#### Honda electric car





### **Metallic nanoparticles: Reinforcement**



### Steel reinforcement

**Reduces surface unevenness** 

printedelectronicsworld.com

V or Mo reinforced bolts



Limits the number of stress risers

### **Reduced fatigue cracking**

#### Improve the delayed fracture problems associated with high strength bolts

#### Cu reinforced steel



Increased safety, less need for monitoring and more efficient materials in constructions prone to fatigue issues. Structural integrity at temperatures up to 1000 F (with regular steel this happens for 750 F) combined with good formability, corrosion resistance and good surface finishing.



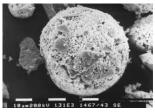


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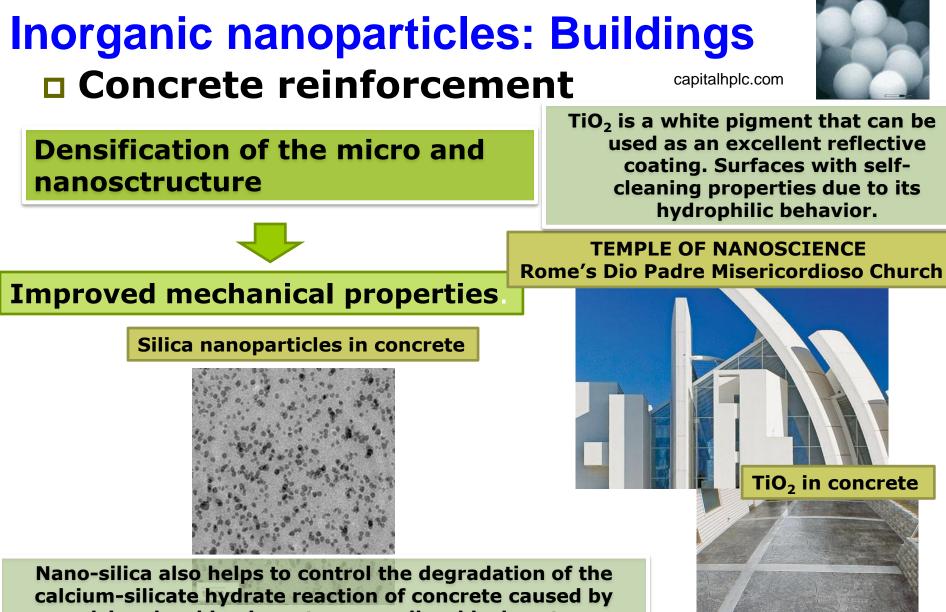
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## **Inorganic nanoparticles**

mtm.kuleuven.be



#### Additives to lubricants **Tungsten disulphide fullerene** nanoprom.it Small and stable lubricant particles **Reduced wear** Reduced friction, noise, heat and vibration results in reduced energy 0.20 consumption and decreased air Raw Oil Nano Oil I (0.01 vol.%) pollution Nano Oil 8 (0.05 vol % Friction Coefficien **High performance lubricants** 0.50 0.05 1000 Load [N] tech-star.it CODATA Workshop on the Description of Nanomaterials, 23-24 February, Paris



calcium leaching in water, as well as block water penetration, leading to improvements in durability.

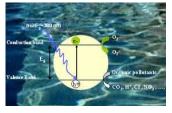


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# **Inorganic nanoparticles: Cleaning**

### Self-cleaning surfaces



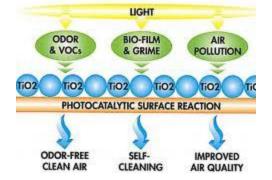
uab.es

### **TiO<sub>2</sub> nanoparticles**



Sterilizing and antifouling properties Hydrophilic nature allows to form sheets out of raindrops, washing off the dirty particles broken down in the previous process.

surfacesolutions.com



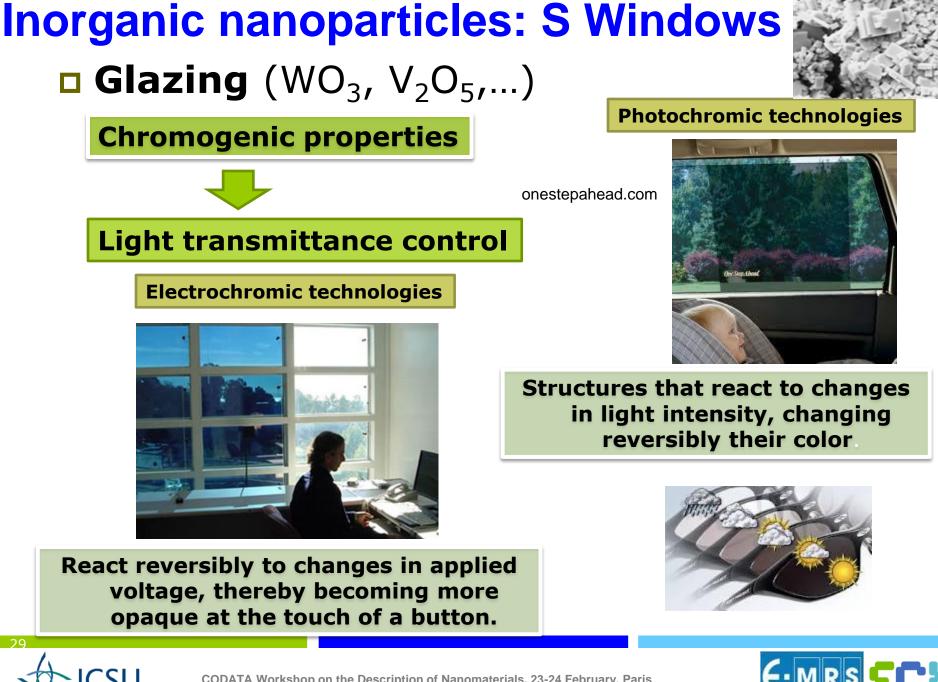
Particles catalyze powerful reactions breaking down organic pollutants, volatile organic compounds and bacterial membranes.



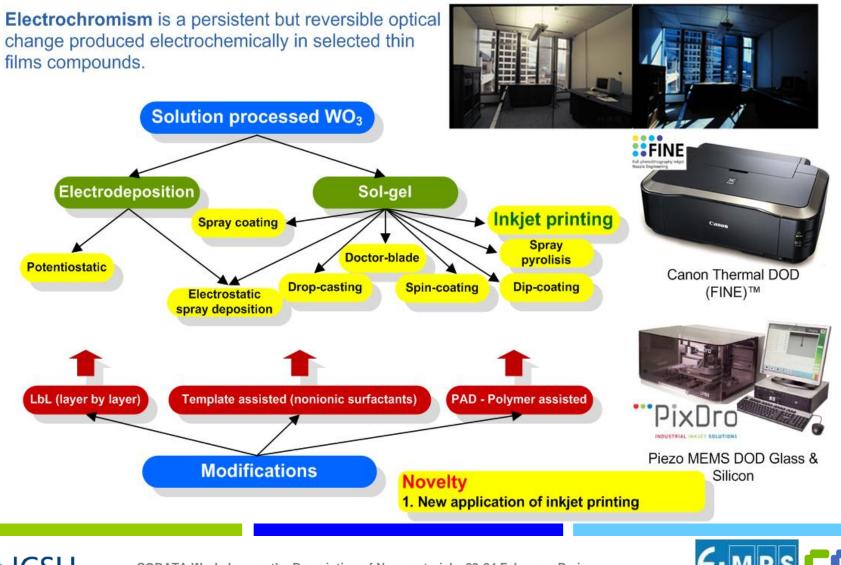


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## **Examples of nanoparticles formulation** Solution-processed WO<sub>3</sub>



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## **Electrochromic ink formulation**

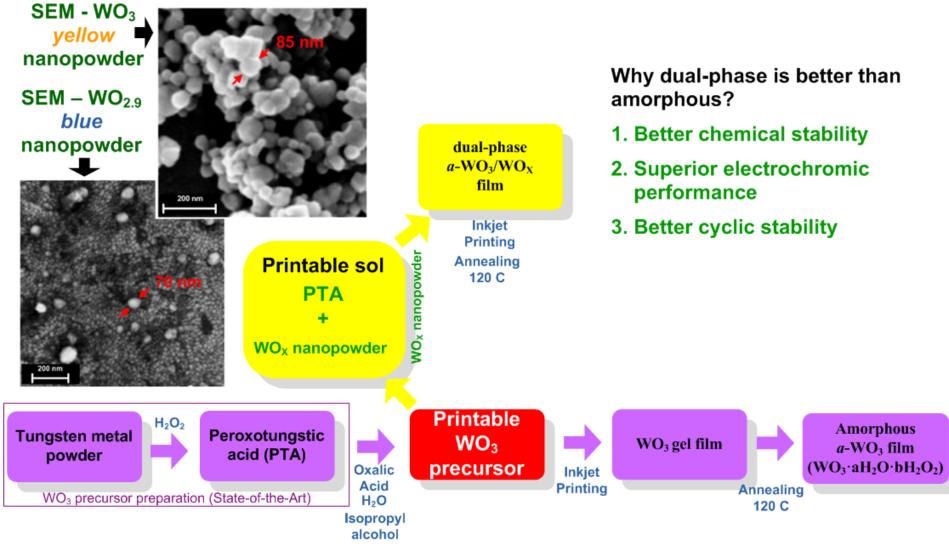




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## **Electrochromic ink formulation**

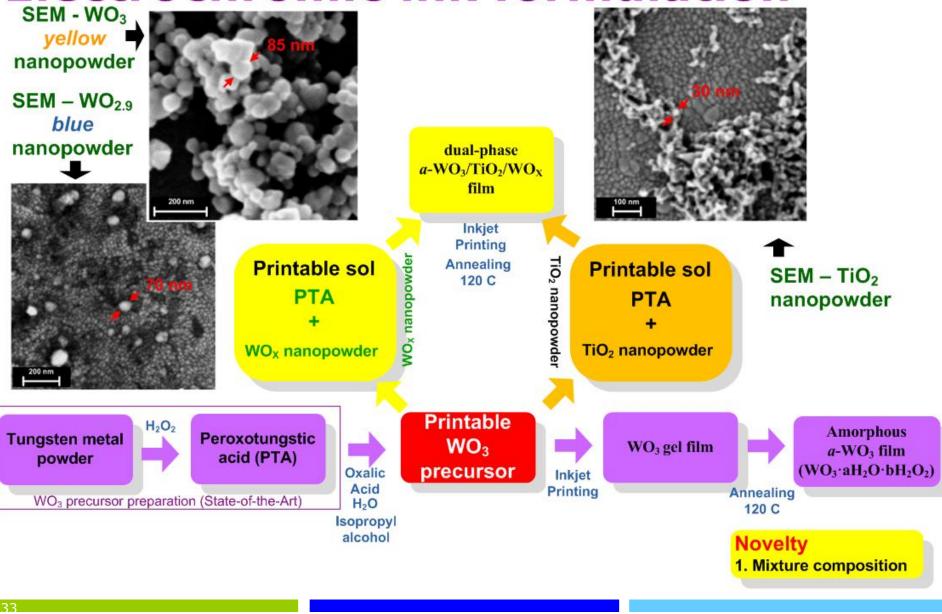




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## **Electrochromic ink formulation**

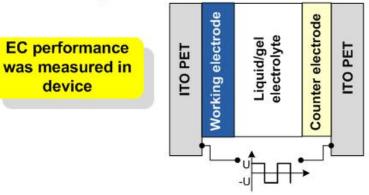


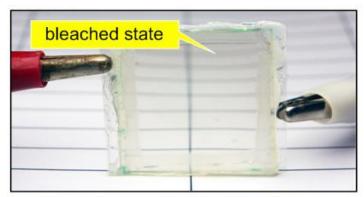


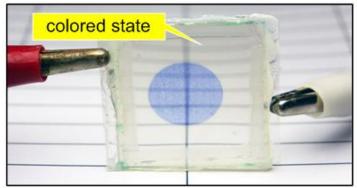
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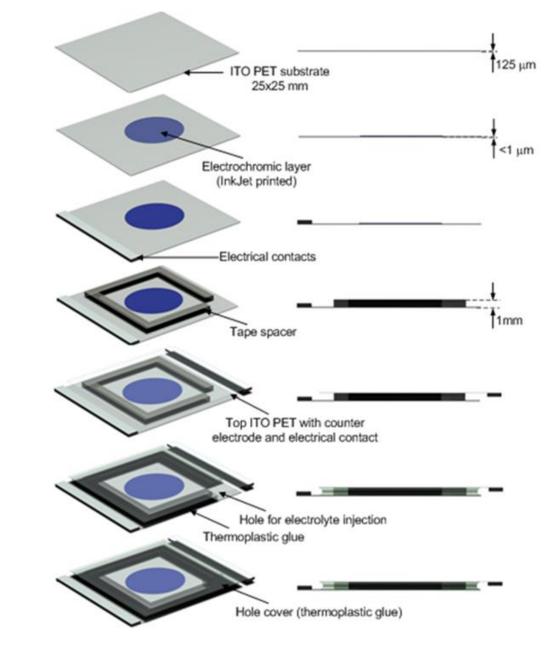
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## Encapsulation











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## Methodology -classically

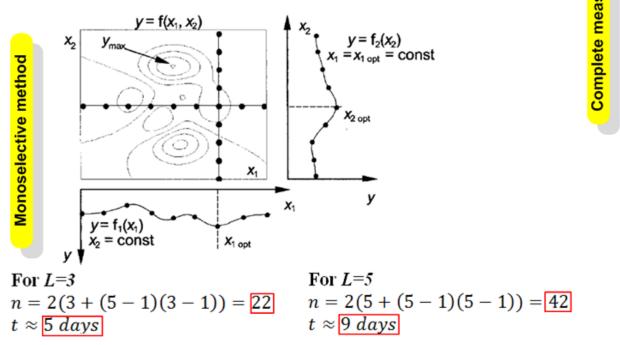
#### Factors to be studied:

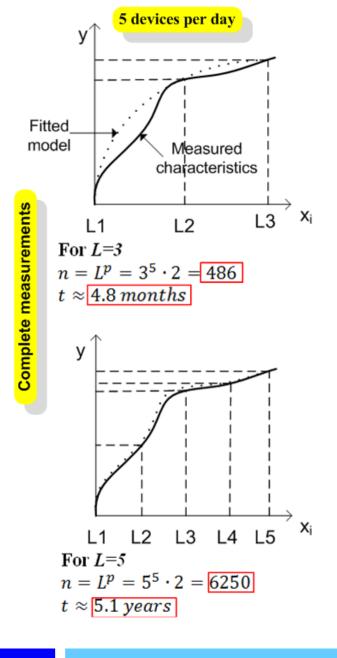
- w<sub>PTA</sub> Peroxotungstic Acid content;
- w<sub>OAD</sub> Oxalic Acid content;

 $w_{TiO2}$  - amount of TiO<sub>2</sub> nanoparticle dispersion;  $w_{WOX}$  - amount of WO<sub>X</sub> nanoparticle dispersion;  $WO_X$  - stoichiometry of tungsten oxide

nanoparticles;

wiso/water - base solution content.







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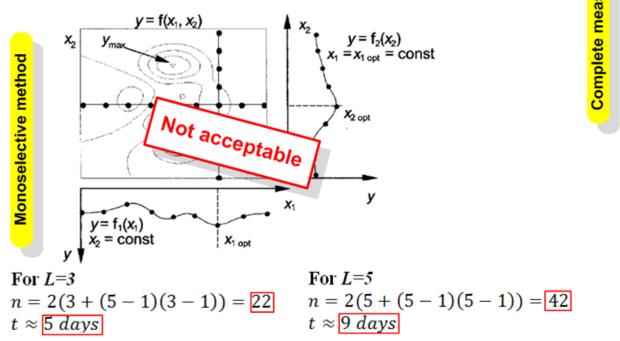
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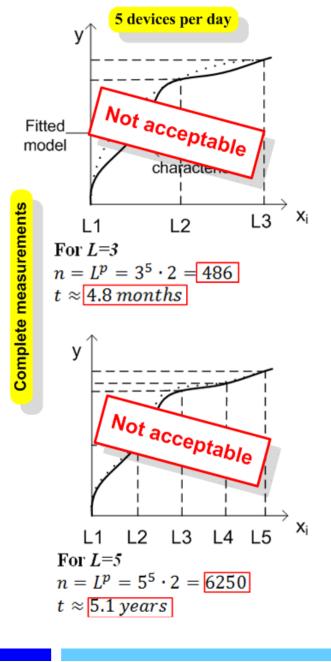
## Methodology -classically

#### Factors to be studied:

- *w*<sub>PTA</sub> Peroxotungstic Acid content;
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  - nanoparticles;

wiso/water - base solution content.



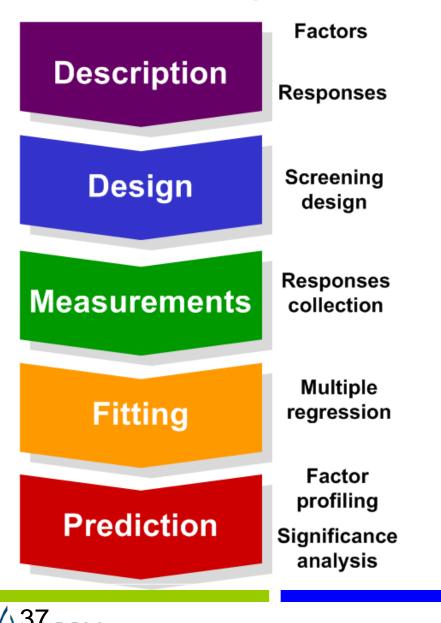




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#### Methodology -Design of Experiment (DOE)



Supported by SAS JMP software

#### Novelty

1. Sophisticated statistical technique applied to complex electrochromic studies

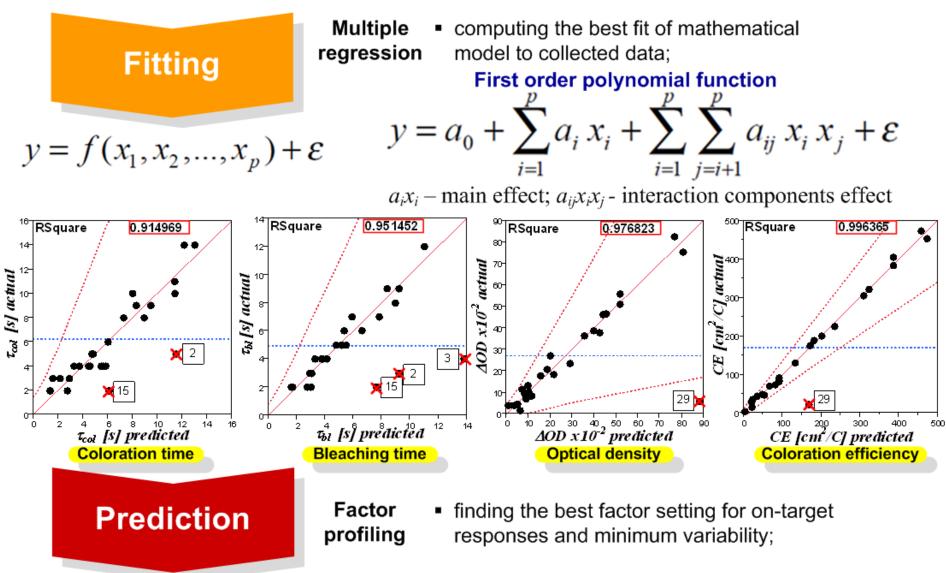


### **Design of Experiment**

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Decerintien	Factors	<ul><li>mixture components (continuous factors);</li><li>type of particles (categorical factors);</li></ul>
Description	Responses	<ul> <li>mechanical, optical and electrical properties of EC layer;</li> <li>fluid (ink) parameters;</li> </ul>
Design	Screening design	<ul> <li>determination of mixture formulations for all devices in a test;</li> </ul>
		D-Optimal designs are most appropriate for screening experiments because the optimality criterion focuses on precise estimates of the coefficients
	Rec	ipes for 30 mixtures (30 devices)
Measurements	Responses collection	<ul> <li>measurements of responses for each device;</li> </ul>

#### Design of Experiment -mathematical model





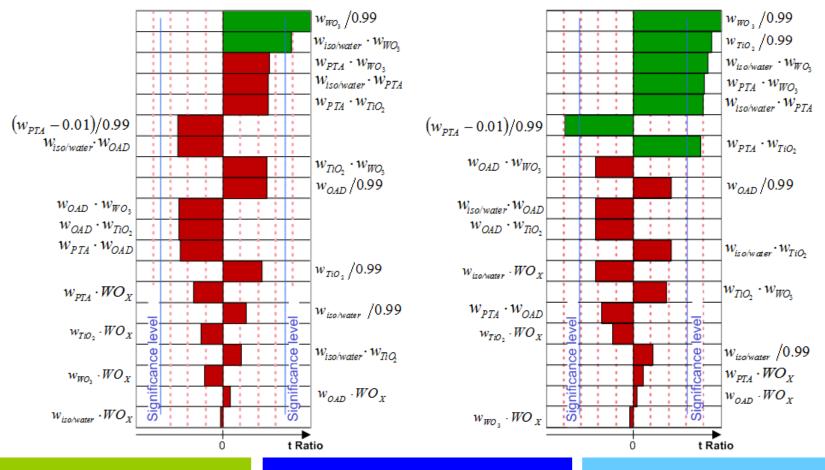
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Significanceexamination of many factors to see which have<br/>the greatest effect on the response

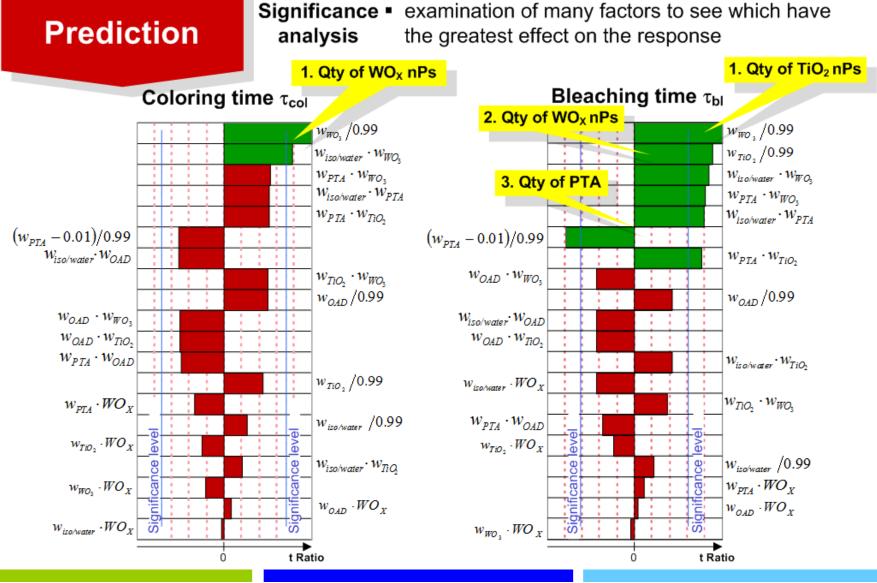
#### Coloring time $\tau_{col}$

#### Bleaching time $\tau_{bl}$





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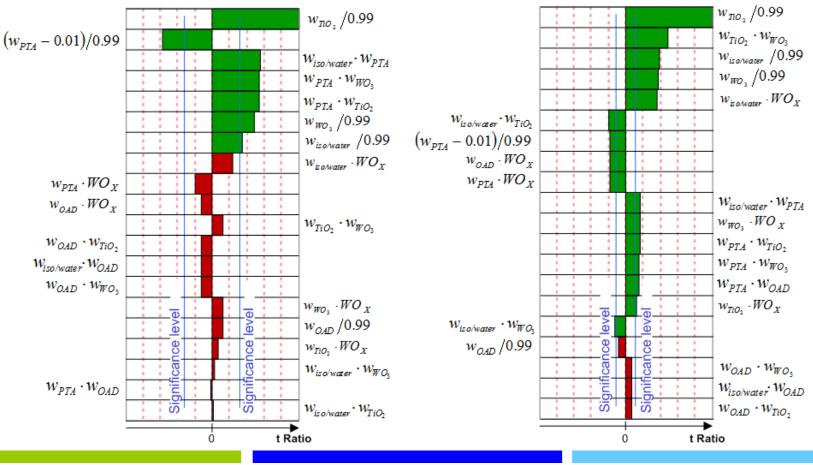
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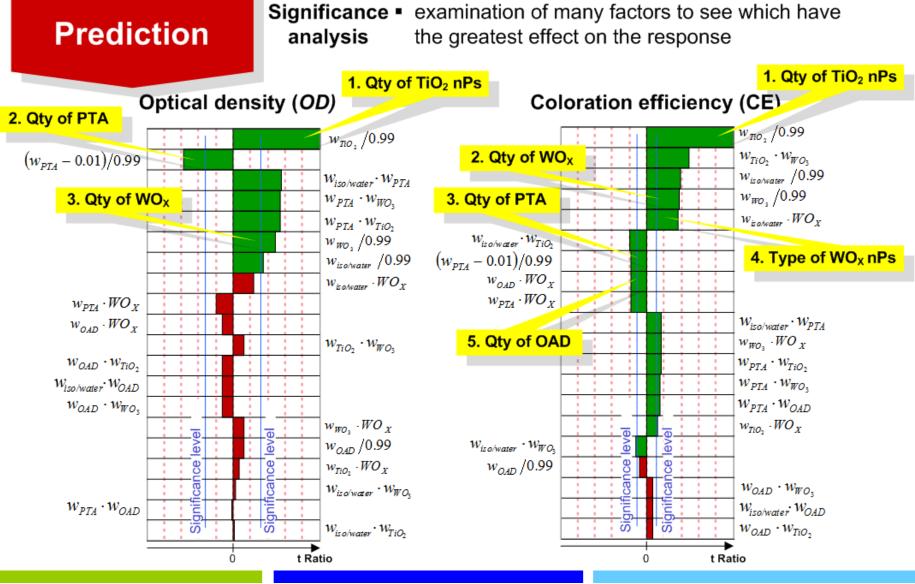
#### Optical density (OD)

#### **Coloration efficiency (CE)**



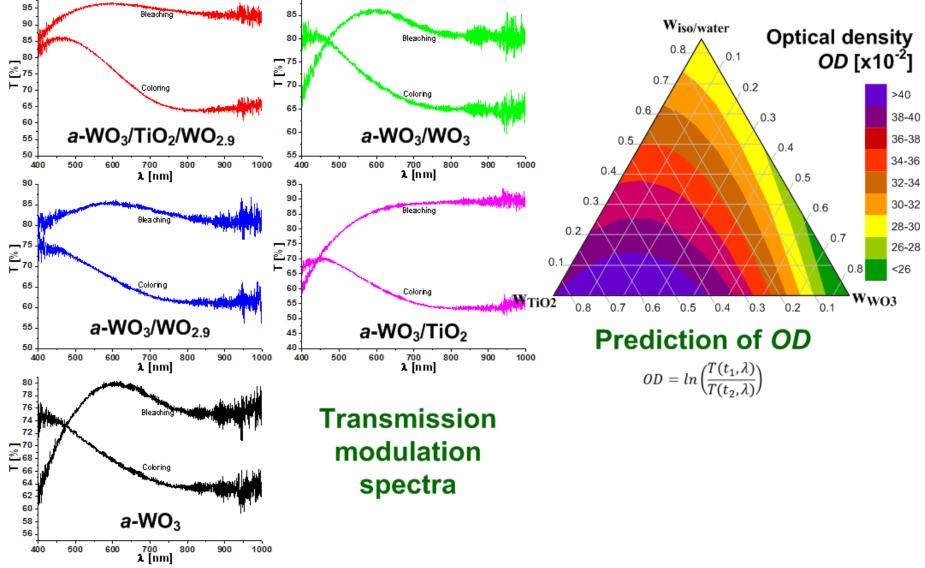


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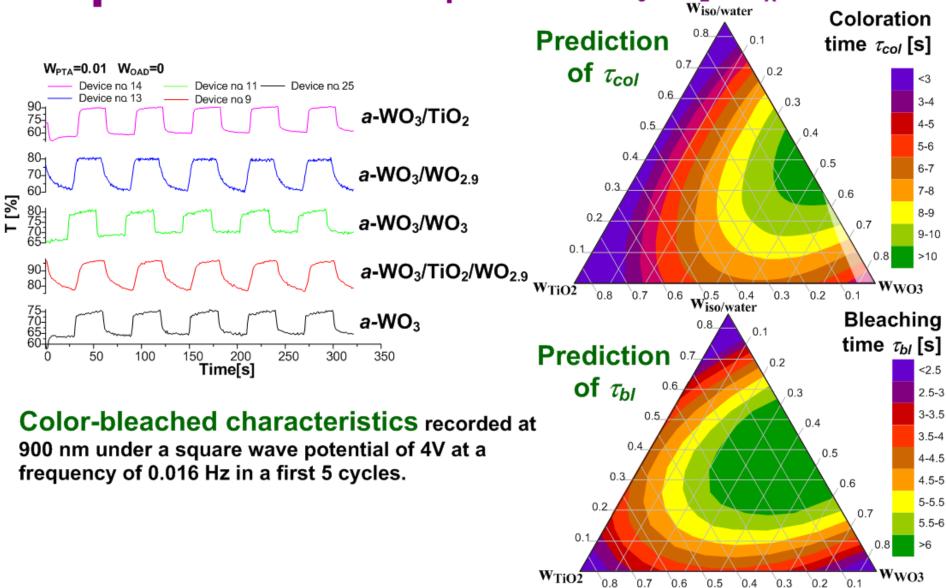




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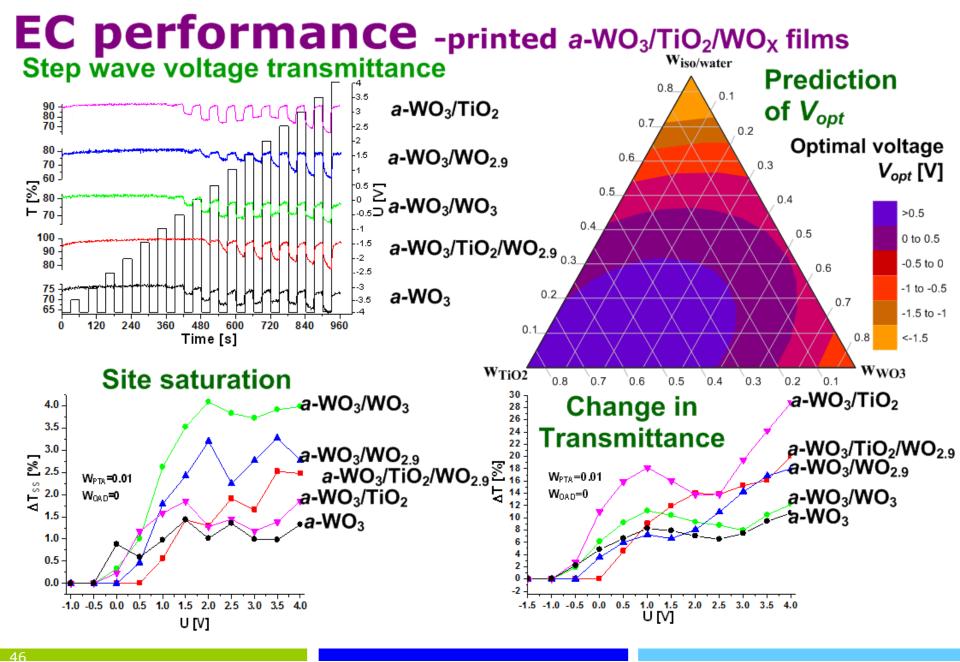
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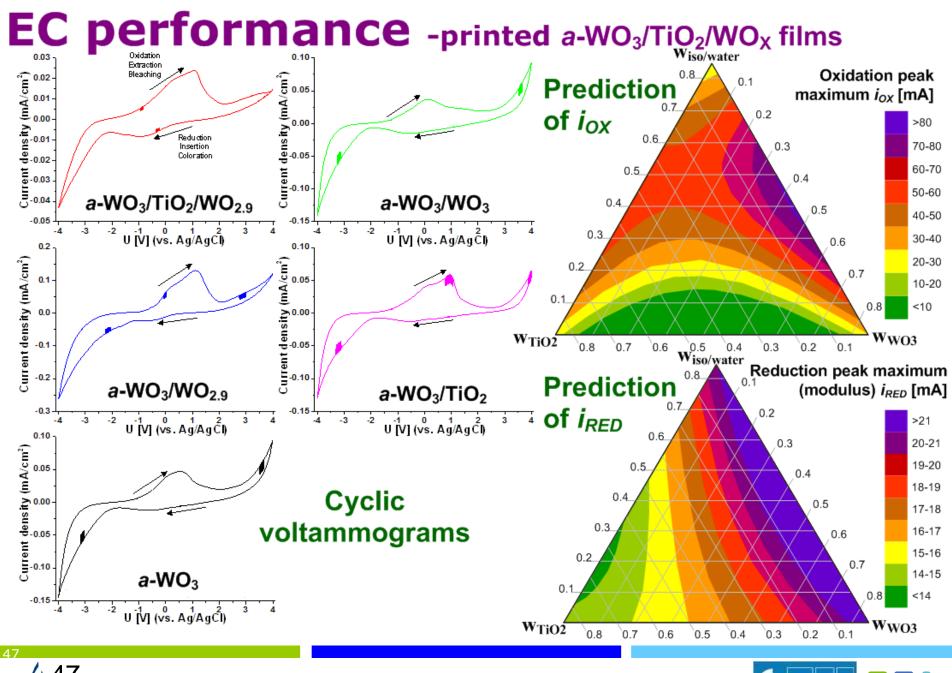
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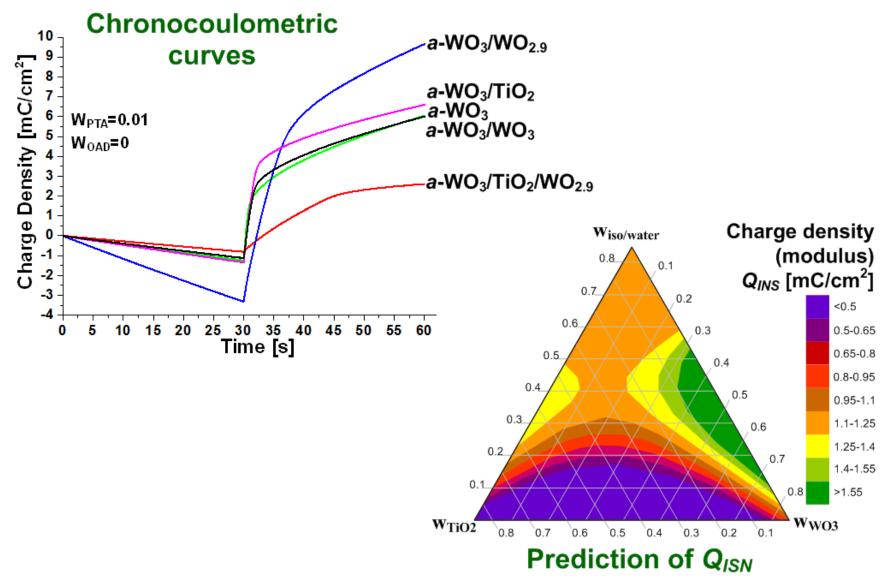
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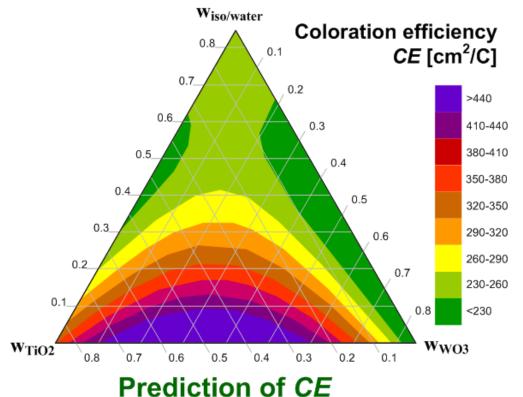


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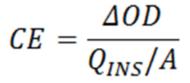
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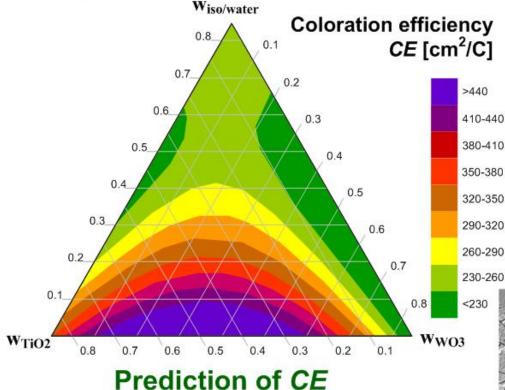
#### **Overall performance**



In State-of-the-Art for PTA based EC devices: CE<120[cm<sup>2</sup>/C]





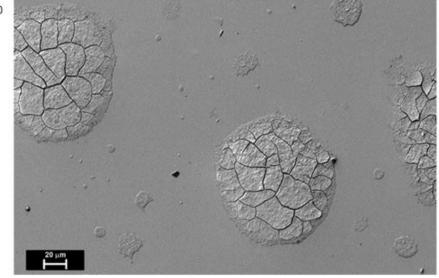


**Overall performance** 

$$CE = \frac{\Delta OD}{Q_{INS}/A}$$

Surface area (A) is overestimated

#### SEM picture of a printed a-WO<sub>3</sub>/TiO<sub>2</sub>/WO<sub>X</sub>





CE<120[cm<sup>2</sup>/C]

In State-of-the-Art for PTA based EC devices:

50



#### Factors

 $w_{TiO2}$  - amount of TiO<sub>2</sub> nanoparticle dispersion;

 $w_{WOX}$ - amount of WO<sub>X</sub> nanoparticle dispersion;

 $w_{PTA}$  - Peroxotungstic Acid content;

 $WO_X$  - stoichiometry of tungsten oxide

We can plot and predict any

relation between factors and

responses

We can test any hypothesis

We can design device with

desired preformance

**Prediction accuracy < 10%** 

 $w_{OAD}$  - Oxalic Acid content;

nanoparticles;

*w*<sub>iso/water</sub>- base solution content.

#### Responses

- 1. Mechanical parameters
  - d film thickness;
  - R<sub>q</sub> film roughness;
  - 2. Optical parameters defined for =900nm
    - $\tau_{col}$  coloration time;
    - $\tau_{bl}$  bleaching time;
    - OD change in optical density;
    - $T_{col}$  transmittance in coloration state;
    - $T_{bl}$  transmittance in bleaching state;
    - $\alpha$  optical absorption coefficient;

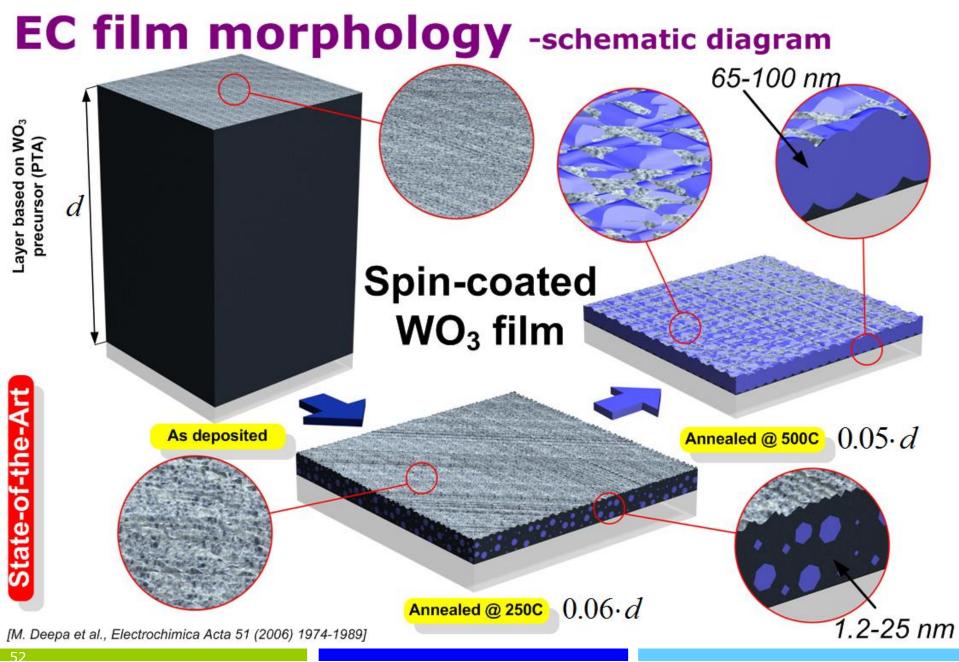
#### 3. Electrical parameters

- $i_{RED}$  reduction peak max.
- $i_{OX}$  oxidation peak max.
- Qins Charge inserted to the device
- 4. Fluid parameters of the ink
  - υ- ink viscosity;
  - $\gamma$  ink surface tension;
  - $\theta$  ink contact angle on ITO PET substrate;  $\rho$ - ink density;
- 5. Overall performance defined for =900nm CE - coloration efficiency



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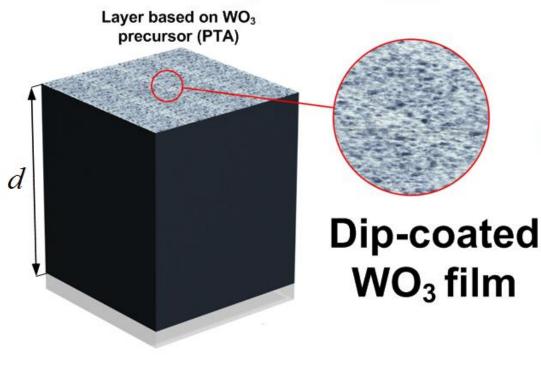






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CSU CC

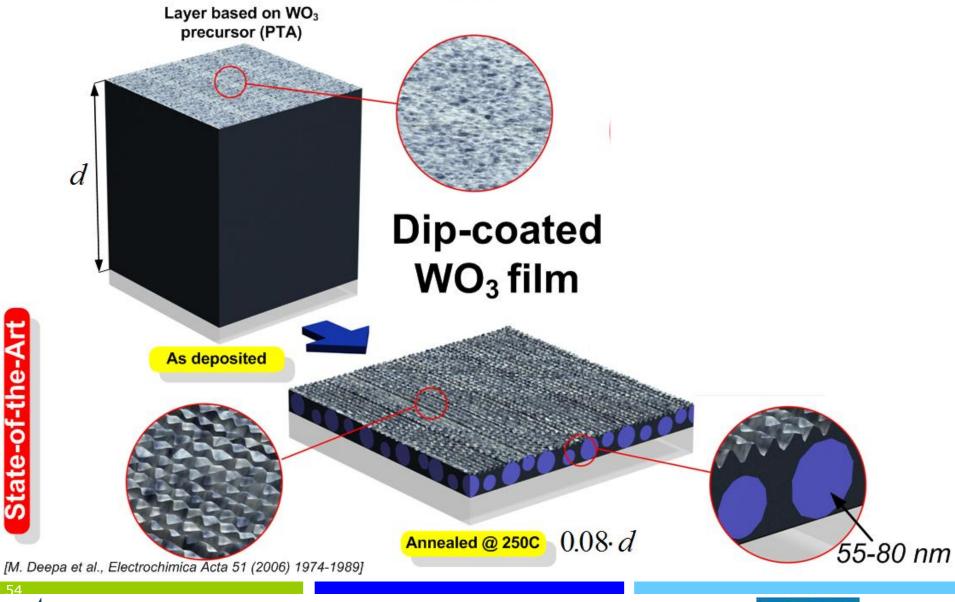


[M. Deepa et al., Electrochimica Acta 51 (2006) 1974-1989]



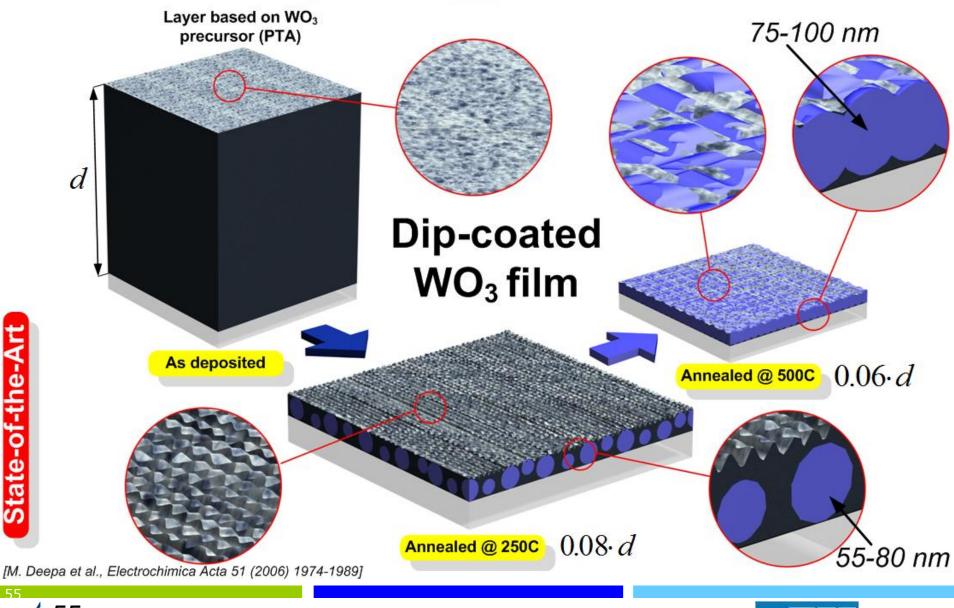
State-of-the-Ar





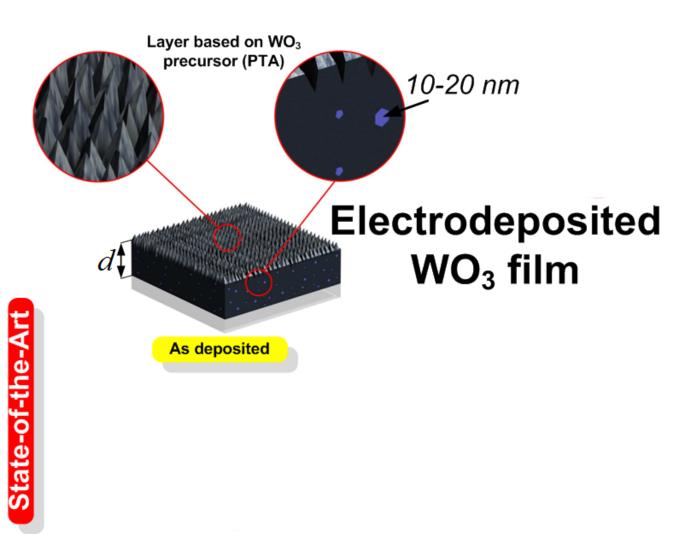








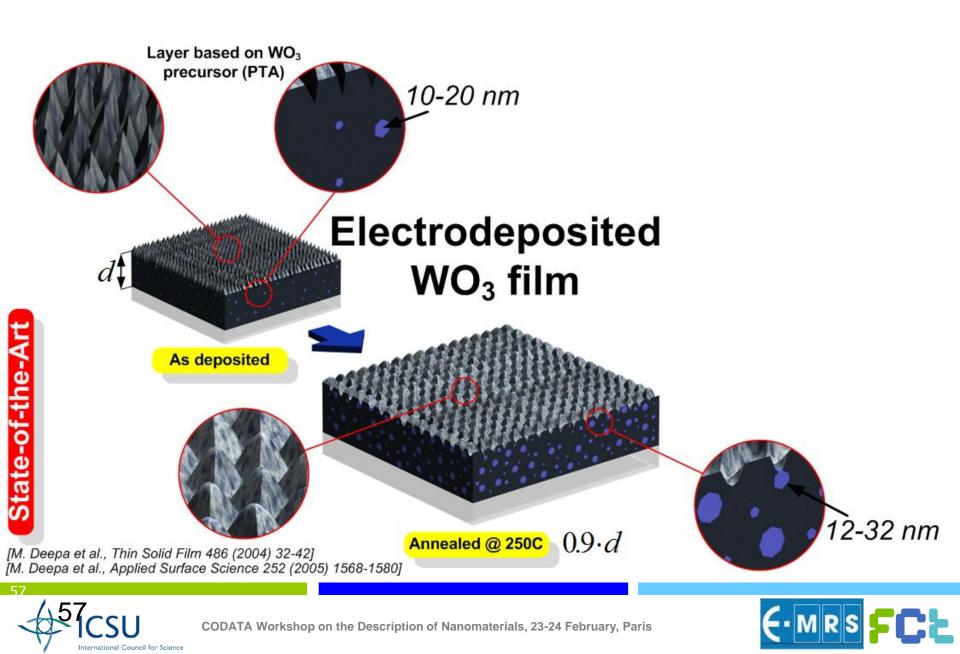


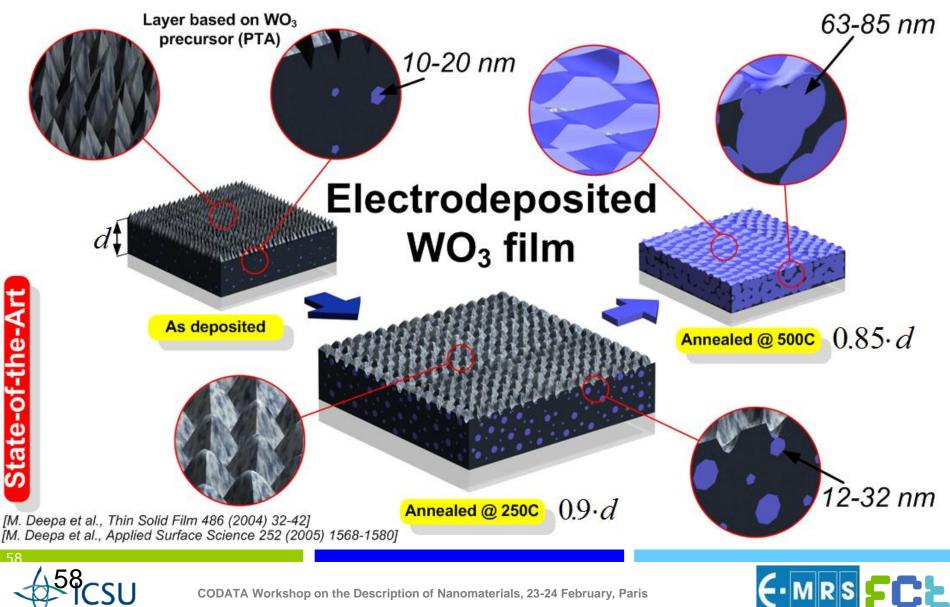


[M. Deepa et al., Thin Solid Film 486 (2004) 32-42] [M. Deepa et al., Applied Surface Science 252 (2005) 1568-1580]

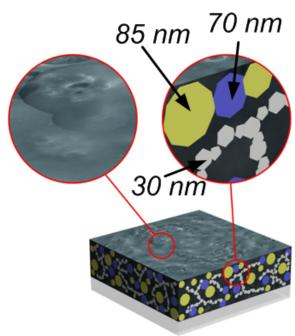


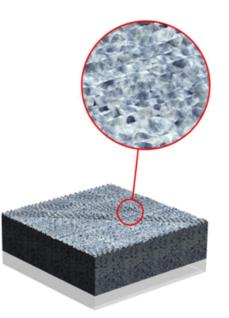






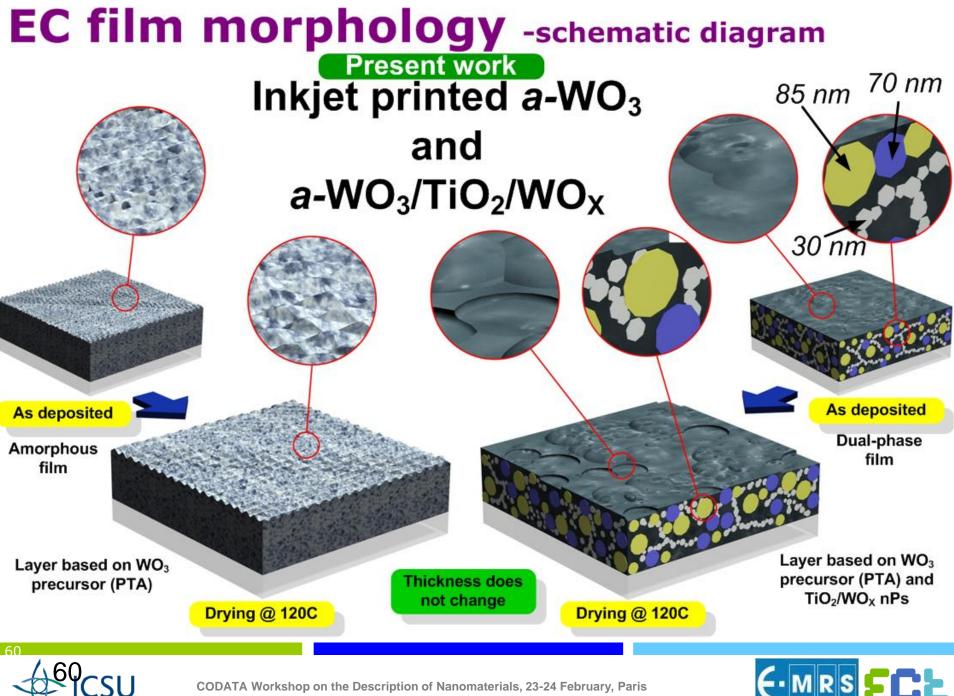
#### Present work Inkjet printed a-WO<sub>3</sub> and a-WO<sub>3</sub>/TiO<sub>2</sub>/WO<sub>x</sub>



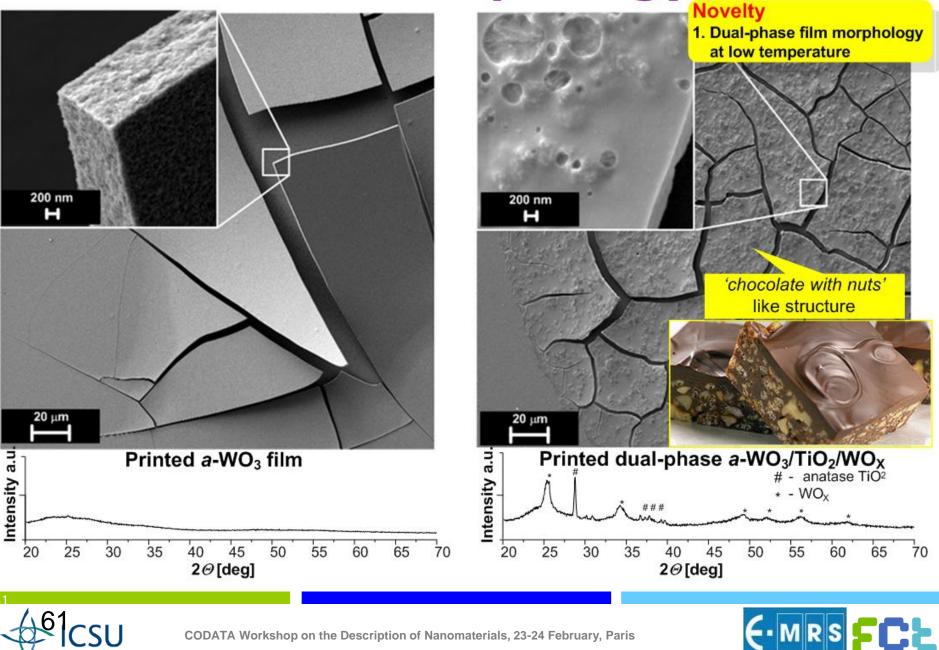




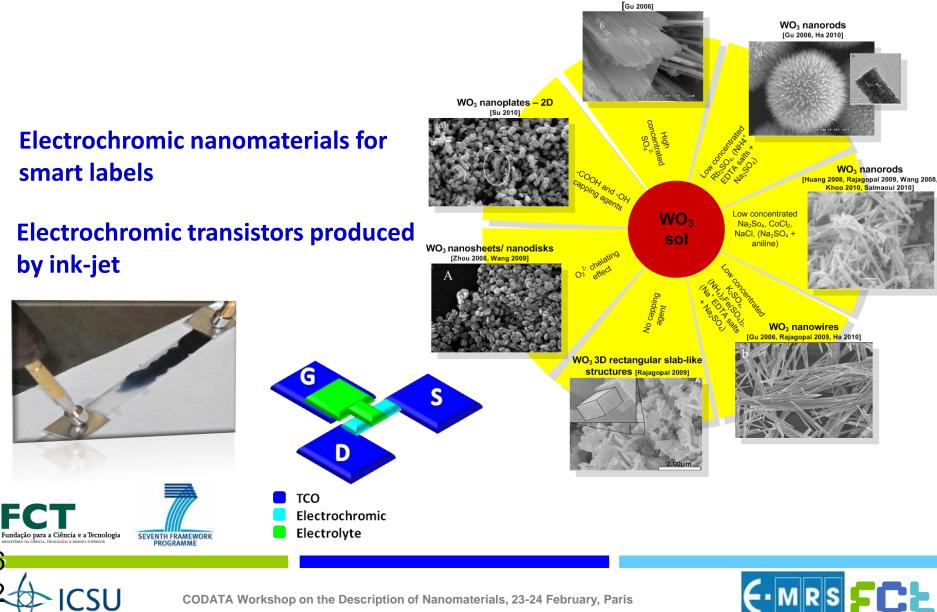




#### Printed EC film morphology -SEM, XRD

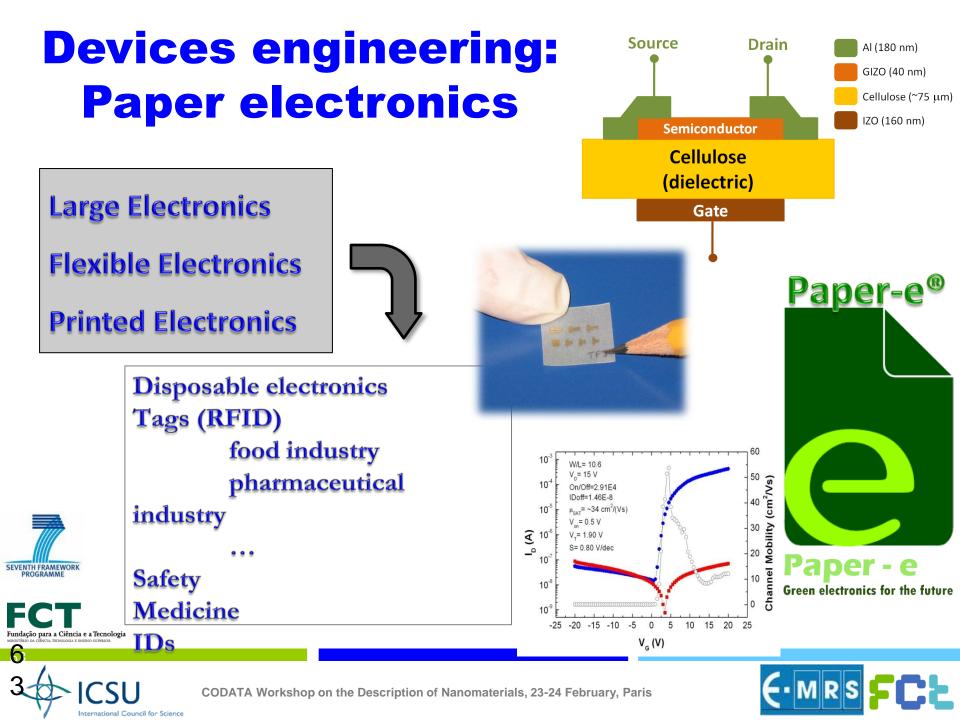


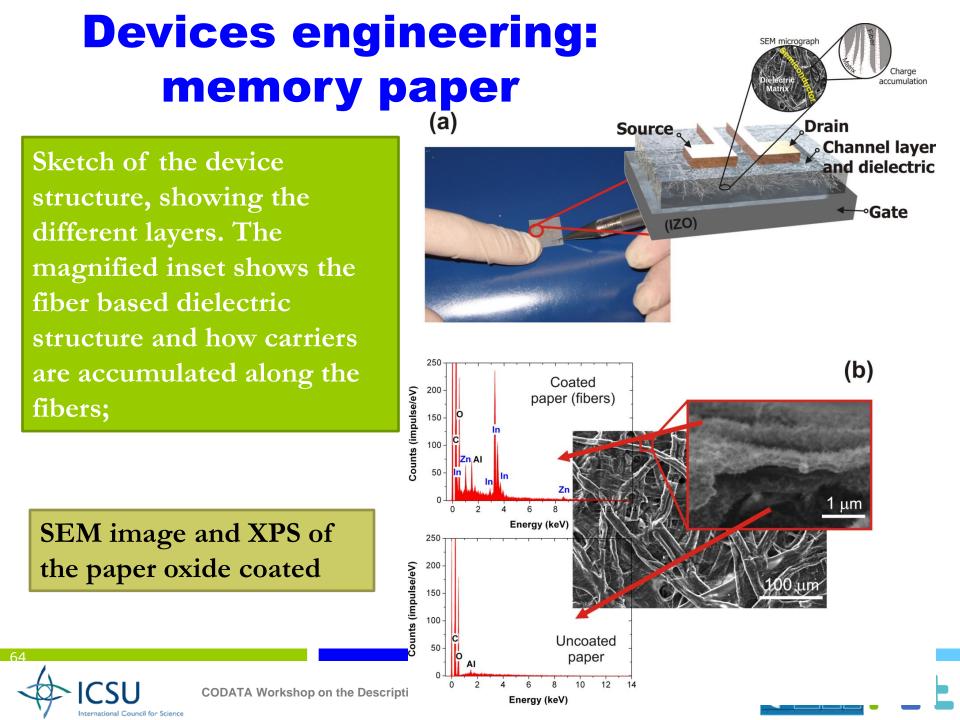
#### **Devices engineering**



WO<sub>3</sub> nanoplates – 2D

ternational Council for Science





## Example of nanofabrication on paper fibres

Lins

COLON P

Inauguração do Laboratório de Nanofabricação CENIMAT - Centro de Investigação de Materiais Departamento de Ciência dos Materiais 28 de Fevereiro de 2011





10 µm



#### **Devices engineering. Bio-batteries**

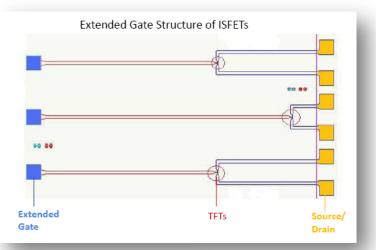
# **Enzyme biosensors based on ion-selective field-effect transistors**

Inkjet printed and "doctor blade" TiO<sub>2</sub> photodetectors for DNA biosensors

Flexible electrochemical device able to generate electrical energy from physiological fluids

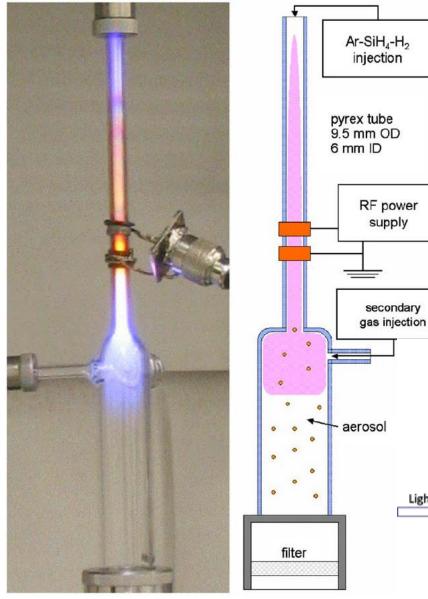


I. Bernacka-Wojcik et al., Biosensors & Bioelectronics, 25 (2010) 1229-1234



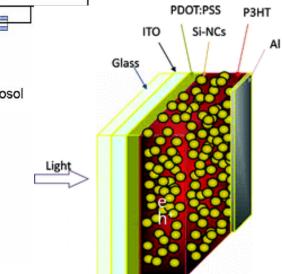


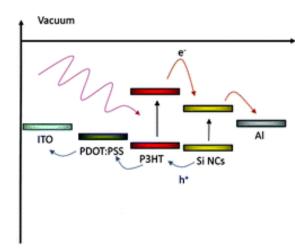




# **Hybrid Solar**

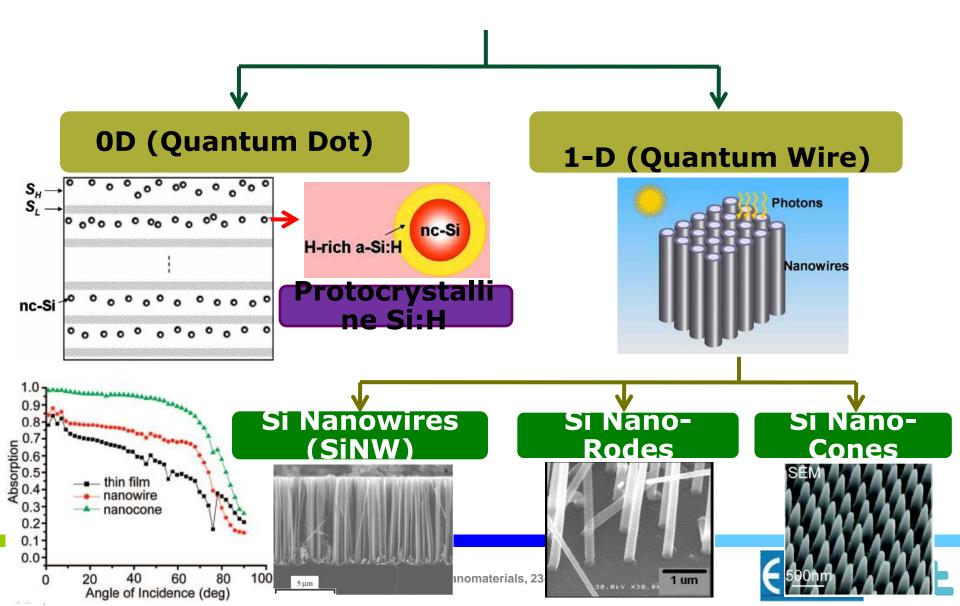
#### *Hybrid Sinanoparticle/polymer layers for solar cell applications*







#### Devices engineering: Nanoscale base solar cells



#### **Nanotech Products**

Examples include

- ICT applications
- •Sporting Goods
- •Clothing and Fabrics
- Medical
- •Other

CSL

Buckyball sculpture created by former physicist Julian Voss-Andreae.





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#### **The Promise of Today**







#### **Nanotech Products**

Other Products, Continued

Window Coatings

**Pilkington** (<u>www.pilkington.com</u>)

creates a coating for window glass that uses a chemical reaction to breakdown and loosen organic dirt particles from the glass when activated by the ultraviolet rays from natural daylight and the oxygen in the air.



Glass coating is hydrophillic.





#### **The Promise of Tomorrow**

Nanotechnology & Nanomaterials has the potential to:

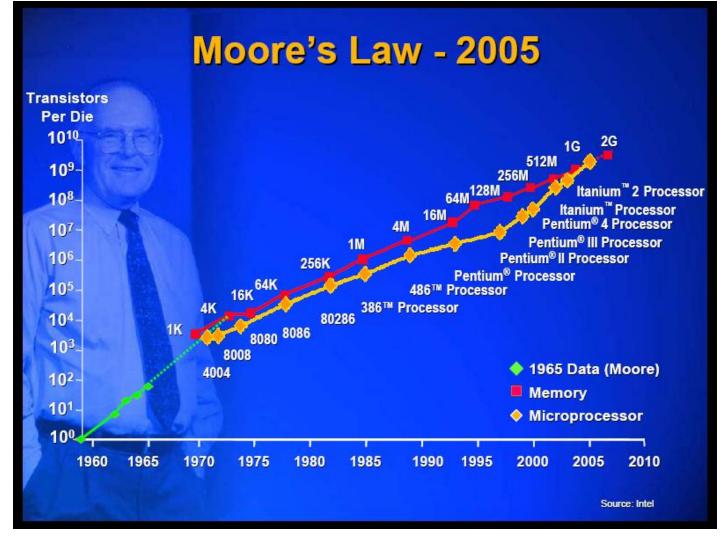
- To promote new outstanding Materials performances
- Solve Information Speed Limitations
- Solve Energy Problems
- Cure Cancer
- Eradicate Disease
- Slow Down Aging
- Solve World Hunger
- Colonize Space

# Without nanotechnology, it is likely none of these are possible.





# The First "Law" of Small(er)

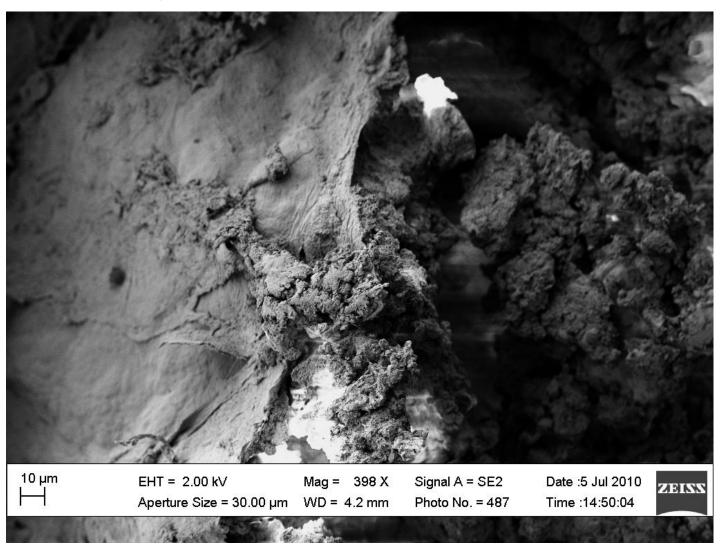


The rapid (exponential) rate of miniaturization of semiconductor devices is unprecedented for any technology or business.





### **Toxicity: Liver of a Zebra Fish**



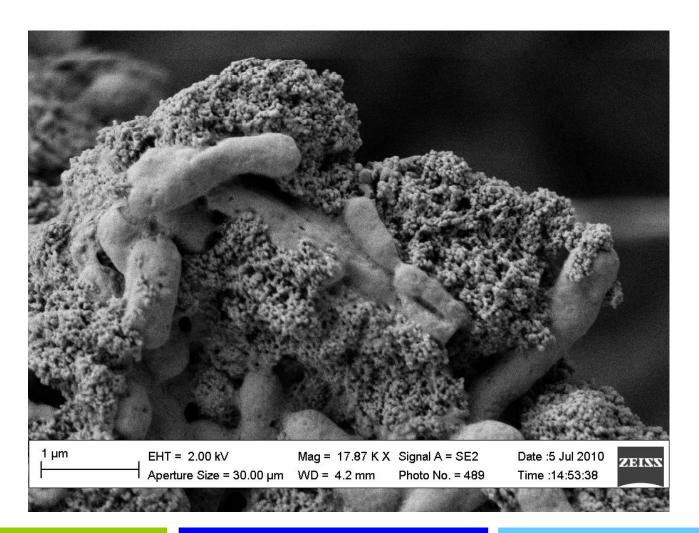


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**ICSU** 

# **Toxicity:** Accumulated TiO<sub>2</sub> nanoparticles on the fish leaver







### **Disadvantages**

- Safety hazards with nanomaterials (size?)
- Some studies detected possible cancercausing properties of carbon nanotubes
- Some nanomaterials bounded with other materials or components (?)

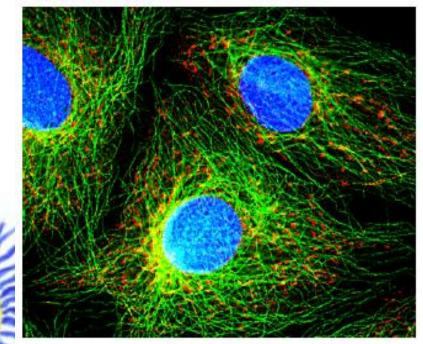




Nanomaterials - Biomarkers Metal and semiconductor nanoparticles are used to label biological samples

Semiconductors are great for fluorescence labeling. Gold is an excellent stain for electron microscopy.

Attach to different structures such as cancer cells by using different molecules on the surface







### **Nanomaterials - Biomarkers**

- 15nm dia FeO nanoparticles injected directly into tumor site.
- Alternating magnetic field (similar to MRI) heats up nanoparticles, destroying tumor from inside with minimal damage to surman manaforce









#### Thanks to all from all of us: CENIMAT/PORTUGAL and E-MRS!



