Vidros eletrocrómicos e revestimentos nanoestruturados

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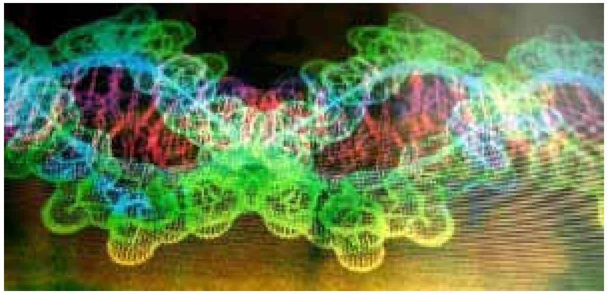


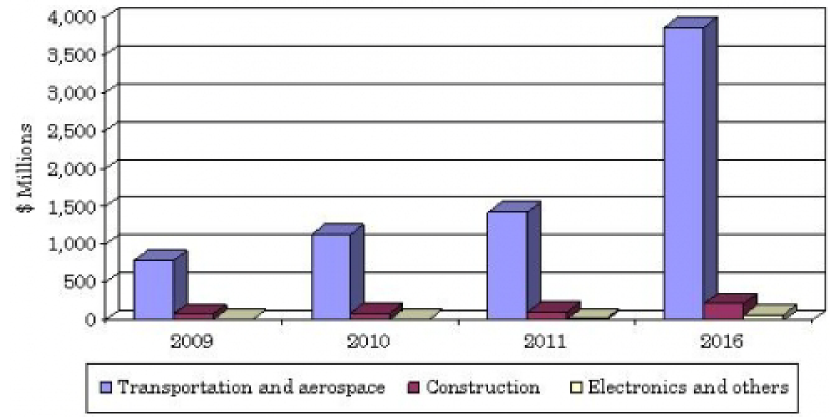
"A Nanotecnologia nos Materiais de Construção"
Ordem dos Engenheiros, 27 Fevereiro 2014

Sumário

- Janelas “inteligentes”
- Mercado e tendências
- Materiais e dispositivos electrocrómicos
- Materiais depositados por impressão
- Materiais de dupla fase
- Desenho e síntese de nanopartículas funcionais
- Electrólitos
- Protótipos e perspectivas

Smart windows

"A glass whose light-control properties change in response to a stimulus such as change in intensity of light or variation in temperature"



Markets:

- **Architectural**
  - Commercial (dominant)
  - Residential
- **Transportation**
  - Automotive
  - Rail
  - Marine
  - Aviation
- **Other**

Players in the market

RavenBrick, LLC (U.S.), Corning (U.S.), Research Frontiers (U.S.), Chameleon (U.S.), Domoticware (Spain), Sage Electrochromics (U.S.), and Saint-Gobain (U.S.)

For construction purposes, in particular, smart glass is analogous to a smart skin for buildings that can automatically change its light transmission properties according to the ambient conditions. It can be used for:

- reduce heating/cooling load,
- reduce lighting load,
- cut the installation and maintenance cost of motorized light screens and blinds or curtains,
- optimize natural light.

Smart windows

Maintain view out

Electrochromic
can require no power to maintain the EC in any switched state for several days. Will dominate.

Photochromic
materials slowly change their tint in response to light intensity. Not commercially available.

Suspended particle device (SPD)
windows switch instantly from a dark blue to a clear slightly hazy state with an applied AC voltage. Commercially available

Do not maintain view out

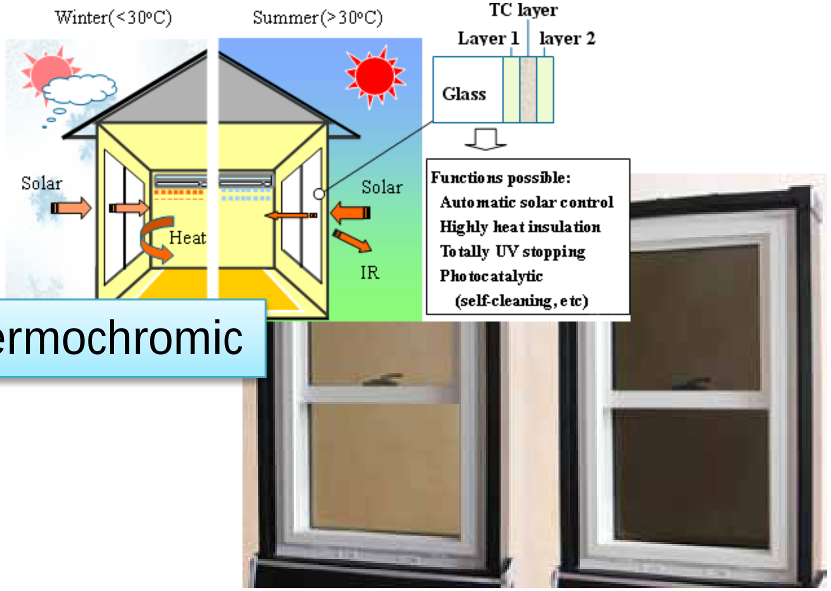
Thermochromic
materials slowly change from a clear state when cold to a more diffuse, white translucent state when hot. Prototype only

Liquid crystal device
windows are translucent when in an unpowered state and become instantly clear (with a noticeable haze) when power is applied. First to be implemented.

Reflective hydride
switches from a transparent to a reflective appearance with the injection of hydrogen gas. R&D stage.

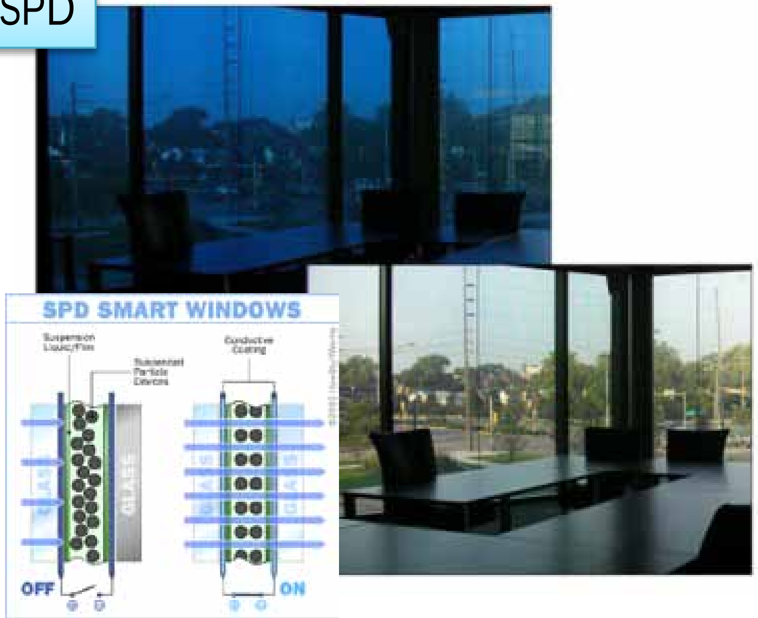
Smart windows

Photochromic

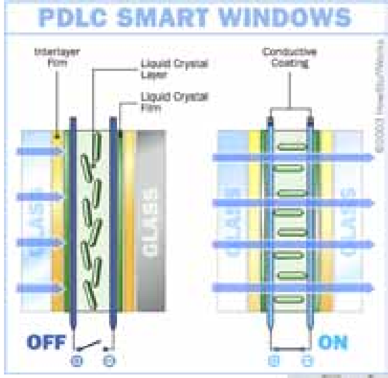


Thermochromic

SPD



PDLC



Smart windows

SUMMARY FORECAST

ELECTROCHROMIC TECHNOLOGY

	2011	2012	2013	2014	2015	2016	2017	2018
Electrochromic Window Glass Volume *(Million Square Meters)*	0.19	0.35	0.61	0.96	1.49	2.30	3.54	5.48
Average Cost per Square Meter *($)*	700.0	609.0	529.8	461.0	401.0	348.9	303.5	264.1
Electrochromic Glass Revenues *($ Million)*	136.0	213.5	321.7	443.9	597.8	800.9	1075.2	1446.3

THERMOCHROMIC TECHNOLOGY

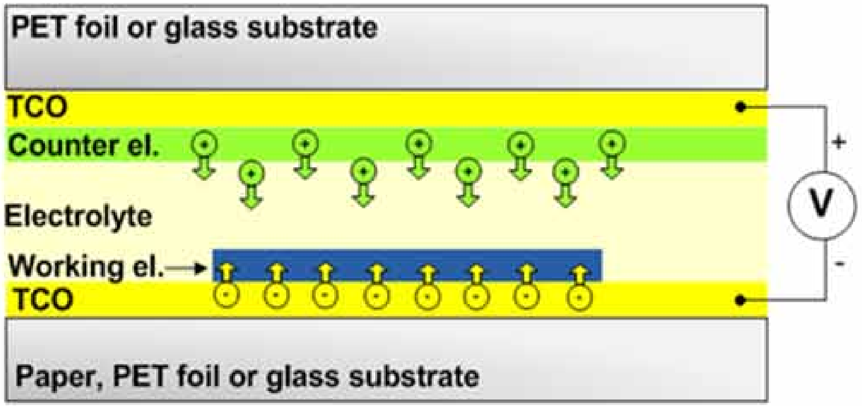
	2011	2012	2013	2014	2015	2016	2017	2018
Thermochromic Window Glass Volume *(Million Square Meters)*	0.07	0.10	0.14	0.26	0.48	0.76	1.06	1.48
Average Cost per Square Meter *($)*	400.0	352.0	309.8	272.6	239.9	211.1	185.8	163.5
Thermochromic Glass Revenues *($ Million)*	30.0	35.7	42.4	71.8	114.9	160.5	196.9	242.3

Source: "Next-Generation Smart Windows: Materials and Markets: 2011," available from Nanomarkets, www.nanomarkets.net.

Electrochromic devices (EC)

Electrochromism is a persistent, but reversible optical change produced electrochemically in selected thin films compounds.

The most typical and widely studied electrochromic material is WO_3



Progress in this area is driven by the need of energy efficient solutions

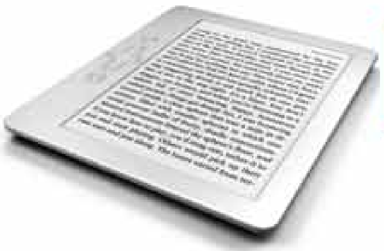
Electrochromic devices (EC)

EC windows

Electrochromic devices (EC)

Bistable EC displays able to work in reflection ➡ Low power consumption

eBook Readers



Automotive

Smart Cards

Smart Packaging

Color display is possible by combinig different layers

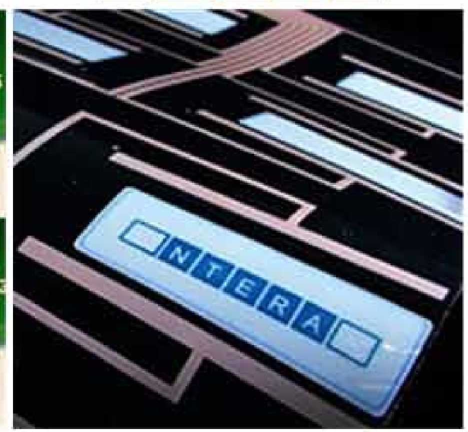
Commercial products

Based on organic EC materials

avēso

acreo

NTERA



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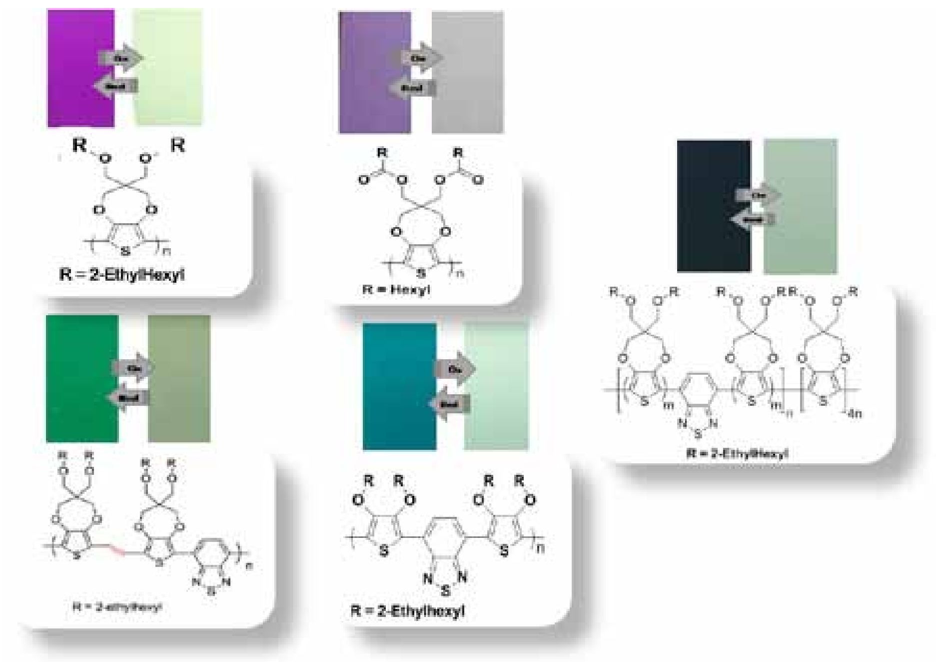
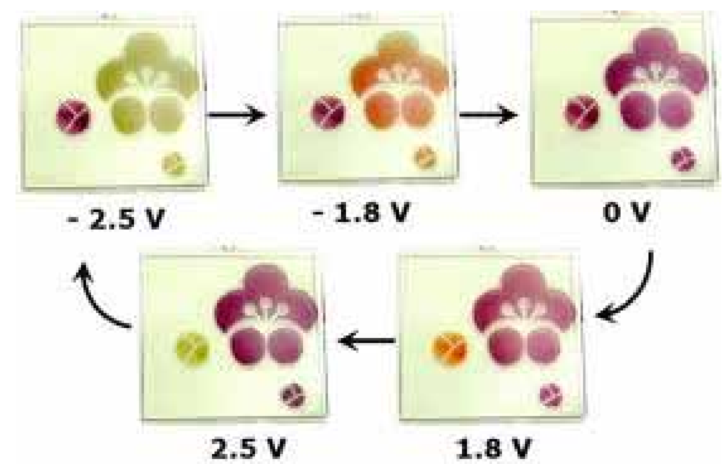
Electrochromic devices (EC)

Organic materials



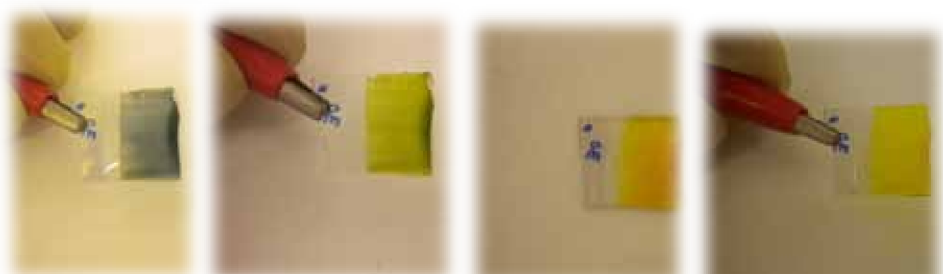
organic/metal hybrid polymer



Different color with different applied voltages

Inorganic materials

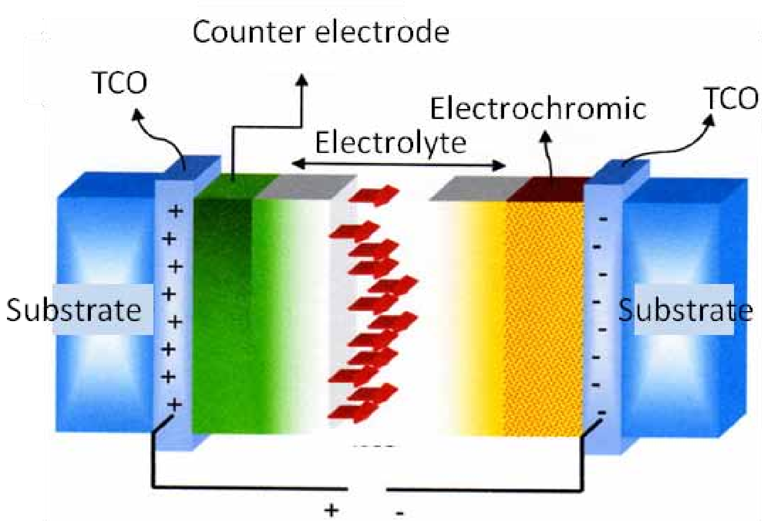
Vanadium oxide



-2V → 2V

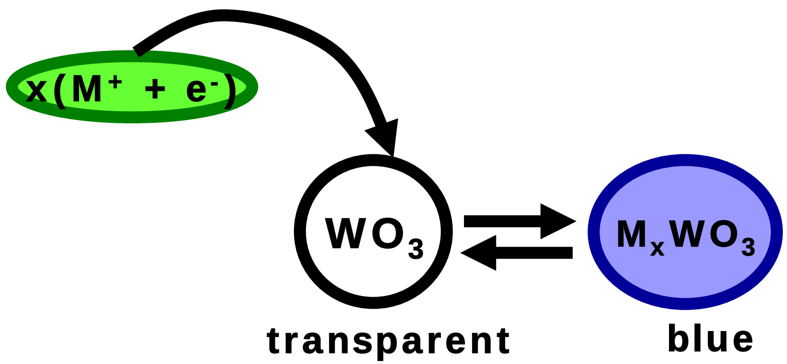
Introduction – Electrochromism and WO_3

Redox reactions

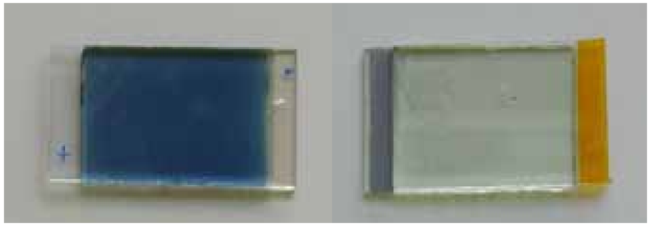


$WO_3 + xM^+ + xe^-$ ó $M_x WO_3$

Transparent Intense Blue



Electrochromic device



After ⇄ Before

voltage

Cathodics – WO_3, MoO_3, TiO_2

Anodics – IrO_2, RhO_2, NiO_2

M^+ (0<x<0,25)- H^+, Li^+, Na^+, K^+

Introduction – Electrochromism and WO_3

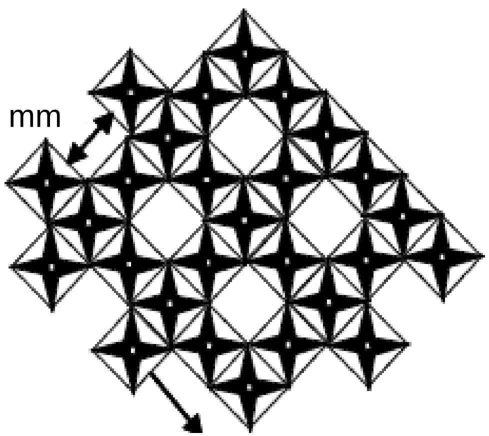
Tungsten oxide – WO_3

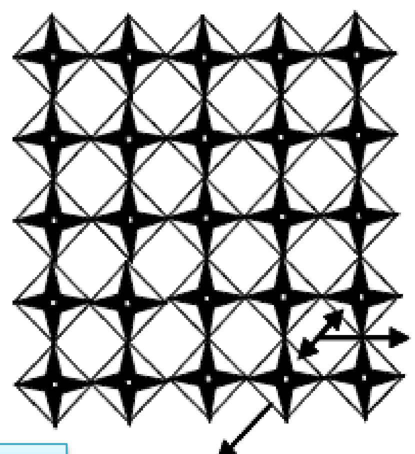
c-WO_3: can be arranged in different configurations, including substoichiometric and hydrated forms

$$WO_3 + x(M^+ + e^-) \longleftrightarrow M_xW^{VI}_{(1-x)}W^{V}_xO_3$$

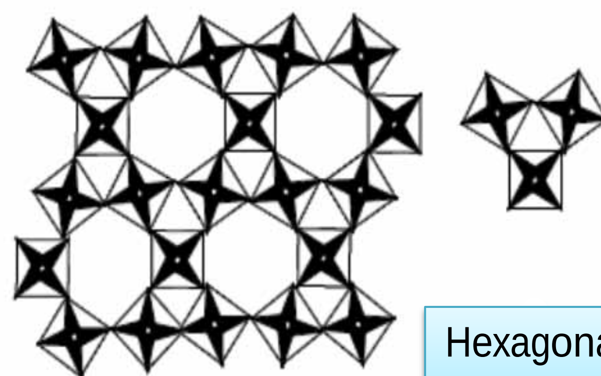
Most accepted theory: photo-effected intervalence charge transfer (IVCT) between adjacent W^V and W^{VI} sites

0.3 mm





0.3 mm



Monoclinic structure

WO_6 octahedra

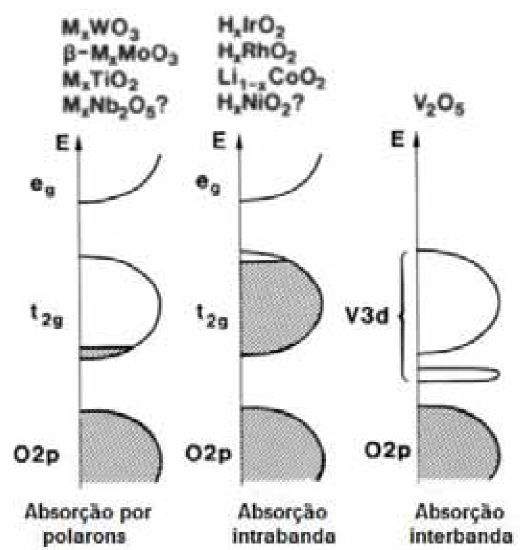
Hexagonal structure

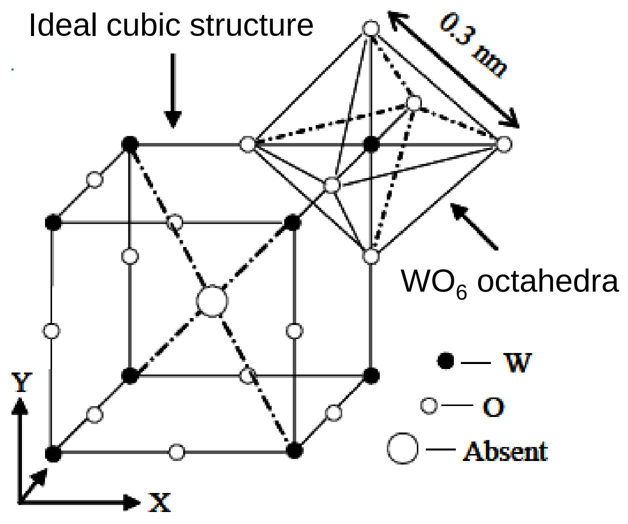
12

Introduction – Electrochromism and WO_3

Tungsten oxide – WO_3

Most studied inorganic material, huge variety of applications like gas sensors, electrocatalyst, thermochromic, photochromic and electrochromic with good color modulation from transparent to dark blue.





***a*-WO_3**: clusters of 3 to 8 WO_6 octahedra

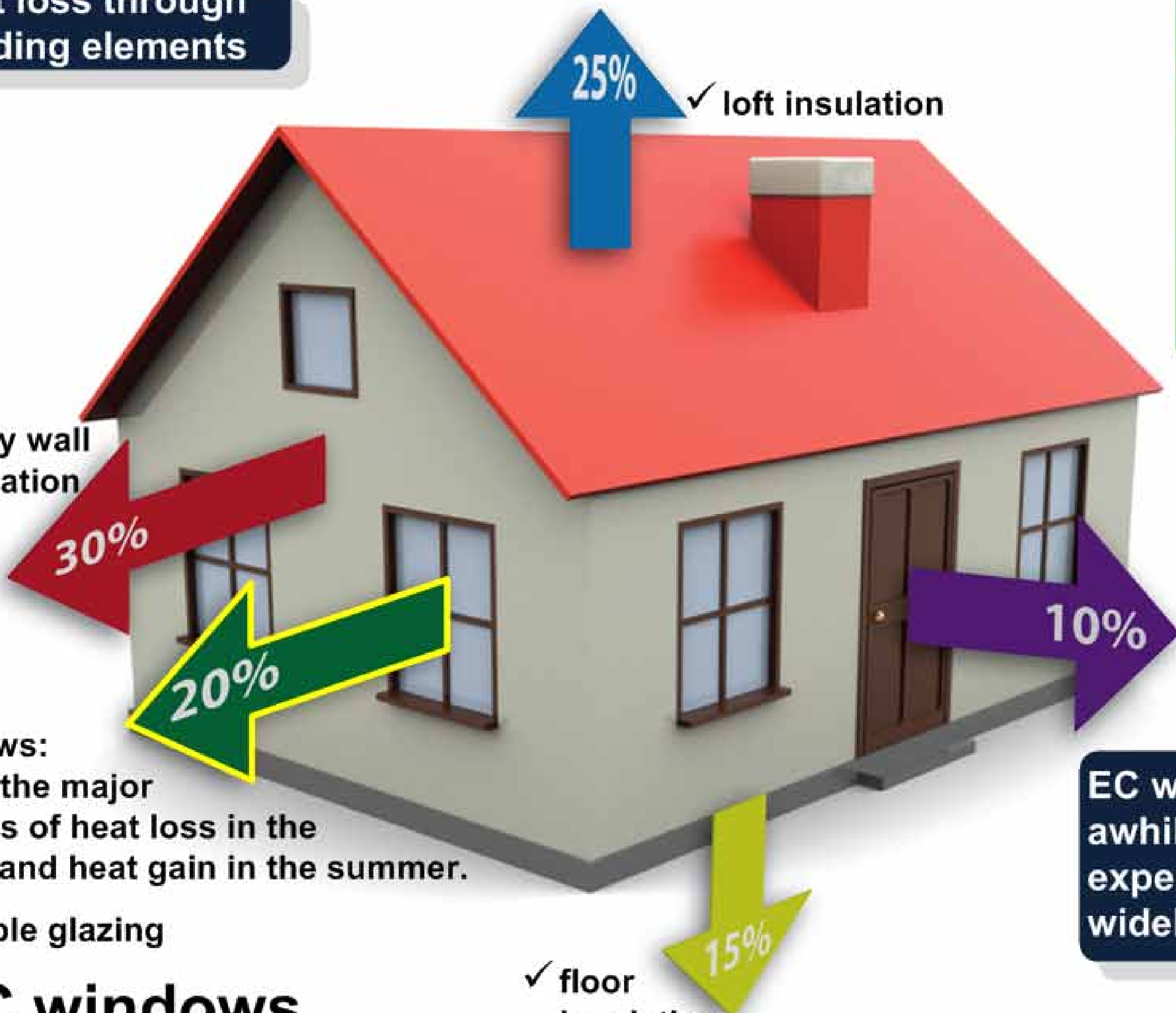
Ionic conduction: proton transfer through chanels or water bridges in pores

Electronic conduction: clusters linked together by W-O-W bonds

Energy efficient EC concepts

Heat loss through building elements

EC windows:
- ✓ Increase solar heat gain in winter
- ✓ Reduce solar heat gain in summer
- ✓ Lighting costs are reduced under all conditions



✓ loft insulation

✓ cavity wall insulation

Windows:
one of the major sources of heat loss in the winter and heat gain in the summer.

✓ double glazing

✓ **EC windows**

✓ floor insulation

EC windows have existed for awhile (2006), but they are expensive and not widely used.

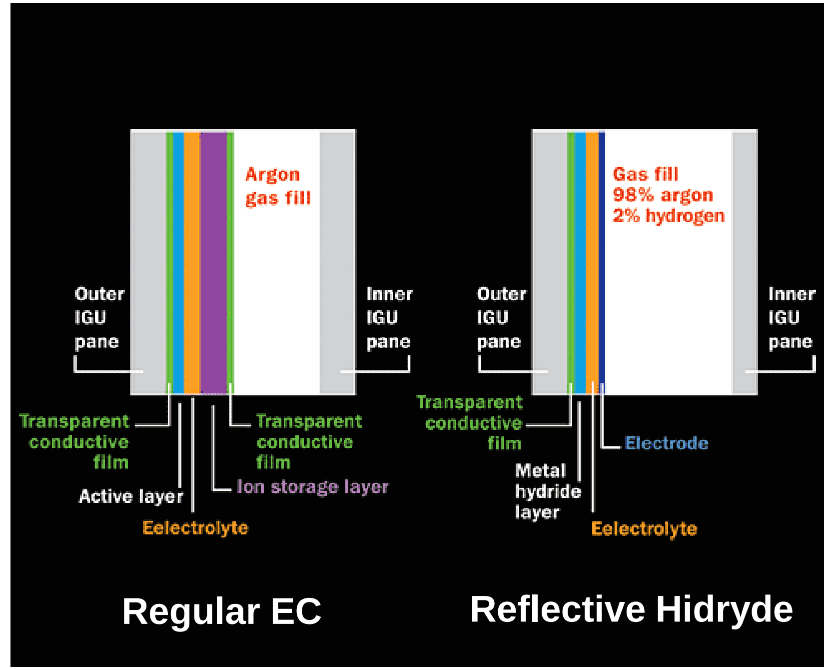
SAGE

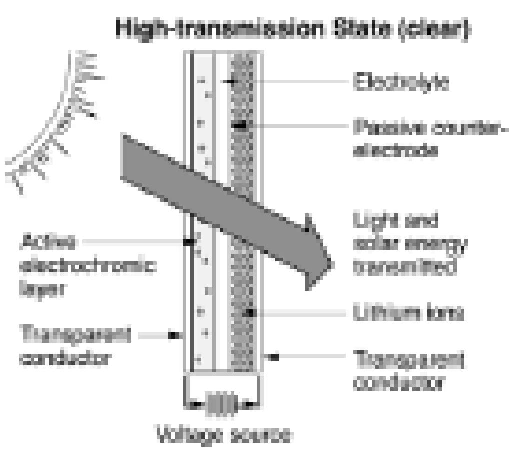
Developed via PVD
Switching time 3-5 min

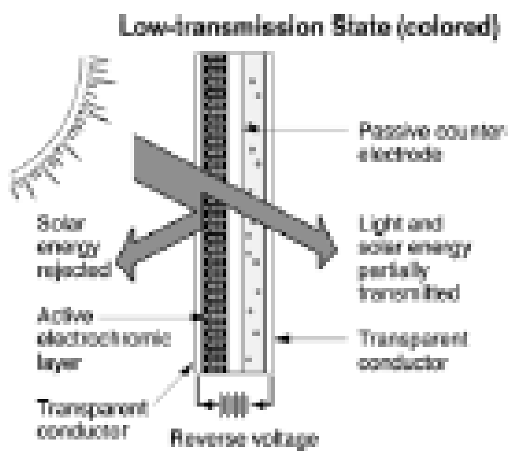
EC windows

Structure

Inert gas is used to improve thermal insulation
(low emissivity coating may also be integrated in the structure)



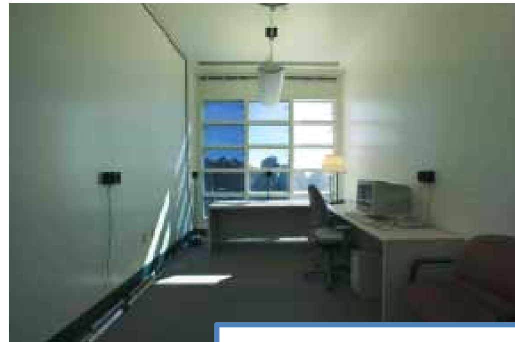




Solar energy reflection may be controlled still keeping viewng out

EC windows

Functionality



Dynamic control of luminosity

The visible transmittance (Tv, typicaly 0.7 to 0.05) and solar heat gain coefficient (SHGC) range of EC coatings vary depending on the material composition. U-factor is not affected by the change in tint. Generally, the wider the switching range, the more control one has under variable sun and sky conditions:

•A high-transmittance clear state lets in more daylight when it is overcast or early morning or late afternoon.

•A dark-transmittance colored state reduces interior window and surface brightness that can cause visual discomfort. A transmittance of less than Tv<0.001 is needed to reduce the brightness of the sun orb down to comfortable levels.

•Generally, commercial buildings in the U.S. tend to be internally-load dominated buildings due to their high occupant and equipment density and operate in a cooling mode even during the winter. For these types of buildings, the SHGC range should be as low as possible compared to the Tv range.

•Whether the windows are small or large, a wide switching range is important.

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EC windows

Power consuption

Low-voltage power is required to switch EC windows and for some types of windows, a small applied voltage is needed to keep the EC in a constant state, irrespective of the level of tint. For example:

- **The polymer laminated WO3 EC window requires power only when switching to a different level of tint**

- **SAGE Electrochromic's window requires constant power:**

  - If no power is applied, the EC window "rests" at the clear state.

  - If the EC window is in the process of being switched, peak power consumption is 0.26-0.32 W/ft2-glazing (5-6 W for a 42.5x60 inch EC window).

  - If the EC is being held constant at any level of tint, steady-state power consumption is 0.07-0.15 W/ft2 -glazing (1.2-2.6 W for a 42.5x60 inch window), assuming a 1-to-1 relationship between the EC window unit and its window controller (excluding losses).

This compares with 0.05-0.5 W/ft2 of glass for SPD, depending o tint level, or 0.5 W/ft2 of glass for PDLC (both require constant power)

EC windows

Switching time

How fast do electrochromic windows switch?

Switching speed varies with the size and exterior surface temperature of the EC window (which is dictated by incident solar radiation leve ls, wind speed, and air temperature):

□

•If the window area is small, the EC will switch faster because the distance between the bus bars is small. For example, for an18-inch distance between bus bars, the fastest switching time is between 1-4 minutes under sunny and/or hot conditions.

•For larger windows, switching time can be significantly longer. Faster switching of large-area EC glass is achieved by applying additional thin conductor line(s), thus allowing for faster distribution of the electrical current over the EC pane.

•When the EC surface temperature is greater than approximately 10ºC, switching speeds are less than 6-7 minutes in 18 inches/side windows. Under sunny, warm conditions, switching speeds can be less than 4 minutes.

•If the EC surface temperature is between –3ºC to –1ºC, it can take 37 minutes to color or bleach between a visible transmittance of 0.56 to 0.13.

EC windows

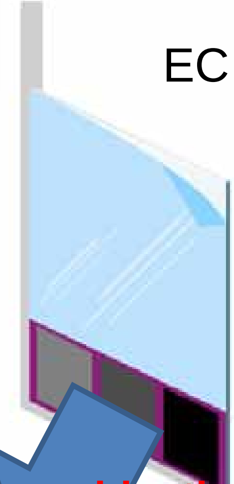
Technology

EXPENSIVE!!!!

EC windows

And if we could adapt the existing ones?

EC Foils

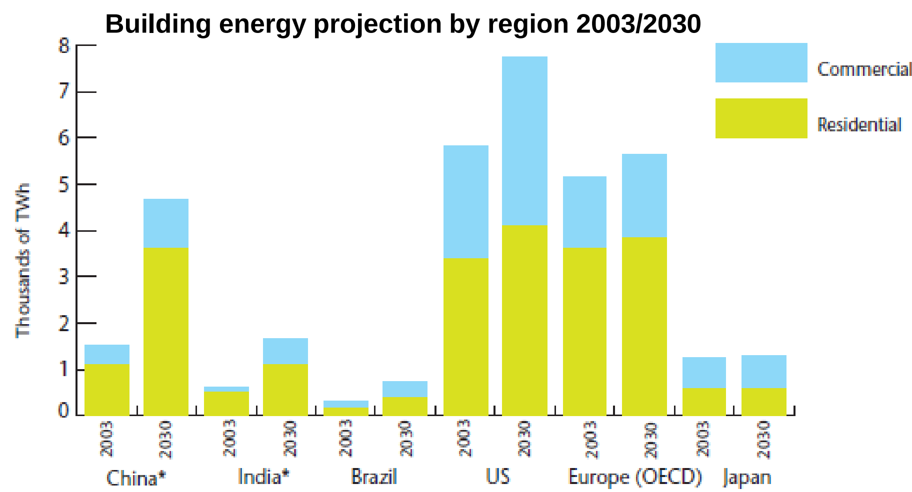


Technology

And if we want to replace the existing windows?

EXPENSIVE!!!!

Would be great in reaching the residential market

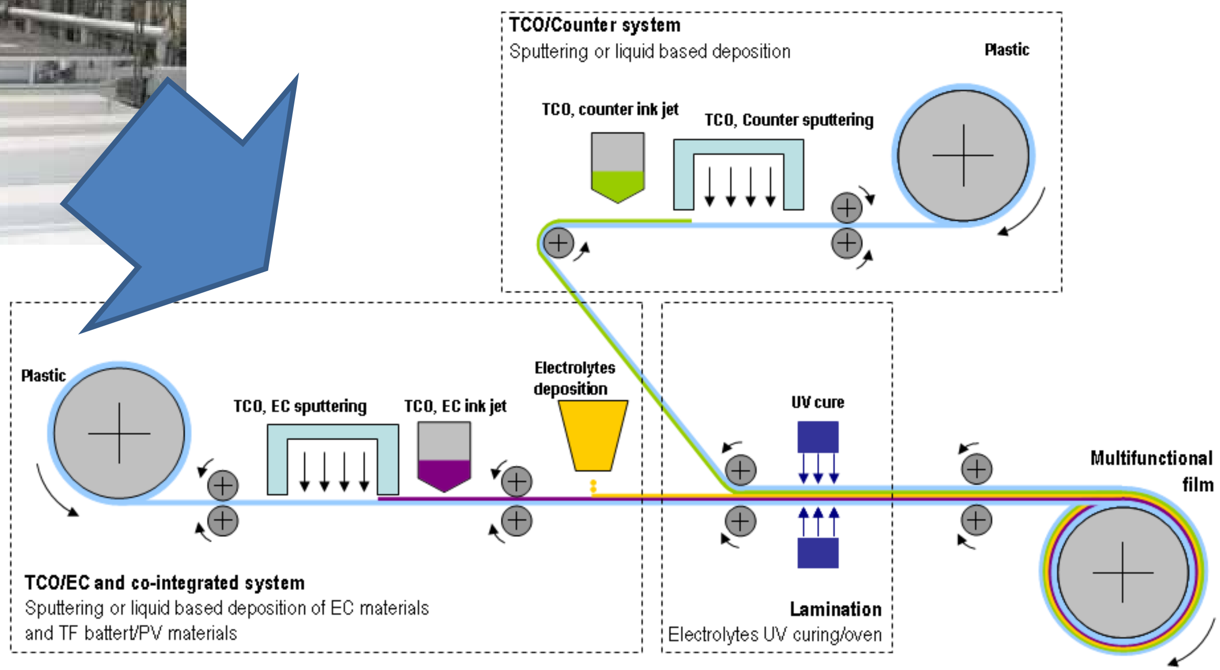


Remember! Buildings account for 40% of the European energy consumption

EC windows

Technology

The ideal would be to move to printing, roll-to-roll sytems



The target

The goal is to develop materials and processes alternative to existing aiming at:

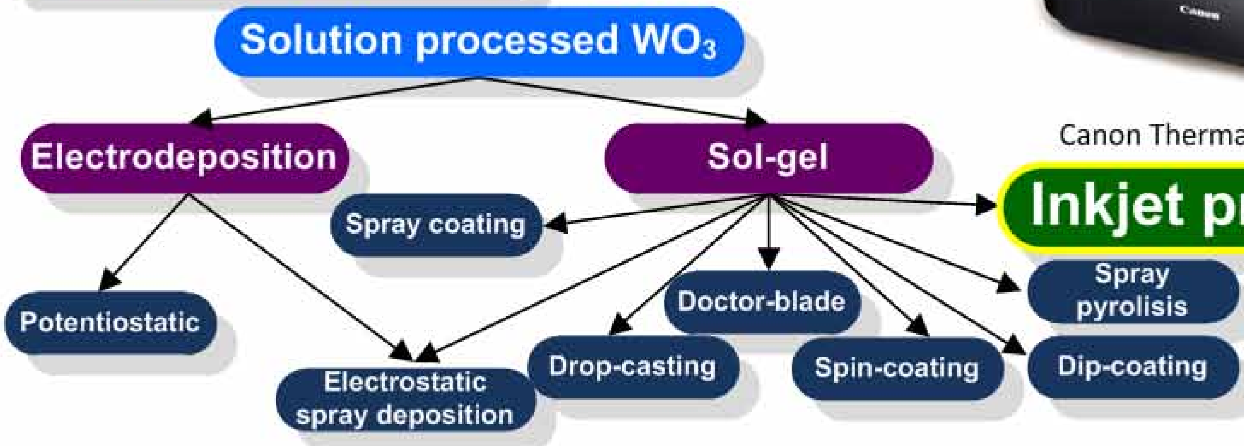
- **low cost (printing techniques)**
- **high performance,**
- **power efficient,**
- **eco-friendly, and**
- **widely accessible solutions.**

A new approach...

1. Inkjet printed EC films

Canon Thermal DOD (FINE)™

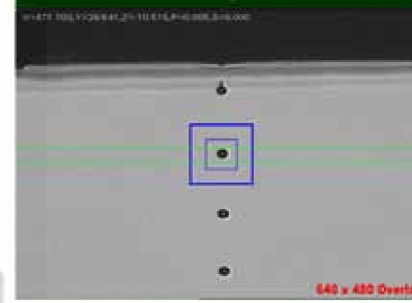
Piezo MEMS DOD Glass & Silicon



Inkjet printing

Novelty
WO_3 sol-gel deposition

10kHz, single nozzle



10kHz, all nozzles

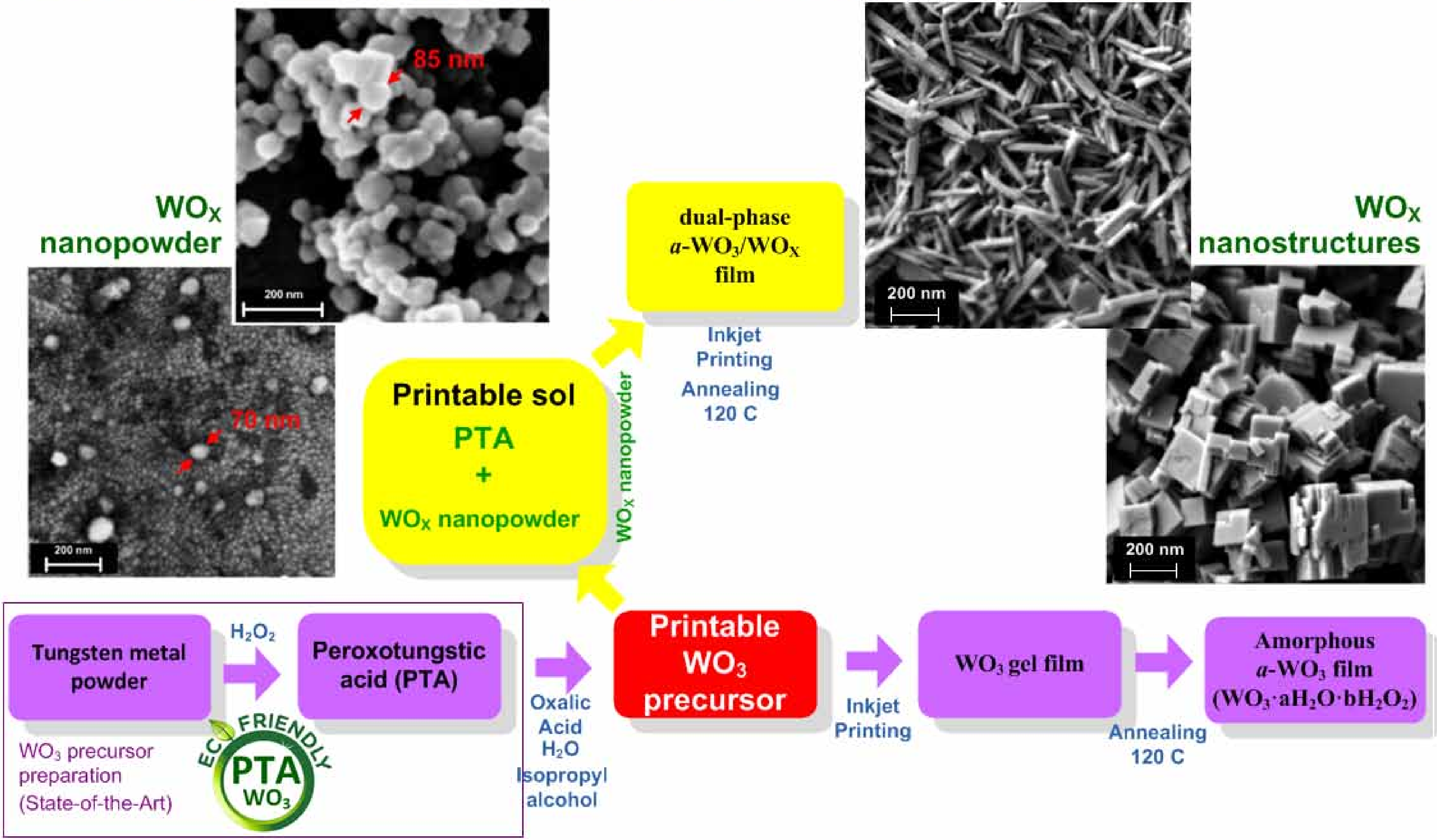
Drop-On-Demand droplet velocity = 5-10m/s, droplet volume = 12-25pl

2. Solid state electrolyte based on thermosetting resin (TCSE)

Novelty
1. A new class of thermosetting electrolyte
2. Low cost and environmental friendly

0.5mm x 10cm x 10cm thermosetting electrolytes

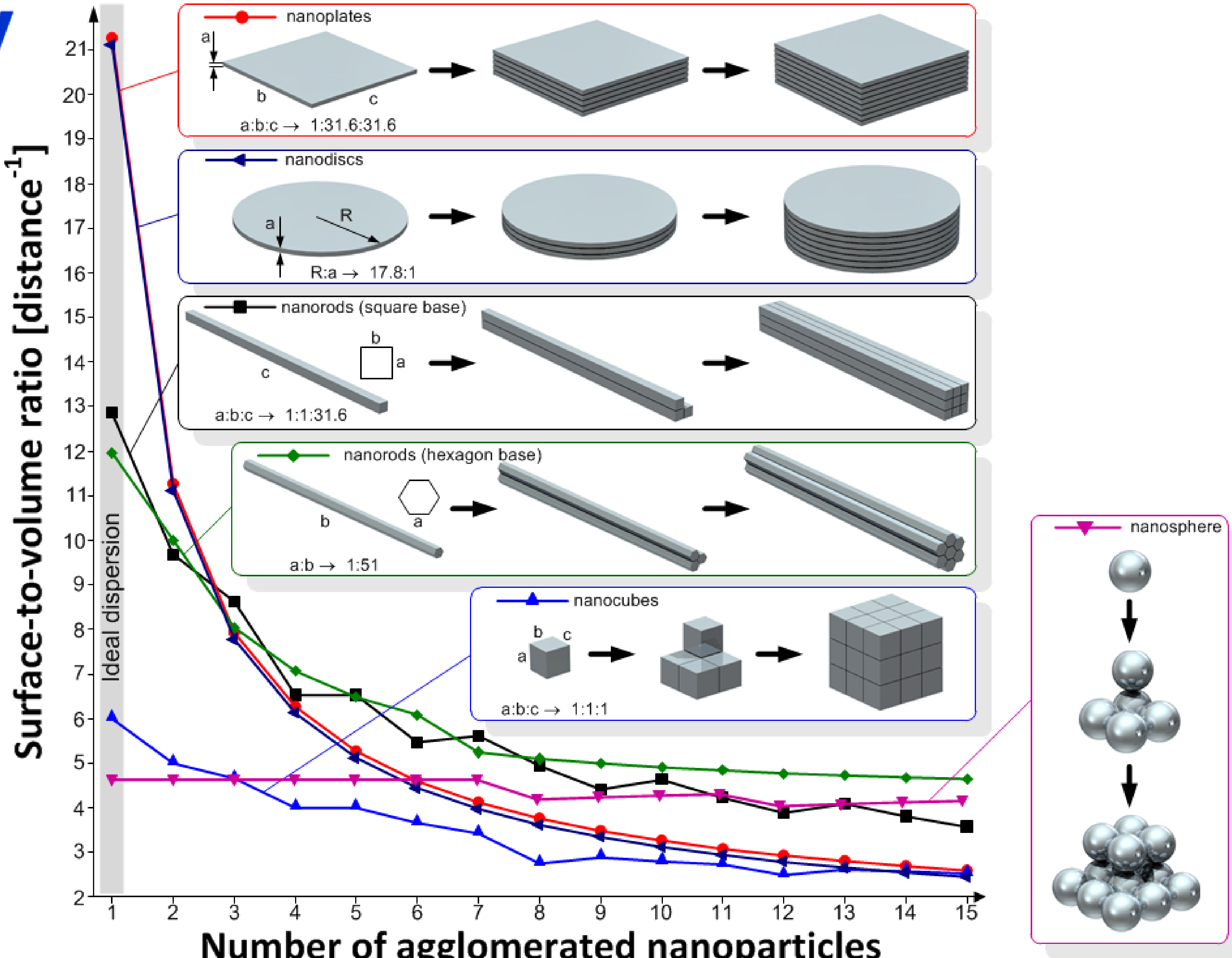
Electrochromic ink formulation



P.J. Wojcik, et al., *J. Mater. Chem.* (**2012**) DOI: 10.1039/c2jm31217d

NPs design

SA:V



Surface-to-volume ratio [distance^{-1}]
Number of agglomerated nanoparticles
Ideal dispersion
nanoplates
a:b:c → 1:31.6:31.6
nanodiscs
R:a → 17.8:1
nanorods (square base)
a:b:c → 1:1:31.6
nanorods (hexagon base)
a:b → 1:51
nanocubes
a:b:c → 1:1:1
nanosphere

NPs synthesis

NPs synthesis

Hydrothermal Synthesis

- The reactants are dissolved (or placed) in water or another solvent (solvothermal) in a closed vessel. Autoclave is heated above boiling point.
- Conventional or Microwave oven

NPs synthesis

Hydrothermal Synthesis

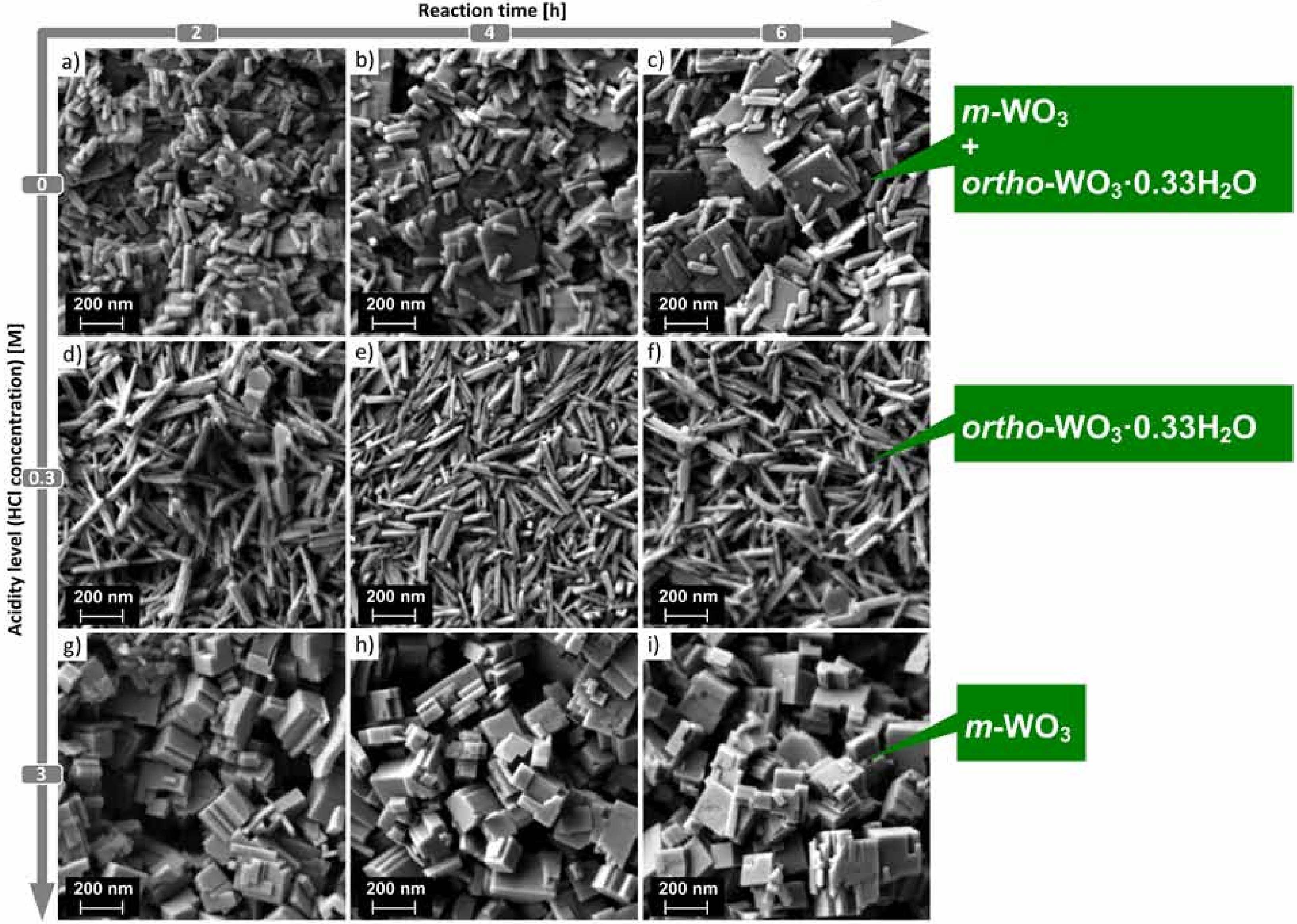
Pros:

- Most materials can be made soluble in proper solvent by heating and pressuring the system close to its critical point;
- Significant improvement in the chemical activity of the reactant, the possibility to replace the solid-state synthesis, and materials which may not be obtained via solid-state reaction may be prepared through hydrothermal / solvothermal synthesis;
- Products of intermediate state, metastable state and specific phase may be easily produced, novel compounds of metastable state and other specific condensed state may be synthesized;
- Easy and precise control of the size, shape distribution, crystallinity of the final product through adjusting the parameters.

Cons:

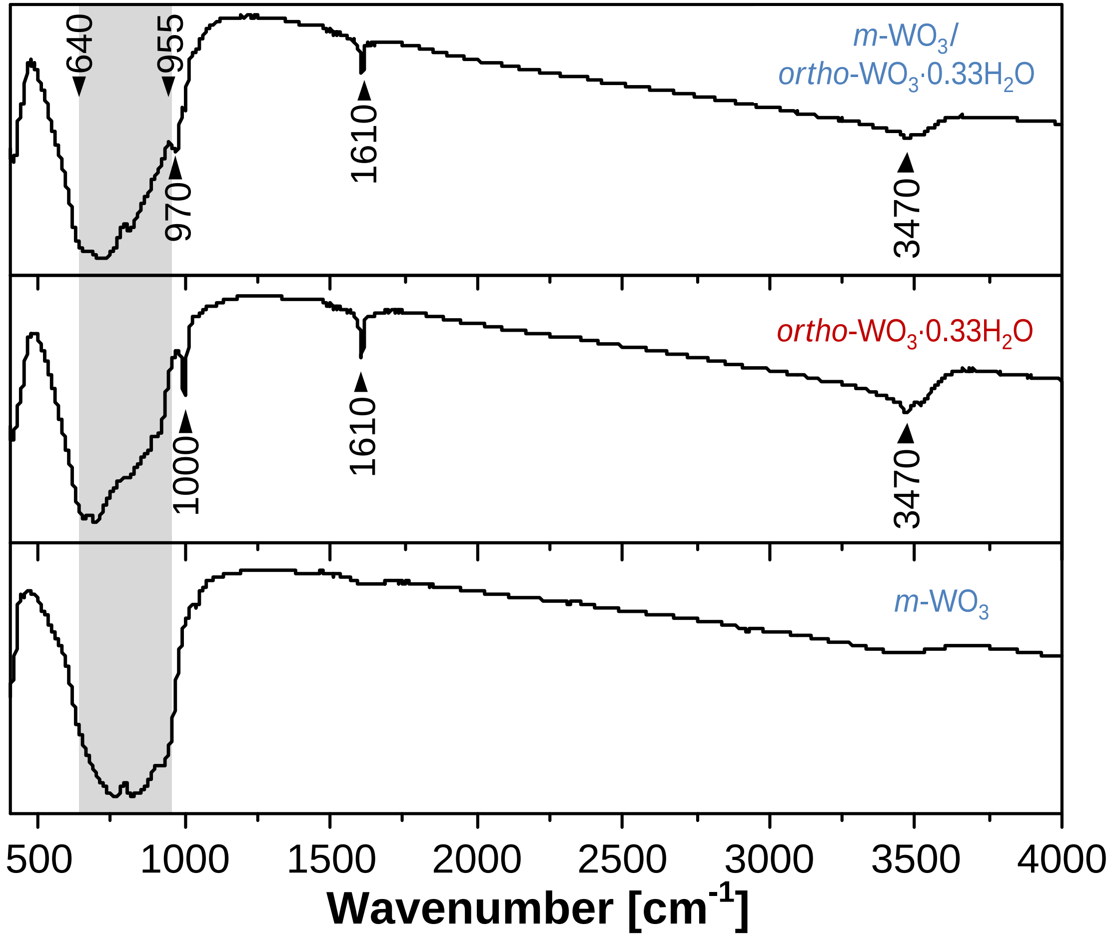
- May obtain variation in size
- The need of autoclaves - Safety issues during the reaction process
- Impossibility of observing the reaction process ("black box")

WO_x NPs – hydrothermal synthesis



WO_x

FT-IR



3470 and 1610 cm^{-1}:
-OH stretching and bending from the water

970/ 1000 cm^{-1}:
W-O stretching from WO_6 octahedra

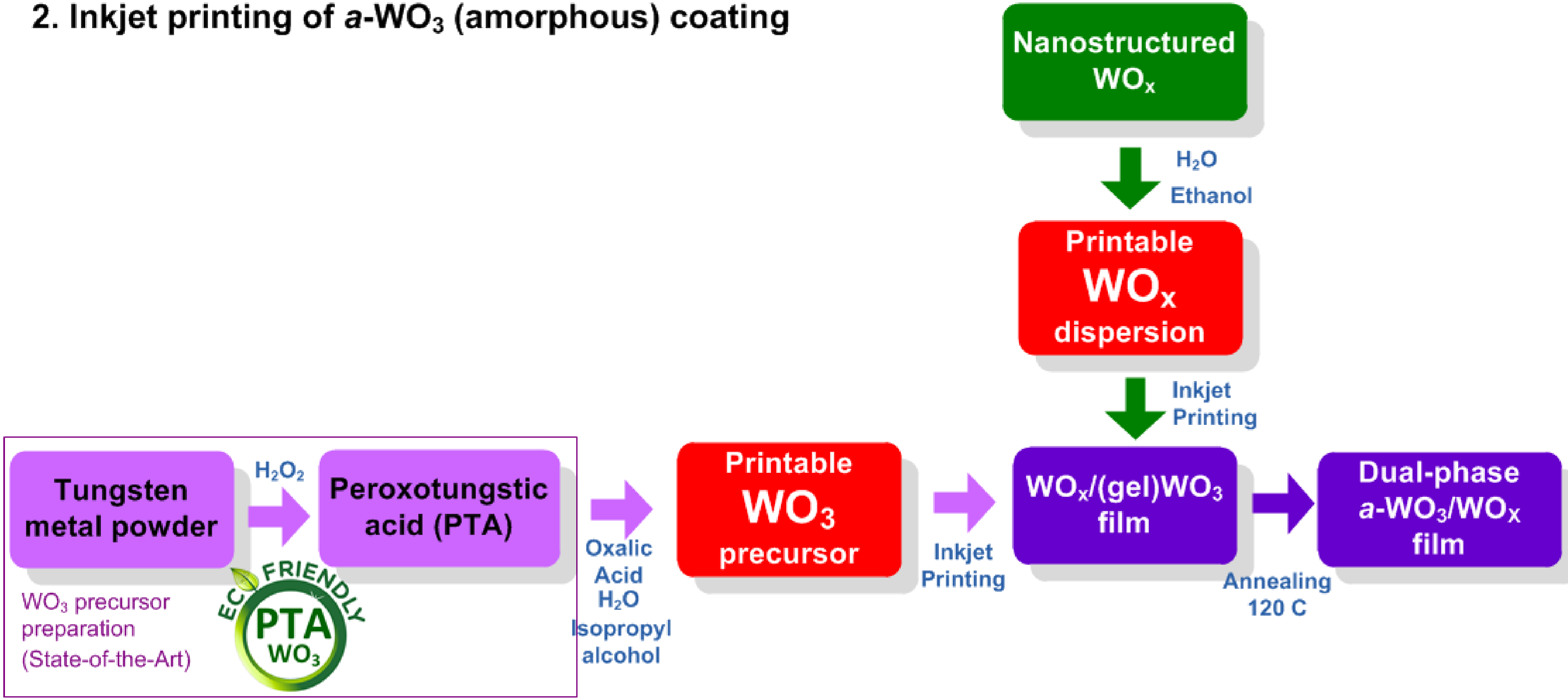
640-955 cm^{-1}:
W-O-W stretching

Dual phase printed films

Dual-phase WO_x film – processing

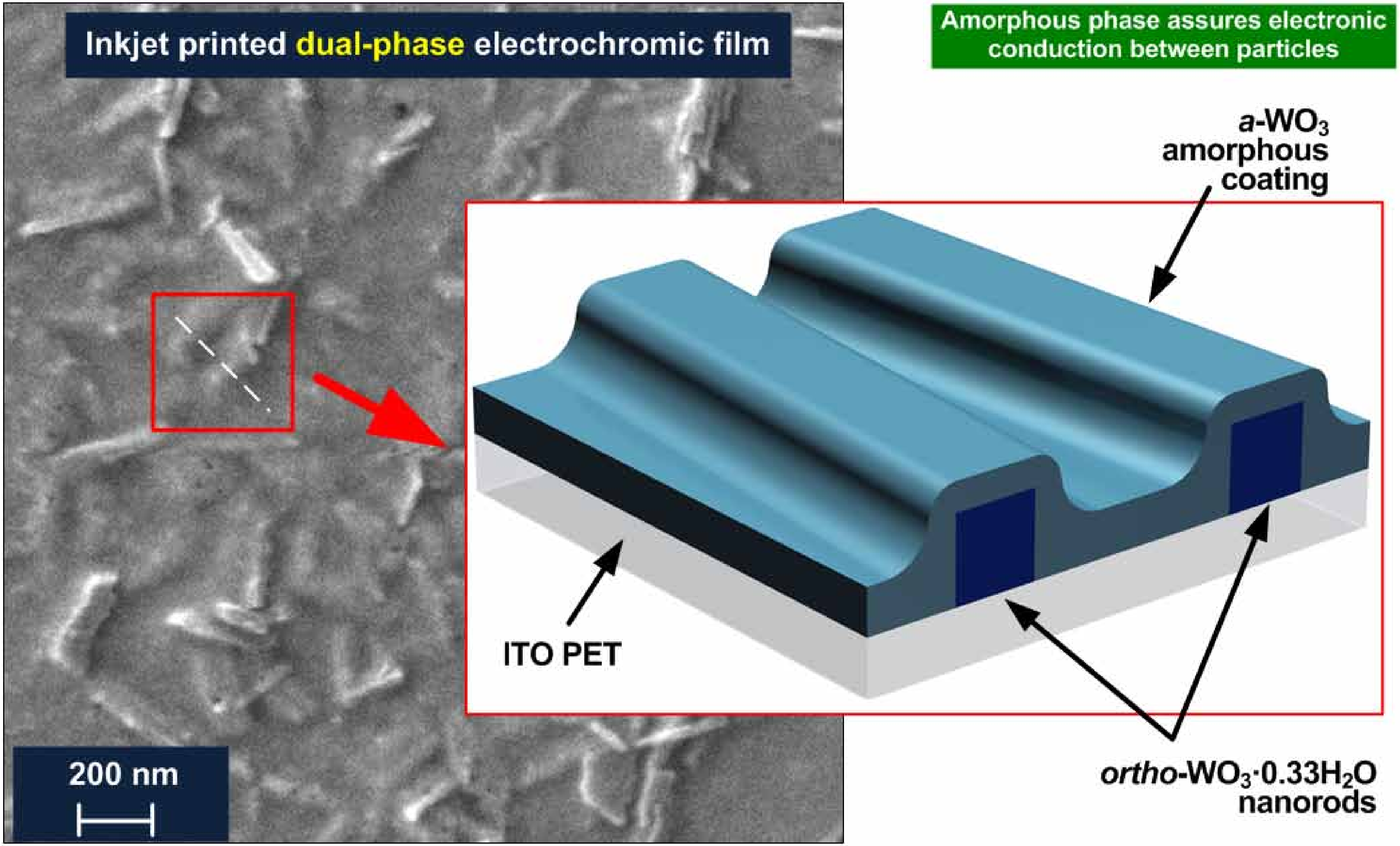
Dual-phase *a*-WO_3/WO_X films were performed in two separated depositions:

1. Inkjet printing of WOx NPs dispersion
2. Inkjet printing of *a*-WO_3 (amorphous) coating

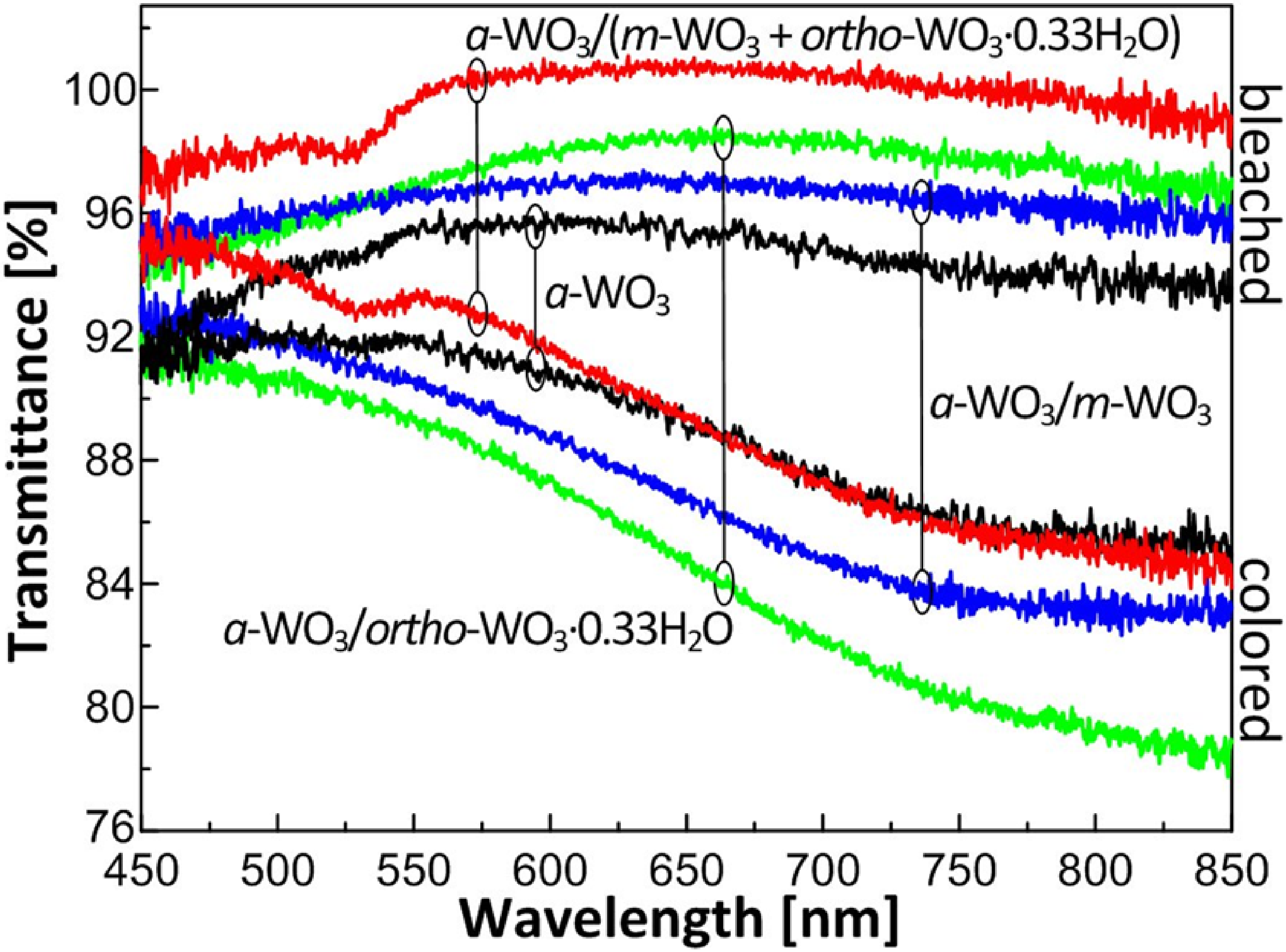


Wojcik, et al., (2012)

Dual-phase WO_x film



Optical modulation

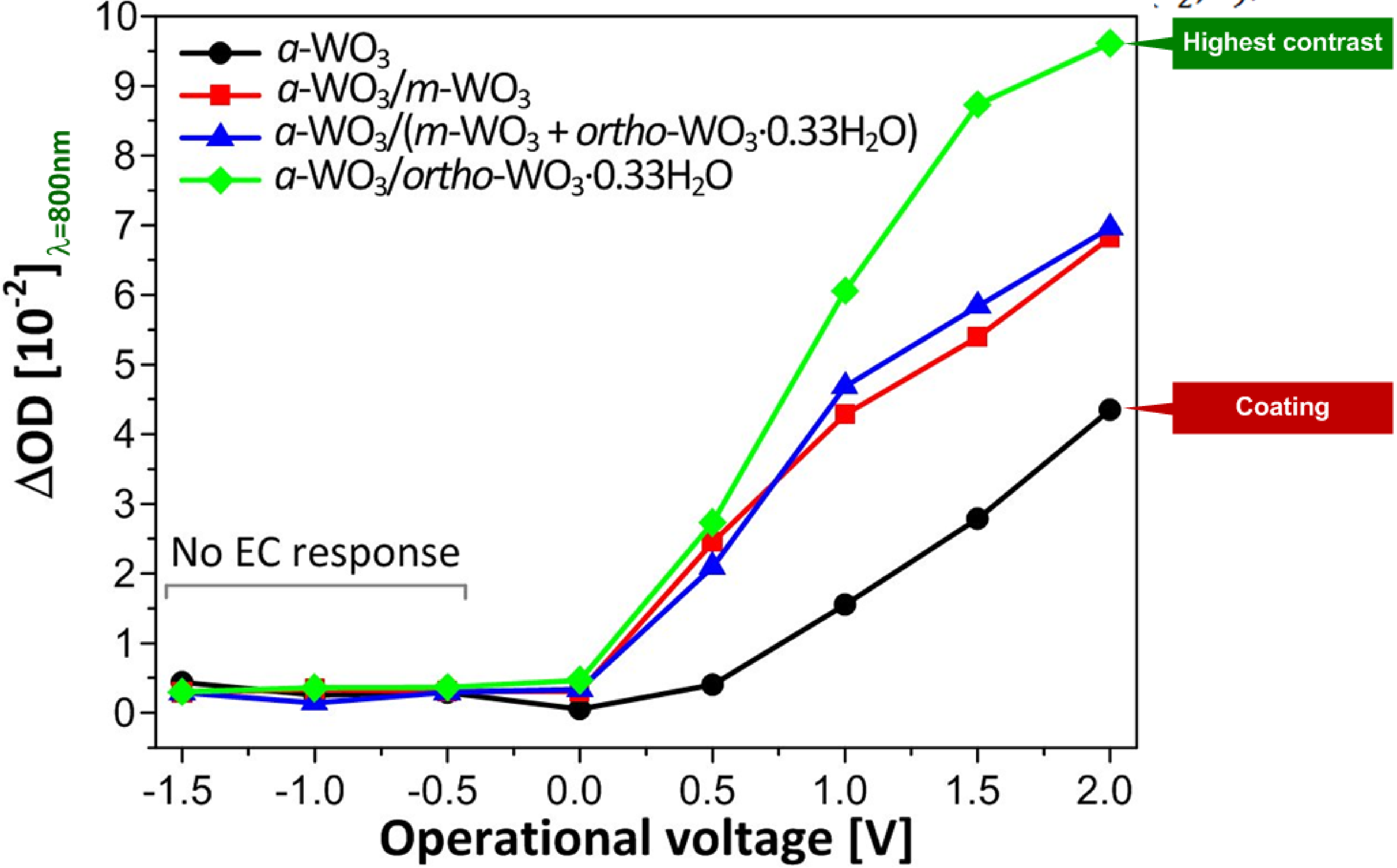


+/-2 V operational voltages

Optical modulation

$$\Delta_{OD} = ln\left(\frac{T(t_1,\lambda)}{T(t_2,\lambda)}\right)$$

← Bleaching
← Coloration



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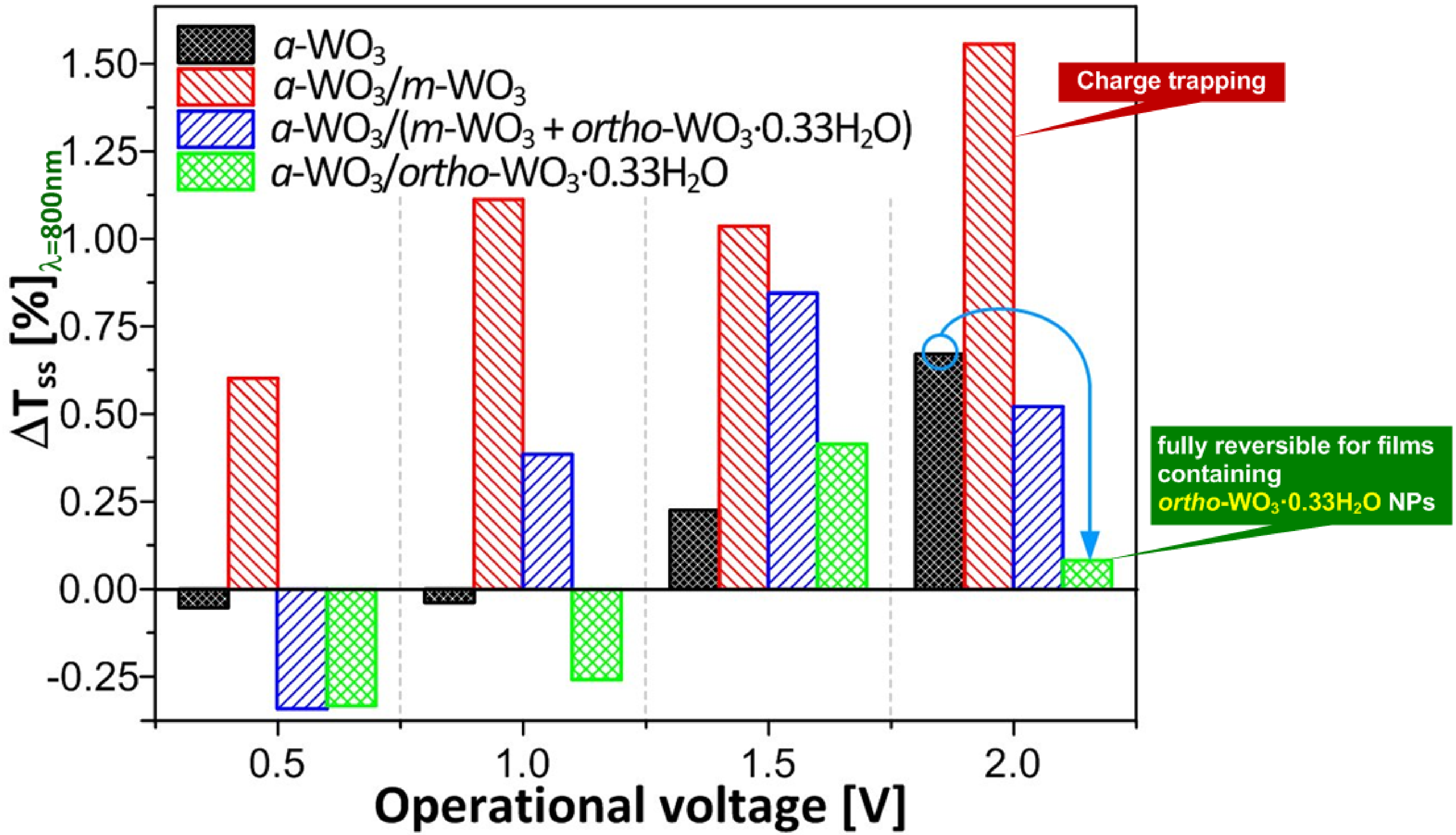
Site saturation effect

ΔT_{SS} - the difference in transmittance of the bleached films to its value before coloration



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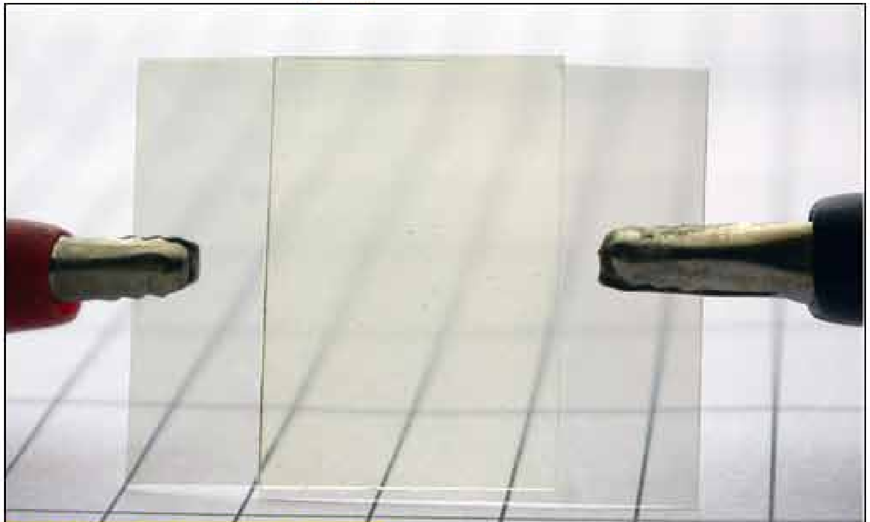
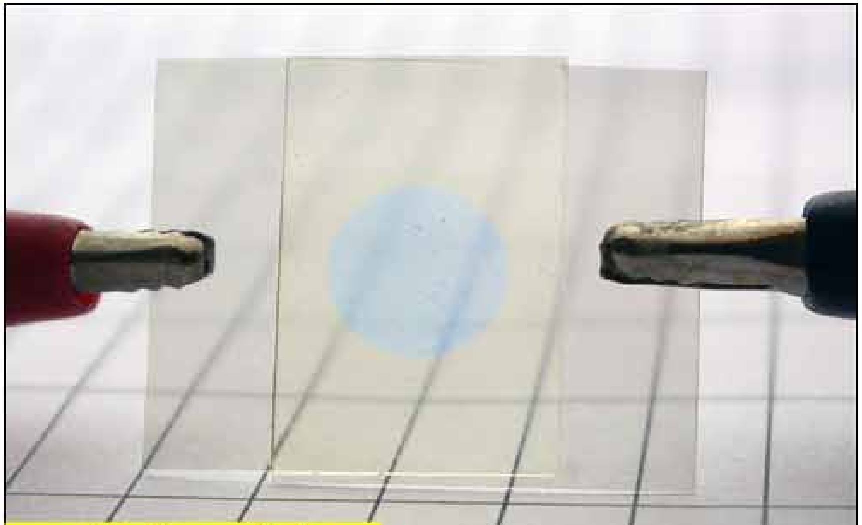
Solid State Electrolytes

All-solid-state EC prototypes (single pixel)

Inkjet printed bendable (transparent) electrochromic pixel based on SCN-Li^+/ thermoset solid state electrolyte



bleaching state



coloring state

UNINOVA CEMOP i3N FCT

All-solid-state EC prototypes (passive matrix)

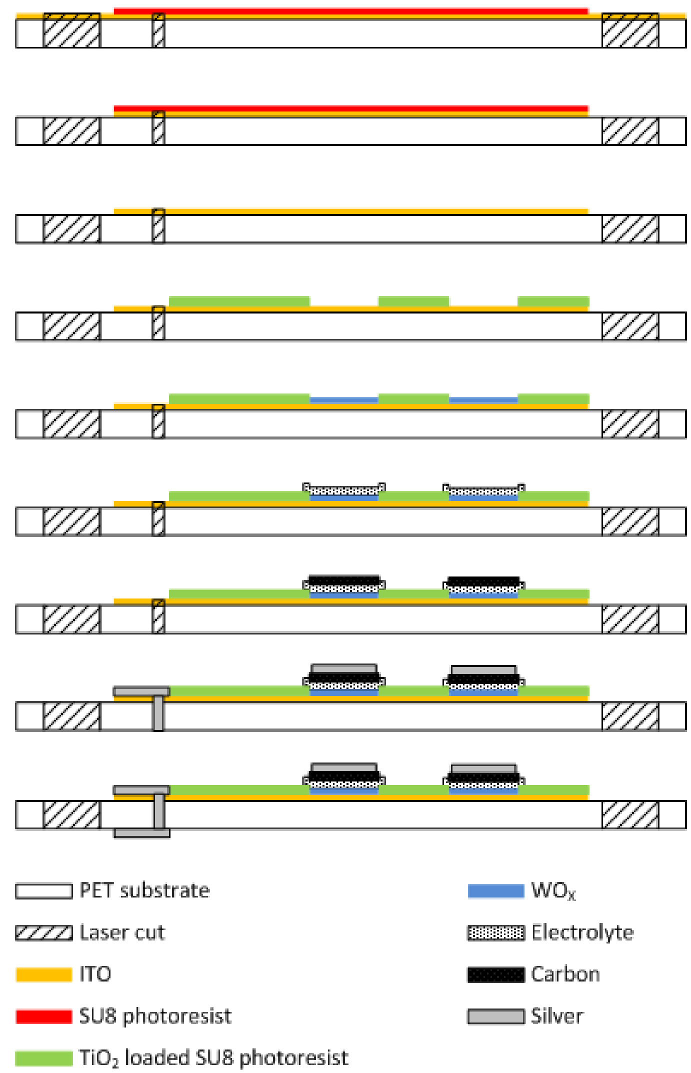
Inkjet printed 8x8 EC passive matrix (transparent) based on SCN-Li^+/thermoset solid state electrolyte (10x10 cm)

Inkjet printed 8x8 EC passive matrix (opaque) based on SCN-Li^+/TiO_2/thermoset solid state electrolyte (10x10 cm)

All-solid-state EC prototypes (passive matrix)

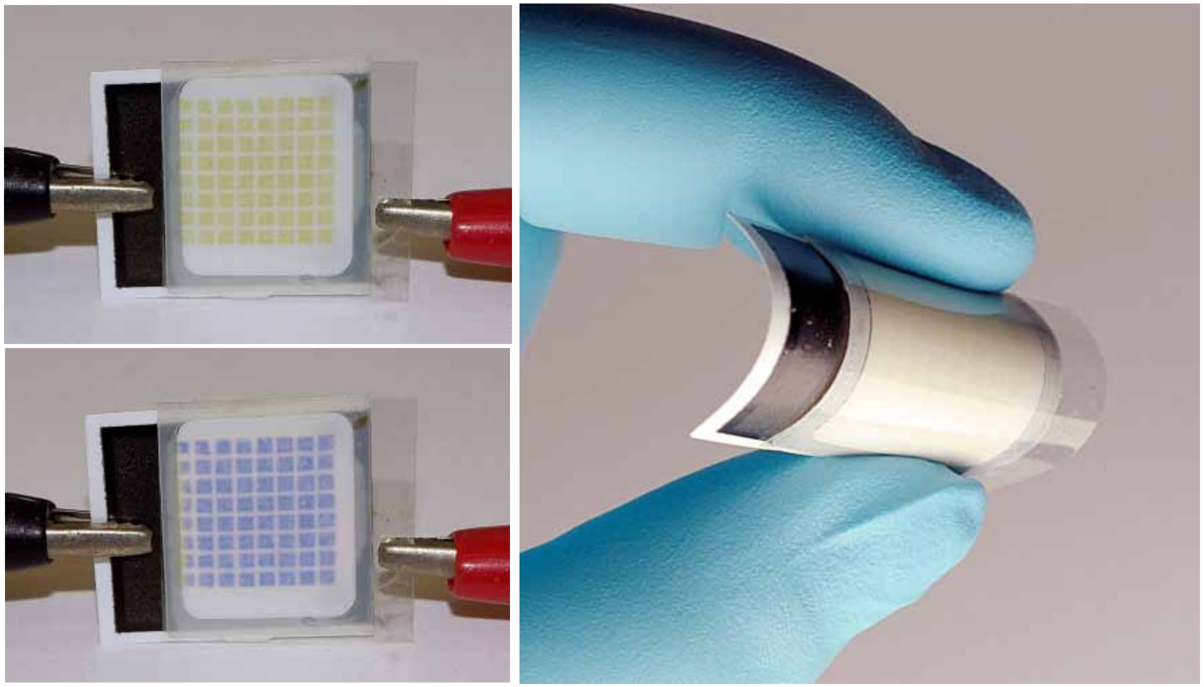
PET Substrate
All layers printed

Screen printed 8x8 passive matrix based on SCN-Li+/TiO2/thermoset solid state electrolyte (3x3 cm)



All-solid-state EC prototypes (passive matrix)

Paper substrate



Flexo printed 8x8 passive matrix based on SCN-Li+/TiO2/thermoset solid state electrolyte (5x2 cm)

All-solid-state EC prototypes

All-solid-state EC prototypes

All-solid-state EC prototypes

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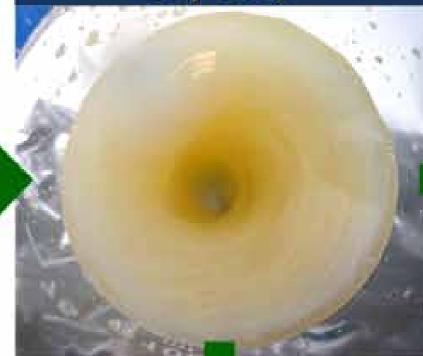
All-solid-state EC prototypes

Recycling

Scrap or waste electrolyte

Grinding in the mill

Water washout of SCN, Li^{+}, ClO_4^{-}



Water evaporation at elevated T (<90C)

SCN, Li^{+} and ClO_4^{-} in their original state:

- Reuse in the synthesis of electrolytes
- SCN degradation and production of lithium carbonate (Li_2CO_3)

Separation of solids

Powdered fillers:

- Reinforcement in composites
- Thermal utilization with energy recovery
- Degradation and reconstitution of the product

Plastic crystal/thermoset/metal oxide

Reprocessing of solid state electrolyte into thermoset filler and Li^{+} doped SCN

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erc

SEVENTH FRAMEWORK PROGRAMME

A3Ple
Autonomous Printed Paper Products for Labels & Electronics

SMART-EC

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Obrigado