Electrochromic Nanomaterials Based on Hybrid Molybdenum-Tungsten Oxide: Synthesis, Wet Coating and Structural / Optoelectronic Characterizations

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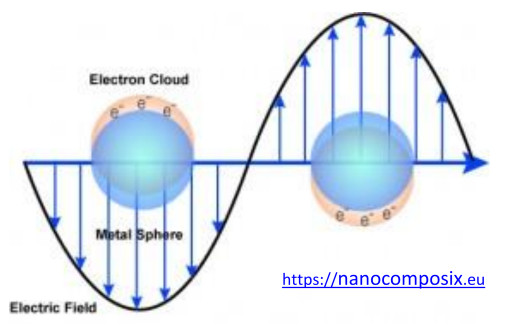
Electrochromic technology for smart windows

Electrochromic (EC) materials display the ability to **reversibly switch between a transparent and a colored state** upon the insertion/extraction of electrons and ions (H^+, Li^+...) during the application of a potential.

In **highly doped metal oxides nanostructures including oxygen vacancy doped tungsten oxide WO_{3-x}**, light absorption can take place through the collective oscillation of free charge carriers via **localized surface plasmon resonance** (LSPR). In this case, the absorbance typically lies in the near infrared (NIR) range.

LSPR principle



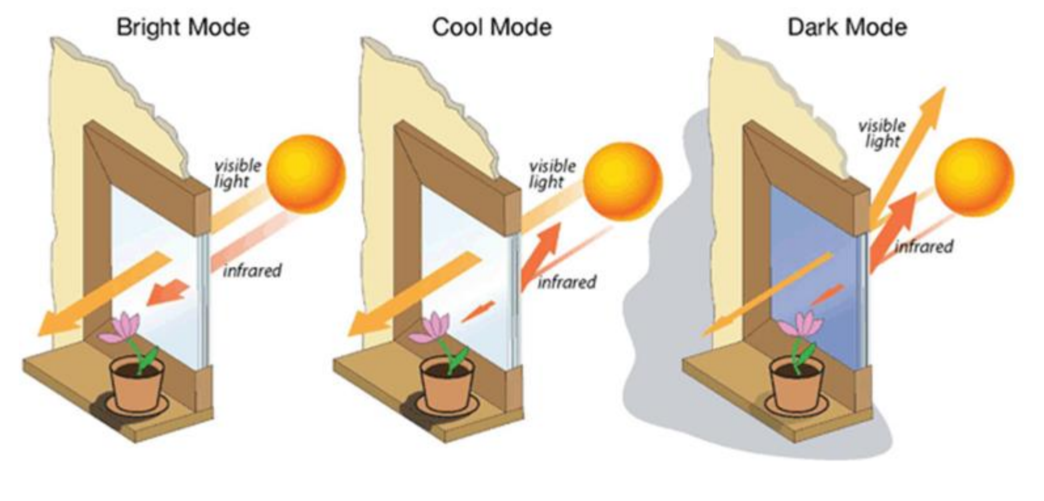
$$\omega_p = \sqrt{\frac{n_e e^2}{\varepsilon_0 m}}$$

n_e = electron density
e = electron charge
m = electron mass

In a recent work, Yamashita *et al.* have reported a great **amplification of the LSPR signal** through the **hybridation of tungsten and molybdenum oxides** ($Mo_{1-y}W_yO_{3-x}$) with a resulting resonance standing at the VIS limit of the NIR range (~900 nm). The application of such material in **electrochromic "smart windows"** could lead to use a single material for **selectively and independently modulating the visible and NIR contributions** of the incident solar radiations.

Yamashita et al. *J. Phys. Chem. C* **2017**, *121*, 23531–23540.

VIS / NIR selective smart windows



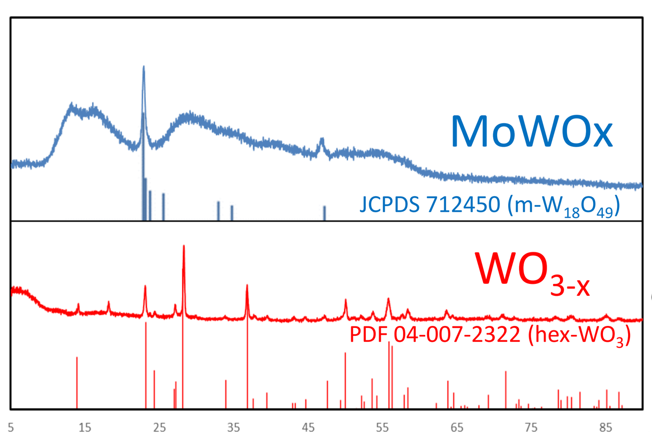
Llordes, A. et al. *Plasmonic Electrochromism of Oxide Nanocrystals. Electrochromic Materials and Devices* **2015**, 363-398

Powder characterizations : $Mo_{1-y}W_yO_{3-x}$ vs WO_{3-x}

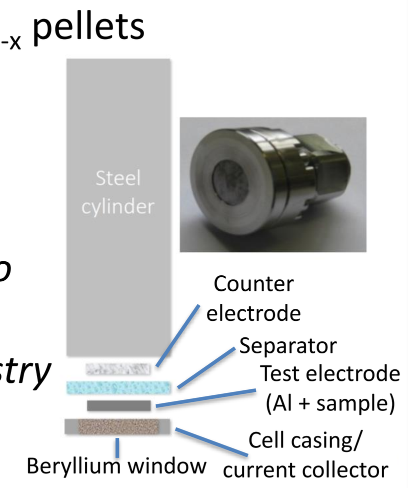
Solvothermal synthetic route : Mo and/or W + H_2O_2 in IPA
(adapted from the work of Yamashita *et al.*)

$Mo_{1-y}W_yO_{3-x}$ (« MoWOx ») urchins

WO_{3-x} pellets



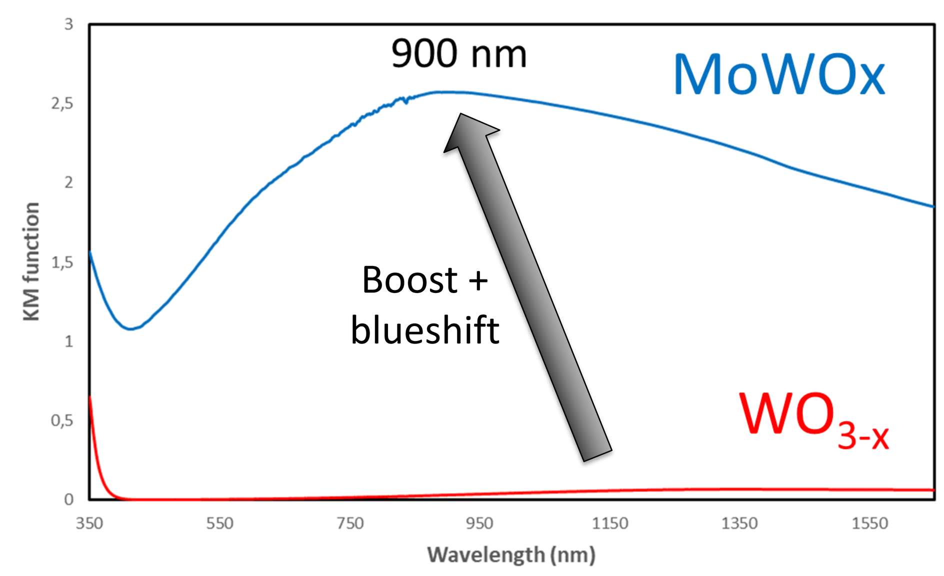
XRD → *In operando with electrochemistry (ongoing)*



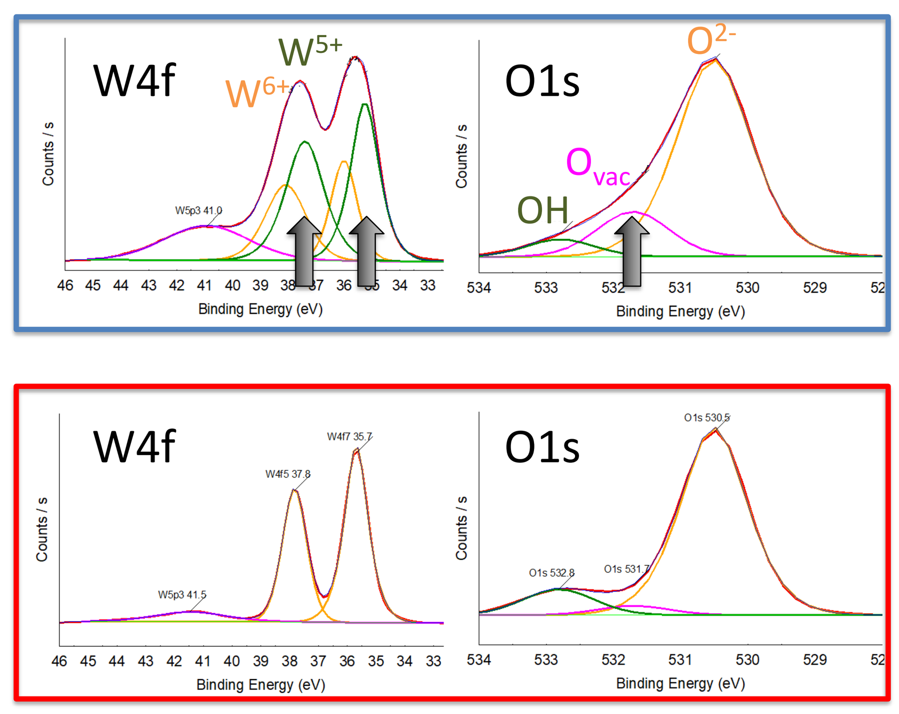
Mahmoud, A. et al. *ACS Appl. Mater. Interfaces* **2018**, *10*, 34202–34211.

Characterization

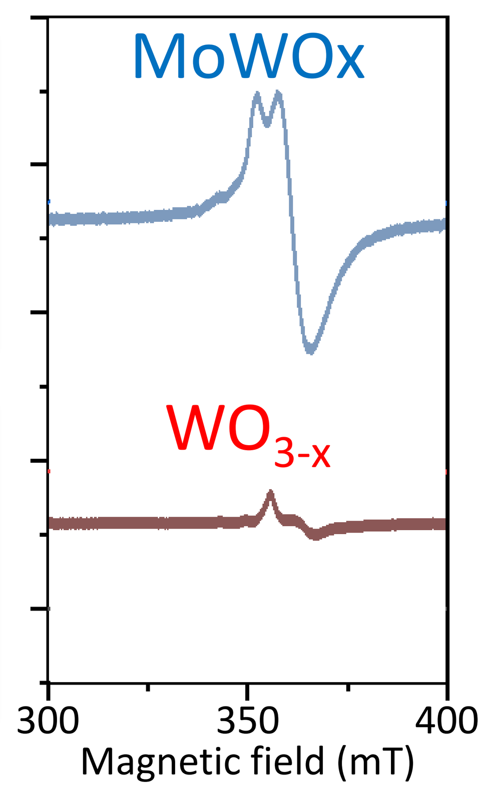
Morpho-structural · Optical · Electronic structure



XPS (collab. UNamur)



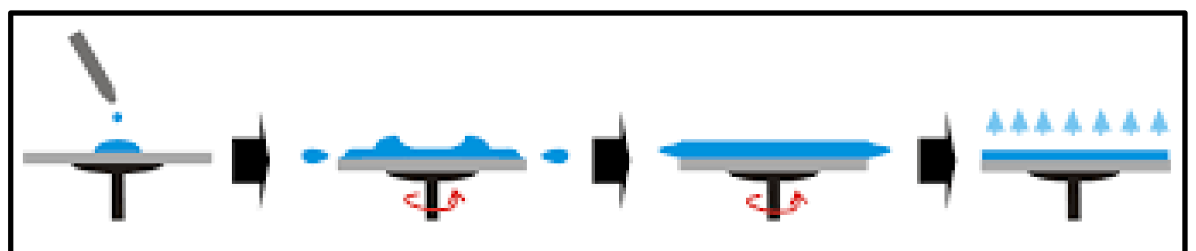
EPR (Collab. ICMCB)



Conc. of **reduced species** and **O_{vac} greater in hybrid**
→ Explains the **increase in the LSPR signal**

Hybrid Molybdenum-Tungsten Oxides nanomaterials as plasmonic EC films

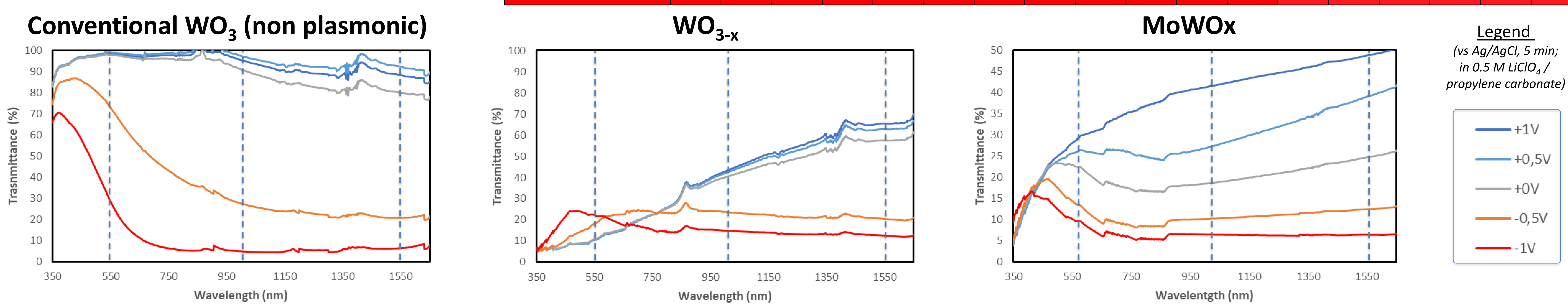
Wet coating on FTO glass by **spin coating**
Powders dispersed in EtOH (200 mg/mL), 2000 rpm, 60 sec



Chebil, Mohamed. (2013). Etude de films ultraminces de polystyrène par réflectivité des rayons X et ellipsométrie en fonction de leur exposition à du CO2.

Spectroelectrochemistry

	Conventional WO_3 (Chatzikyriakou, D. *Microporous and Mesoporous Materials* **2017**, *240*, 31–38.)						WO_{3-x}						MoWOx					
	$T_{550\,nm}$	ΔT_{bl}	$T_{1000\,nm}$	ΔT_{bl}	$T_{1550\,nm}$	ΔT_{bl}	$T_{550\,nm}$	ΔT_{bl}	$T_{1000\,nm}$	ΔT_{bl}	$T_{1550\,nm}$	ΔT_{bl}	$T_{550\,nm}$	ΔT_{bl}	$T_{1000\,nm}$	ΔT_{bl}	$T_{1550\,nm}$	ΔT_{bl}
+1 V (bleached)	98,5		95,5		88,4		10,4		42,8		65,4		28		41,2		48,7	
+0 V (NIR selective)	98,1	***0,4***	91,1	***4,4***	80,1	***8,3***	10,8	***-0,4***	40,1	***2,7***	57,6	***7,8***	22,9	***5,1***	18,4	***22,8***	24,6	***24,1***
-1 V (colored)	28,4	***70,1***	4,8	***90,7***	6,3	***82,1***	22,4	***-12***	15	***27,8***	12,7	***52,7***	10,1	***17,9***	6,4	***34,8***	6,4	***42,3***



→ Lower contrasts in « MoWOx » than with conventional, non-plasmonic WO_3 but **selective and independent modulation** of **VIS & NIR** as a function of V

Conclusions

Hybrid Molybdenum-Tungsten oxides nanomaterials are obtained by **solvothermal synthesis**. In comparaison with undoped WO_{3-x}, a **boost in the optical signature** has been observed, which can be linked to a **concentration increase of reduced species and oxygen vacancies** in the material. The « MoWOx » powder is then wet-processed as thin film by spin coating and succesfully **used as plasmonic EC material**, dispalying a **selective and independent modulation of both visible and NIR wavelengths** as a function of the applied potential.

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