Hybrid Molybdenum-Tungsten Oxide as Plasmonic Electrochromic Material for Dual-Band VIS-NIR Smart Windows

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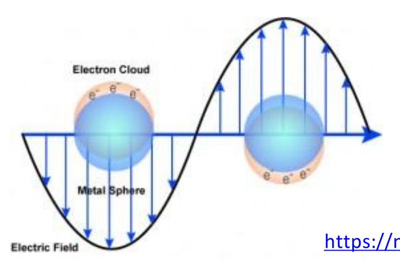
Plasmonic nanomaterials for electrochromic smart windows

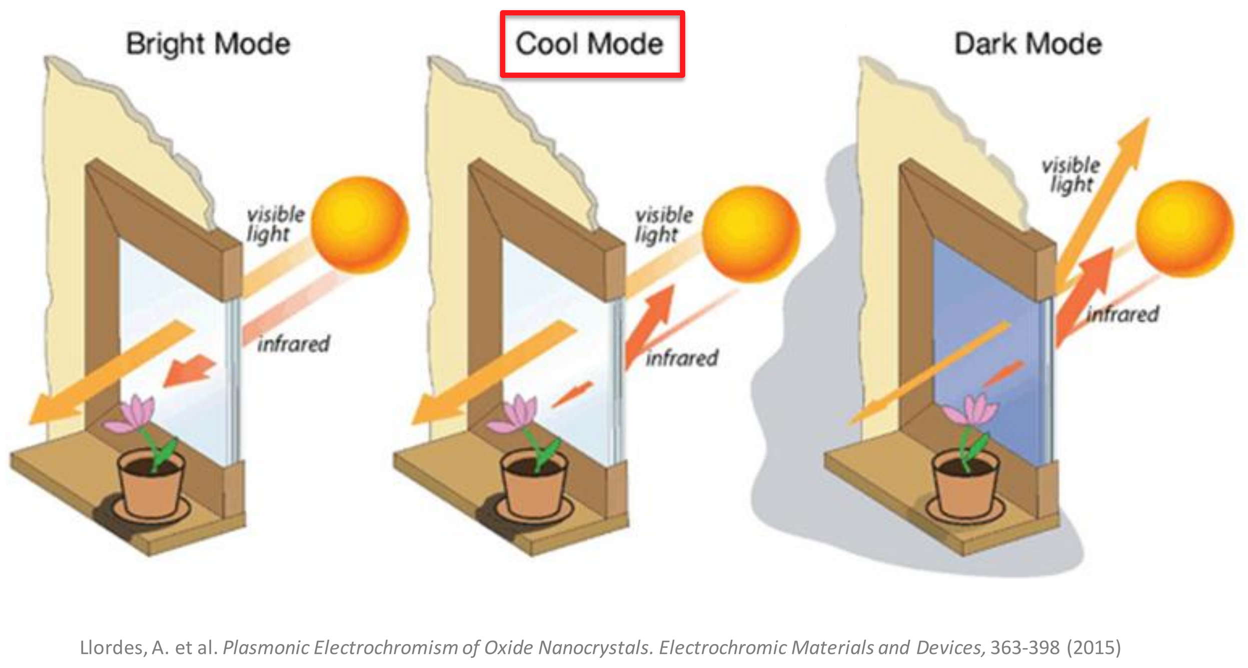
In selective nanomaterials, light absorption can take place through the collective oscillation of free charge carriers as **localized surface plasmon resonance (LSPR)**. In the case of **highly doped metal oxide nanocrystals**, absorption typically lies in the near-infrared (NIR), leading to optically-active systems where such radiations can be controlled independently from visible VIS light.

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



Plasmonic metal oxide nanomaterials can notably be used in **electrochromic "smart windows"**, able to reversibly switch between optical states upon charge insertion/extraction, leading to a **selective and independent control of light (VIS) and heat (NIR) contributions of the solar radiation** (*dual-band modulation*), and providing access to a **"cool" filtration mode** combining VIS transparency and NIR darkening.

Recently, **hybrid molybdenum-tungsten substoichiometric oxides $Mo_{1-y}W_yO_{3-x}$ ("MoWOx")** have been shown to present LSPR absorption of increased intensity around ~900 nm, which appears of strong topical interest for the design of **novel dual-band plasmonic EC materials**.



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

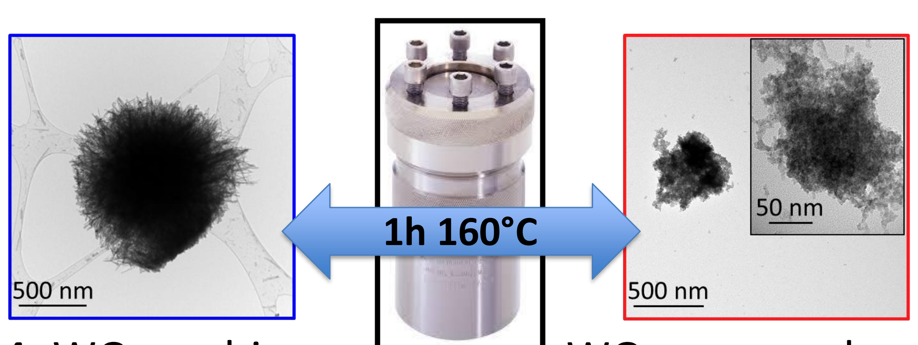
Synthesis and characterization of MoWOx powders

Morpho-structural

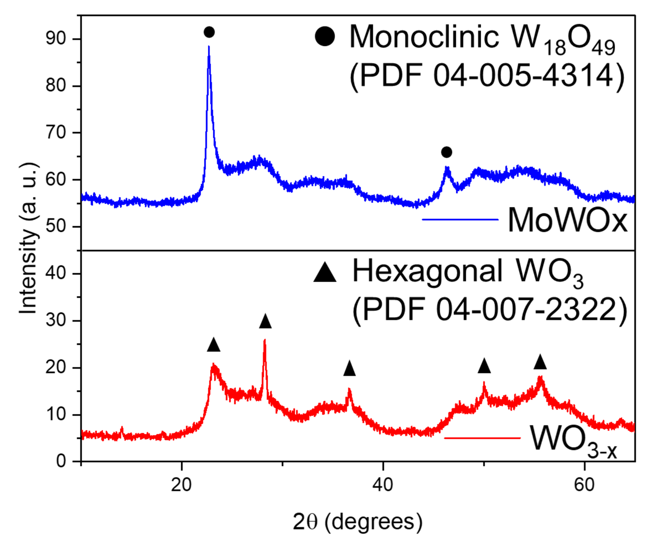
Solvothermal synthetic route

Mo and/or W + H_2O_2 in isopropanol

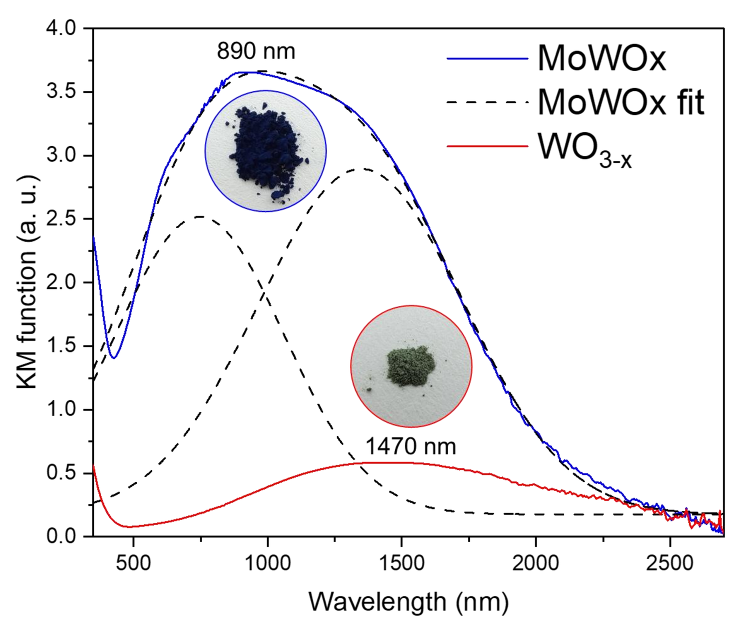
(adapted from Yamashita *et al.*, J. Phys. Chem. C 2017)



MoWOx urchins | WO_{3-x} nanospheres



Optical

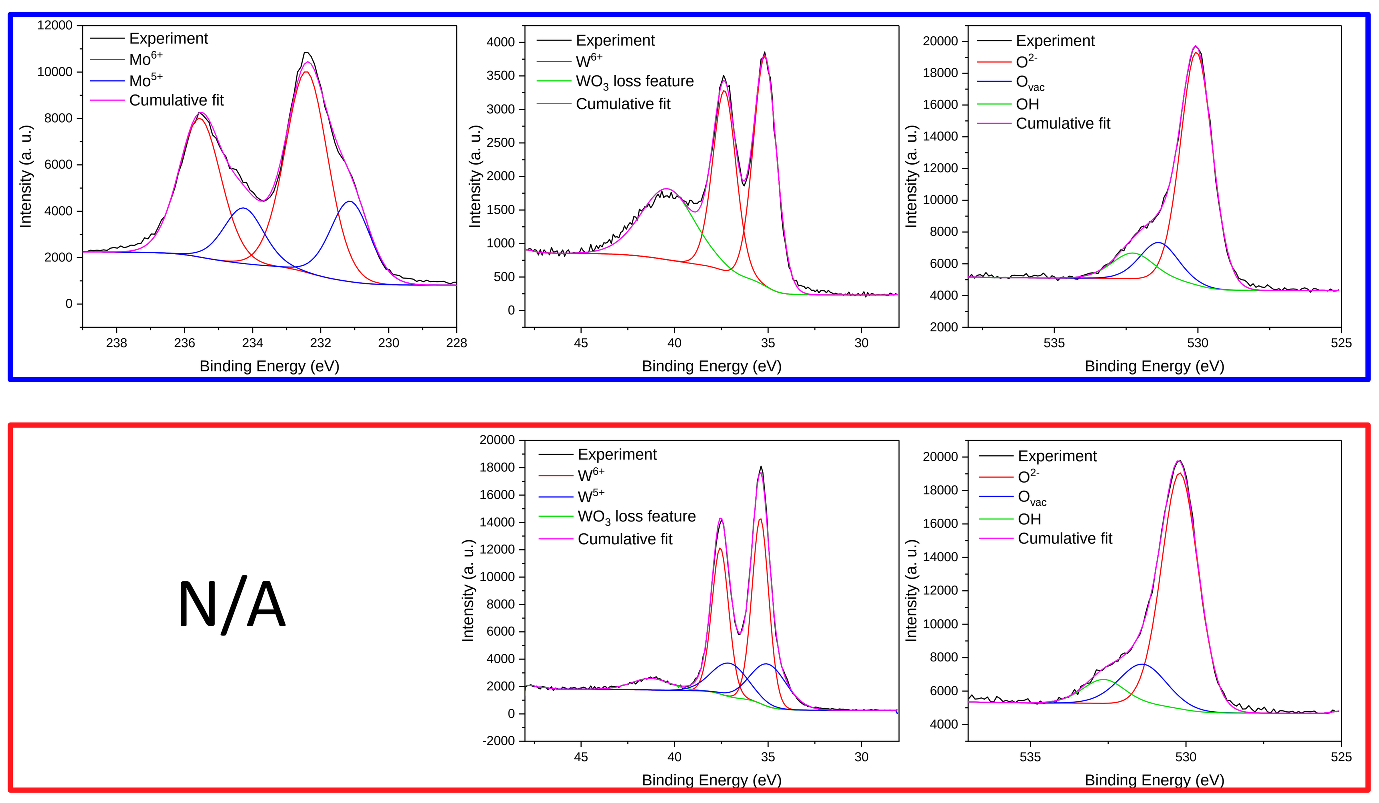


Increase in LSPR signal intensity upon **hybridization; blue tinted** powders indicating **more O_{vac}**

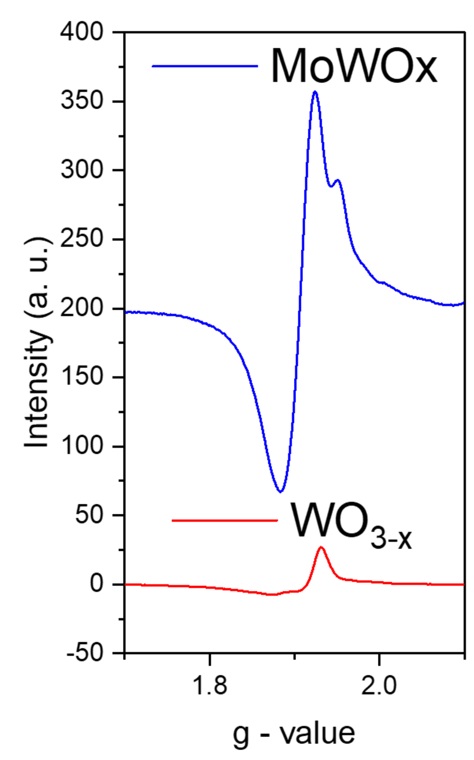
Electronic structure

XPS (collab. UNamur)

Mo3d | W4f | O1s



EPR (collab. ICMCB)



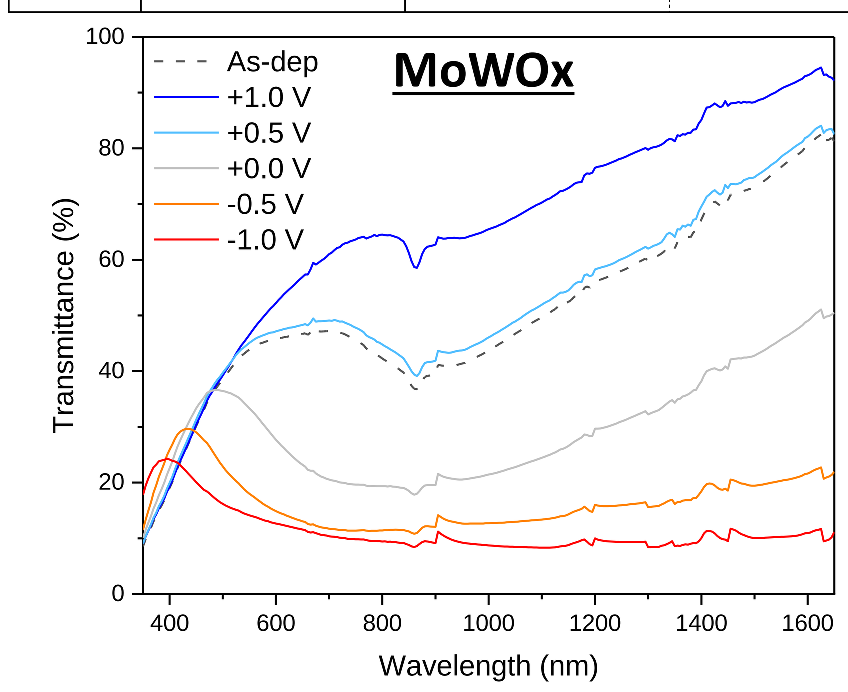
Concentration of **reduced species** and **O_{vac} larger in MoWOx**

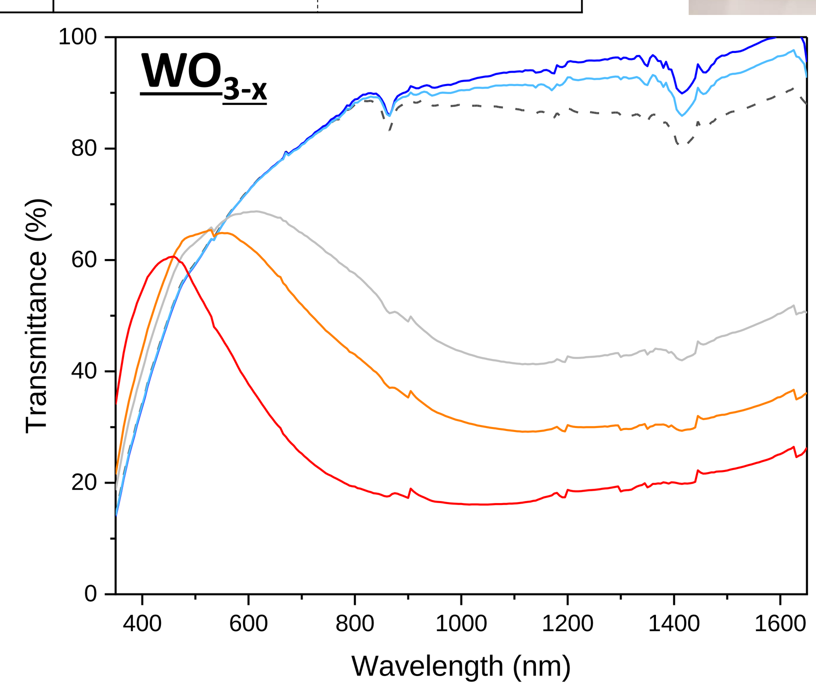
→ Responsible for the **increase in LSPR signal**

MoWOx as plasmonic electrochromic films

Li⁺ electrolyte (small cation)

	Bleached (+1V)		Intermediate (+0V)				Dark (-1V)			
	%T		%T		ΔT		%T		ΔT	
	VIS	*NIR*	VIS	*NIR*	VIS	*NIR*	VIS	*NIR*	VIS	*NIR*
MoWOx	46.8	*76.1*	31.1	*30.8*	15.8	*45.3*	23.3	*9.5*	23.5	*66.6*
WO_{3-x}	61.3	*93.8*	58.7	*46.3*	2.6	*47.5*	42.6	*19.4*	18.7	*74.5*



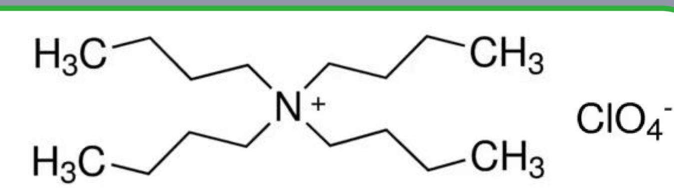


→ Dual-band behavior in both formulations, with « warm » mode (VIS-darkened, NIR-transparent) observed for MoWOx

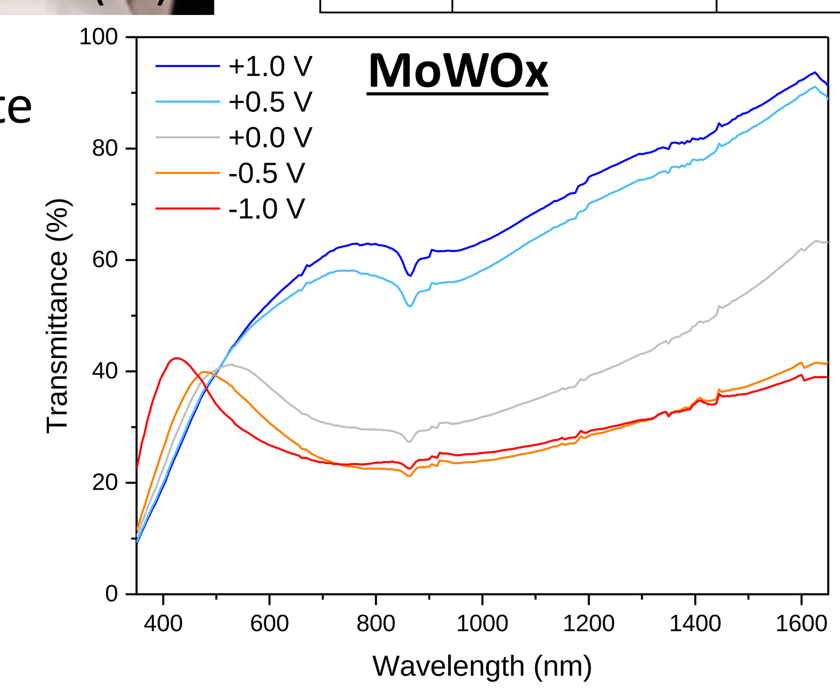
3 electrodes cell

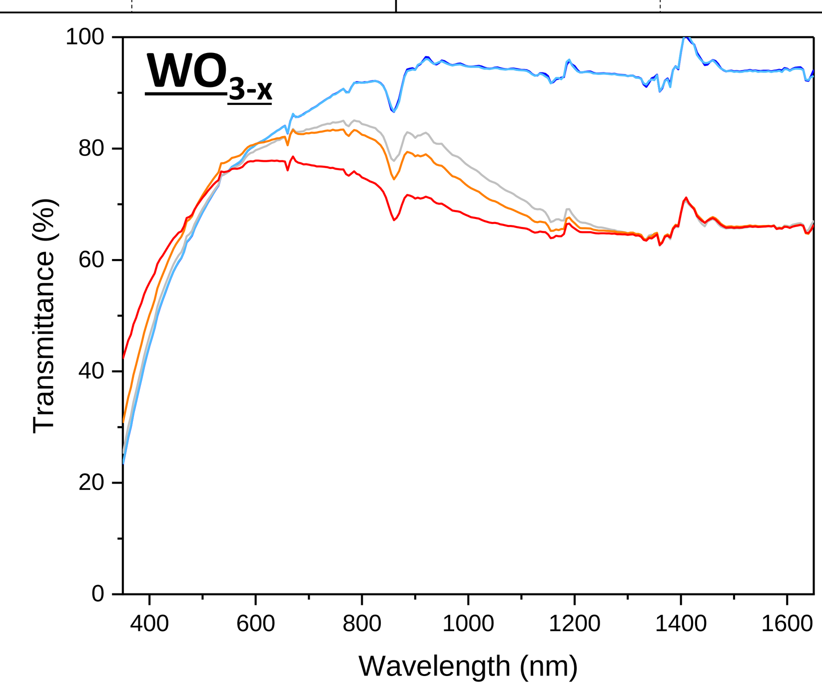
Liquid electrolyte

TBA⁺ electrolyte (large cation)



	Bleached (+1V)		Intermediate (+0V)				Dark (-1V)			
	%T		%T		ΔT		%T		ΔT	
	VIS	*NIR*	VIS	*NIR*	VIS	*NIR*	VIS	*NIR*	VIS	*NIR*
MoWOx	43.0	*74.2*	32.6	*41.3*	10.4	*32.9*	30.6	*29.9*	12.3	*44.3*
WO_{3-x}	69.7	*93.7*	69.1	*71.5*	0.5	*22.2*	70.1	*67.4*	-0.4	*26.3*





→ Confirmation of the capacitive (plasmonic) behavior for the NIR modulation through electrochemistry in $TBAClO_4$/PC

Conclusions

Hybrid molybdenum-tungsten oxides have been obtained by solvothermal route, observing an expected **boost of optical absorption** that can be linked to an **increase in the concentration of reduced species and oxygen vacancies** in the material.

Films of both formulations succesfully **display dual-band electrochromic behavior**, with **MoWOx exhibiting a "warm" mode** in its oxidized state.

Acknowledgements: PLASMON_EC Project (# 35271134), FRS-FNRS, Prof. Luc Henrard and co-workers @ UNamur (Belgium) and Dr. Aline Rougier and co-workers @ ICMCB Bordeaux (France)