Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2018

Tungsten oxide ion gel-gated transistors: how structural and electrochemical properties affect the

doping mechanism

M. S. Barbosa,^{a,b} F. M. B. Oliveira,^{a,c} X. Meng,^b F. Soavi,^{d*} C. Santato,^{b*} and M. O. Orlandi^{a*}

^a Departamento de Físico-Química, Universidade Estadual Paulista (UNESP), Rua Professor Degni, 55,

Araraquara, 14800-060, Brazil.

^b Département de Génie physique, Polytechnique Montréal, C.P. 6079, Succ. Centre-Ville, Montréal,

H3C 3A7, Canada.

^c Department of Chemistry, Federal University of São Carlos, CEP 13565-905, P.O. Box 676, São

Carlos, Brazil.

^d Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via Selmi, 2, Bologna, 40126, Italy. Dual beam microscopy (Focused Ion Beam and Scanning Electron Microscopy) was used to examine the interfaces in the devices and determine the thickness of the tungsten oxide films. The interfaces in the devices were examined after the deposition of the oxide film on patterned substrates (Si/SiO₂ patterned with Ti/Au electrodes) and before the incorporation of the ion gel. A Ga⁺ beam was used to etch a squared hole in the channel (10 μ m-deep) for cross-section analysis. Figures S2 - S4 show the secondary electrons SEM images (left) and EDS maps (right) of relevant chemical elements, with the intensity of the signal indicated by the intensity of the color. For W, the selected energy for the EDS analysis was 8.396 eV, which corresponds to the L α energy, despite a much more intense M line available at 1.774 eV. Our choice was motivated by the need to avoid the superposition of the signal with the Si K α energy, at 1.739 eV. Au was analyzed at the M α 1 energy, 2.120 eV. O was analysed at the K α energy, 0.525 eV.



Figure S1: Cross-sectional SEM/EDS of granular films on Au patterned substrates. Secondary electron SEM image (a) and EDS maps of Au M α 1 (b); Si K α (c); W M (d); O K α (e).



Figure S2: Cross-sectional SEM/EDS of nanofibers on Au patterned substrates. Secondary electrons SEM image (a) and EDS maps of Au M α 1 (b); Si K α (c); W M (d); O K α (e).



Figure. S3: Cross-sectional SEM/EDS of nanoplates deposited on Au patterned substrates. Secondary electrons SEM image (a) and EDS maps of Au M α 1 (b); Si K α (c); W M (purple, d); O K α (e).



Figure S4: Survey XPS scan, for the tungsten oxides (granular, nanofibers and nanoplates) considered in this work. Sn from Fluorine-doped Tin Oxide glass substrate) was detected in granular films.



Figure S5: Cyclic voltammetry of tungsten oxide samples, at 5mV/s, interfaced to the two different ion gels studied in this work (first 4 cycles). [EMIM][TFSI]SOS (a) hexagonal granular (b) hexagonal nanofiber (c) monoclinic nanoplate. [EMIM][TFSI]SMS as gating medium: (d) hexagonal granular, (e) hexagonal nanofiber (f) monoclinic nanoplate. Current normalized over the BET surface area (see main text).



Figure S6: a) Source and drain electrode size (not in scale); b) geometric area considered for granular films and nanoplates (external rectangle) and nanofibers (internal rectangle).

For granular films and nanoplates, tungsten oxides cover the whole substrate, therefore the geometric area was the area covered by the ion gel ($0.5 \text{ cm} \times 1 \text{ cm}$). For nanofiber films, the electrodes and channel region area was considered as geometric area ($0.4 \text{ cm} \times 0.1 \text{ cm}$).



Figure S7: Transistor characteristics, up to V_{gs} =0.9 V, of the tungsten oxide samples investigated in this work. Forward transfer at V_{ds} =0.5 V and output (V_{gs} =0, 0.6, 0.8, 0.9 V) for [EMIM][TFSI]SOS as the gating medium: (a) hexagonal granular (b) hexagonal nanofiber (c) monoclinic nanoplate. For [EMIM][TFSI]SMS as the gating medium: (d) hexagonal granular (e) hexagonal nanofiber (f) monoclinic nanoplate.



Figure S8: Forward transfer characteristics of tungsten oxide samples investigated in this work (V_{ds} =0.5 V), plotted in semi-logarithm scale. For [EMIM][TFSI]SOS as the gating medium: (a) hexagonal granular, (b) hexagonal nanofiber, (c) monoclinic nanoplate. For [EMIM][TFSI]SMS as the gating medium: (d) hexagonal granular, (e) hexagonal nanofiber, (f) monoclinic nanoplate.

Hexagonal tungsten oxide (JCPDS #85-22459)		Granular films		Nanofibers	
2 0	Ι	2	Ι	2 0	Ι
13.95	89	13.86	64	13.88	42
23.19	79	23.34	79	23.24	55
24.28	33	24.14	27	24.2	35
28.11	100	27.97	100	27.95	100
49.75	23	36.72	13	36.81	8

Table S1: Comparison between literature and our experimental data for peak position (2 theta) and signal intensity (I) for hexagonal granular and nanofiber tungsten oxides.

Monoclinic tungsten oxide (JCPDS #72-677)		Nanoplates		
2 0	Ι	2 0	Ι	
23.11	99	23.05	100	
23.58	96	23.52	29	
24.35	99	25.28	38	
28.61	16	28.43	14	
28.87	16	28.84	15	
33.23	38	33.23	12	
33.55	24	33.55	12	
34.15	56	34.08	13	
47.23	9	47.22	10	
49.89	22	49.84	7	

Table S2: Comparison between literature and our experimental data for peak position and signal intensity for monoclinic nanoplates.

Tungsten oxide	Thickness	BET specific	RBS density	Surface area
	(nm)	area (m²/g)	(g/cm ³)*	(m ²)
Granular	50	8	7.1	1.5×10-4
Nanofibers	500	60	7.0	4.3×10-4
Nanoplates	400	9.8	6.0	1.2×10 ⁻³

Table S3: Film thickness, BET specific surface area and estimated material surface area.

Brunauer Elmett Teller (BET) analysis was used to measure the specific surface area of the tungsten oxide materials investigated in this work. To estimate the surface area available for doping, initially the film geometric area (please see Figure S6) was multiplied by film thickness (obtained by FIB measurements, please see S2-S4) to find the film volume. Multiplying the film volume by the density (deduced by Rutherford Backscattering Spectroscopy, RBS) and we estimated the mass of the tungsten oxide available for doping. Eventually, the value of the mass was multiplied by the values of the BET specific surface area obtained experimentally to get the surface area available for doping.

*Tungsten oxide bulk density reported in literature is 7.16 g/cm^{3.1} Lower values of the density were expected for nanofibers and nanoplates given the porosity of these materials.

Channel material reference	Gating Medium	Charge carrier density (cm ⁻²)	Mobility (cm ² /Vs)	Modulation	Mechanism
Epitaxial WO ₃ [2]	HMIM-TFSI Ionic Liquid	-	-	On/Off 10 ⁶ at V _{gs} =3 V	Oxygen electromigr.
Porous hexagonal WO ₃ films [3]	DEME-TFSI ionic liquid	10 ¹⁶	-	5 o.o.m. decrease in sheet resistance	Electrostatic Electrochem
Amorphous and crystalline WO ₃ Films [4]	Li ⁺ doped plastic resin	-	-	On/Off 10 ⁶ at V _{gs} =4V	Elecrochem. (Li+ insertion)
Atomically flat WO ₃ films [5]	DEME-TFSI ionic liquid	-	1	6 o.o.m. decrease in sheet resistance at $V_{gs}=2.2$ V	Electrochem: residual proton insertion
Monoclinic WO ₃ films [6]	EMIM-TFSI ionic liquid	-	6x 10 ⁻¹	10 ³ at 1.5 V	Elecromigr. and electrochem.
Epitaxial WO ₃ films [7]	HMIM-TFSI ionic liquid	-	-	-	Oxygen electromigr.
Monoclinic WO ₃ films [8]	DEME-TFSI	10 ¹⁶	-	4 o.o.m. decrease in sheet resistance at V_{gs} =4.5 V	Electrochem: residual proton insertion Chemical: H ₂ evolution
Granular hexagonal WO ₃ films (this work)	[EMIM][TFSI] SOS ion-gel	10^{14} (BET) 10^{15} (geometric)	2.2×10 ⁻³ (BET) $8x10^{-4}$ (geometric)	On/Off: 10 at V_{gs} =0.9V 50 at V_{gs} =1.2V	Electrochem: Residual proton insertion Chemical: H ₂ evolution
Nanofiber hexagonal WO ₃ films (this work)	[EMIM][TFSI] SOS ion-gel	10^{14} (BET) 10^{16} (geometric)	5.5×10 ⁻³ (BET) 2.6×10 ⁻⁵ (geometric)	On/off: 10^2 at V _{gs} =0.9V 10^3 at V _{gs} =1.2V	Electrochem.: residual proton insertion Chemical: H ₂ evolution
Nanoplate monoclinic WO ₃ films (this work)	[EMIM][TFSI] SOS ion-gel	10^{14} (BET) 10^{15} (geometric)	$ \begin{array}{c} 1.2 \times 10^{-2} \\ (BET) \\ 5.0 \times 10^{-4} \\ (geometric) \end{array} $	$\begin{array}{c} \text{On/Off:} \\ 10^3 \text{ at } V_{gs} = 0.9 \text{V} \\ 10^4 \text{ at } V_{gs} = 1.2 \text{V} \end{array}$	Electrochemical : residual proton insertion Chemical: H ₂ evolution

Table S4: Film characteristics, electrolyte interface, device figures of merit, and proposed gating mechanisms reported on recent WO₃ electrolyte-gating studies.

References:

- 1 S. H. Lee, R. Deshpande, P. A. Parilla, K. M. Jones, B. To, A. H. Mahan and A. C. Dillon, *Adv. Mater.*, 2006, **18**, 763–766.
- 2 S. G. Altendorf, J. Jeong, D. Passarello, N. B. Aetukuri, M. G. Samant and S. S. P. Parkin, *Adv. Mater.*, 2016, **28**, 5284–5292.
- 3 P. M. Wu, S. Ishii, K. Tanabe, K. Munakata, R. H. Hammond, K. Tokiwa, T. H. Geballe and M. R. Beasley, *Appl. Phys. Lett.*, 2015, **106**, 5–9.
- 4 P. Barquinha, S. Pereira, L. Pereira, P. Wojcik, P. Grey, R. Martins and E. Fortunato, *Adv. Electron. Mater.*, 2015, **1**, 1–7.
- 5 X. Leng, J. Pereiro, J. Strle, G. Dubuis, A. T. Bollinger, A. Gozar, J. Wu, N. Litombe, C. Panagopoulos, D. Pavuna and I. Božović, *npj Quantum Mater.*, 2017, **2**, 1–7.
- 6 H. Kalhori, M. Coey, I. Abdolhosseini Sarsari, K. Borisov, S. B. Porter, G. Atcheson, M. Ranjbar, H. Salamati and P. Stamenov, *Sci. Rep.*, 2017, **7**, 1–7.
- 7 C. ViolBarbosa, J. Karel, J. Kiss, O. Gordan, S. G. Altendorf, Y. Utsumi, M. G. Samant, Y.-H. Wu, K.-D. Tsuei, C. Felser and S. S. P. Parkin, *Proc. Natl. Acad. Sci.*, 2016, **113**, 11148–11151.
- 8 M. Wang, S. Shen, J. Ni, N. Lu, Z. Li, H.-B. Li, S. Yang, T. Chen, J. Guo, Y. Wang, H. Xiang and P. Yu, *Adv. Mater.*, 2017, **1703628**, 1–7.