Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Fluoride additive in epoxide-initiated sol–gel synthesis enables thin-film applications of SnO_2 aerogels

Juan Pablo Correa Baena,[1,2]* David A. Kriz,[3] Marcus Giotto,[4] Steven L. Suib,[3,4] and Alexander G. Agrios[1,2]*

[1]Civil and Environmental Engineering, [2]Center for Clean Energy Engineering, [3]Department of Chemistry and [4]Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States.

JPCB and DAK contributed equally to this work.

*Corresponding authors: A.G.A. agrios@engr.uconn.edu; Tel: +1 860 486 1350;
J.P.C.B juan.correa@eplf.ch; Tel: +41 788 135459

Keywords: Sol-gel synthesis, porous materials, tin oxide, TCOs.

Table S1. Nitrogen physisorption information as a function of precursor fluorine (F:Sn) content in SnO_2 materials before and after calcination at 450˚C for 30 minutes.

F:Sn	BET surface area (m^2g^{-1})		BJH pore volume (cm^3g^{-1})	
	Uncalcined	450˚C	Uncalcined	450˚C
0:1	516	84	2.18	0.94
0.25:1	451	98	1.62	1.24
0.5:1	357	149	1.66	1.10
0.75:1	257	135	1.07	1.06
1:1	183	101	0.77	0.89

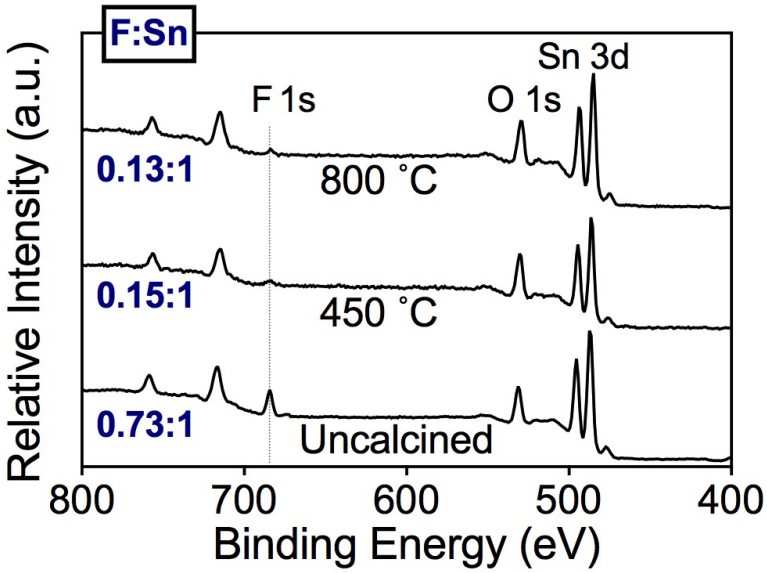

Figure S1. X-ray photoelectron spectra showing the Sn 3d, O 1s and F 1s peaks as a function of heat treatment after supercritical drying, for samples with precursor F:Sn of 1:1. Tin peaks corresponding to Sn $3d_{3/2}$ and $3d_{5/2}$ were found at 495 and 488 eV, which corroborates the oxidation state of Sn(IV). The uncalcined samples showed a ratio of 0.73:1 of F:Sn, lower than the original 1:1 in the precursor, which suggests that some of the fluorine was washed out during the solvent exchange process. F content decreases dramatically to 0.15:1 (F:Sn ratio) for materials calcined at 450˚C for 30 min. A similar F:Sn ratio is observed after calcination at 800˚C for 6 h.

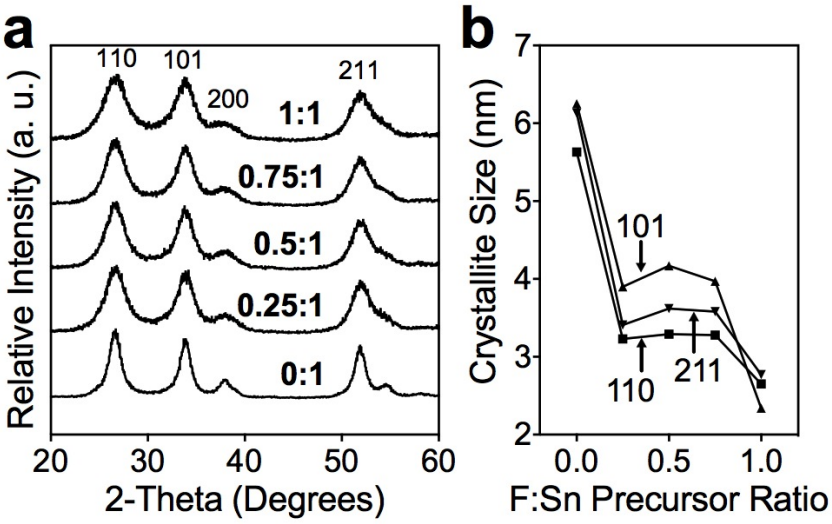

Figure S2. Powder XRD patterns for calcined SnO_2 aerogels plotted by F:Sn precursor ratio (a) and crystallite size calculated with the Scherrer equation from the three main peaks (b). All samples (calcined at 450˚C) have the tetragonal rutile phase of SnO_2 (JCPDS card no. 041-1445) which belongs to the space group P42/mnm (no. 136). No other crystal phases were detected in any of the materials. Major peaks for the (110), (101), (200) and (211) orientations were detected with high intensities, although a preferred orientation was found to be along (110). The peaks became noticeably broader with the addition of F, regardless of concentration. The crystallite size was calculated with the Scherrer equation from the well-defined peaks of (110), (101) and (211) with fairly invariable results from peak to peak. There is a significant decrease in crystallite size with even small amounts of F added with the smallest crystallite size found when F is introduced at a precursor ratio of 1:1 F:Sn.

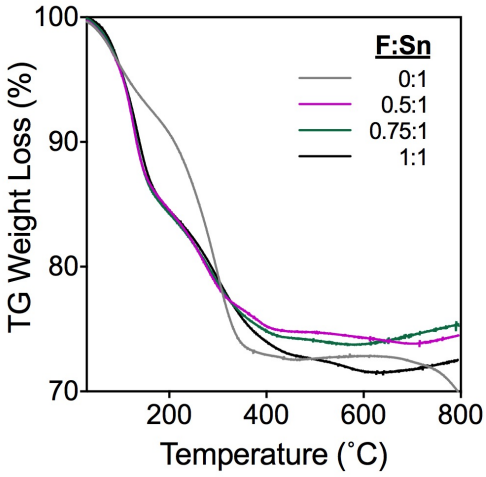

Figure S3. Thermogravimetric curves for SnO_2 samples with different amounts of precursor NH_4F. Fluorinated samples exhibit a sharp drop between room temperature and 170 °C, followed by a second, less rapid mass loss between 170 and 350 °C. The unfluorinated sample exhibits a more gradual mass loss between room temperature and 200 °C, followed by a rapid loss between 200 and 350 °C.