SUPPLEMENTARY INFORMATION

Liquid –Mix synthesis of SnO₂ nanoparticles doped with Li:

The Liquid-Mix chemistry method¹ (LM) used for the synthesis of the SnO₂ and Li doped nanoparticles is shown schematically in Figure S1(a). Initially a mixture with the desired stoichiometry of cations is added to a citric acid dissolution at room temperature. Once these cations are completely dissolved, a 3% (v/v) of EG is added under stirring at a temperature between 100-200 °C, until a 3D vitreous polymeric resin is formed with the homogeneously trapped nanoparticles. Figure S1(b) shows the thermal treatment carried out once the resin is obtained during the last process of the synthesis. First, the resin is grounded in an agate mortar several times until it becomes into a very fine black / grayish powder. This powder is then transferred to a large surface alumina nacelle, in order to increase the surface area and promote the calcination of the organic matter. This process was carried out at 350 °C during 30 hours. After this time, the residual powder containing the synthesized nanoparticles is extracted by quenching and gently re-grounded. Finally, they are reintroduced in a furnace for 12 hours at 450 °C, in order to obtain the crystalline SnO₂ material avoiding the formation of secondary phases such as SnO brookite or ternary compounds.



Fig. S1. (a) Schematic representation of the soft chemistry method used for the npLix synthesised nanoparticles. (b) Thermal treatment carried out in order to obtain SnO_2 nanoparticles with cassiterite structure.

Photoluminescence and quantitative evolution of defects with Li content:

The photoluminescence (PL) spectra was recorded at 300 K and shown in Figure S2. A 325 nm excimer laser was used to record the spectra which consist of an asymmetric broad band in the visible region with the maximum placed around 2.25 eV and a shoulder at the higher energy side. From the deconvolution of these spectra, four bands are identified with energy levels approximately corresponding with the CL bands described in the main text of the article.

The normalized PL spectra (Fig. S2) show a competition between the orange and the blue-violet bands. By increasing the amount of lithium incorporated to the nanoparticles, the orange band starts to decrease and is partially quenched whereas the blue and violet bands increase. As a result, the green band is the predominant in the PL spectra of the high Li doped samples whereas the blue region is more favoured in the CL measurements due to the different excitation mechanisms of both techniques.



Figure S2. Normalized PL spectra and its deconvolution for the complete set of studied nanoparticles.

In Table S.I, the quantitative parameters used in the Gaussian fitting of the four emission bands are presented, together with the most commonly attributed origin of the responsible defects.

npLi0						
Band	Peak position	FWHM (eV)	Peak Intensity (a.u.)	Area	Defect ^(Ref)	
Dunu	(eV)			(a.u)	•	
Orange	1,95	0,522	0,248	0,301	$(V_0)_{2,3}$	
Green	2,29	0,456	0,783	0,431	$(V_0 - Sn - V_0)_3$	
Blue	2,49	0,391	0,216	0,137	$(V_0^+)_{iso 4}$	
Violet	2,89	0,592	0,248	0,194	$(V_0^{"})_{5-7}$	

Table S.I. Fitted parameters of the PL for the different Li cat. %, in the npLix and its structure of defects. (The upper index in defect column indicates the reference for the most commonly attributed origin defect)

npLi10					
Band	Peak position	FWHM (eV)	Peak Intensity (a.u.)	Area	Defect ^(Ref)
	(eV)			(a.u)	
Orange	1,91	0,477	0,636	0,335	$(V_0)_{2,3}$
Green	2.26	0 471	0.750	0 387	$(V_0 - Sn - V_0)_3$
Green	2,20	0,171	0,700	0,007	STH ⁸
Blue	2,49	0,520	0,136	0,087	$(V_{0}^{+})_{iso^{4}}$
Violet	2,97	0,552	0,137	0,091	$(V_0^{"})_{5-7}$

npLi20						
Band	Peak position	FWHM (eV)	Peak Intensity (a.u.)	Area	Defect ^(Ref)	
	(eV)			(a.u)		
Orange	1,98	0,440	0,320	0,170	$(V_0)_{2,3}$	
Green	2 30	0.432	0.843	0 408	$(V_0 - Sn - V_0)_3$	
Gitten	2,30	0,102	0,010	0,100	STH ⁸	
Blue	2,49	0,346	0,196	0,095	$(V_0^+)_{iso^4}$	
Violet	2,89	0,580	0,369	0,246	$(V_0^{"})_{5-7}$	

npLi30							
Band	Peak position	FWHM (eV)	Peak Intensity (a.u.)	Area	Defect ^(Ref)		

	(eV)			(a.u)	
Orange	1,96	0,632	0,558	0,406	$(V_0)_{2,3}$
Green	2,29	0,372	0,382	0,203	$(V_0 - Sn - V_0)_3$ STH ⁸
Blue	2,58	0,530	0,741	0,460	$(V_0^+)_{iso^4}$
Violet	3,00	0,712	0,335	0,282	$(V_0^{"})_{5-7}$

The evolution with Li content of the peak energy position, FWHM and the relative intensity of the emission bands are shown in Figure S3. The relative intensity is calculated as the ratio of the integrated area under the Gaussian fitting curve for each band and the total emission intensity. As a general result, the blue and green bands do not significantly shift their position with the incorporation of lithium, whereas the violet and orange bands suffer from a complementary slight shift. Analogously, the relative intensity of the orange and violet band develops in a complementary form, so that the increase of one of these bands evolves parallel with the decrease of the other. Taking into account that the violet and orange bands are related to oxygen vacancies, the evolution of the corresponding defect concentration seems to be related to the accommodation of most of the charge imbalance due to the Li⁺ incorporation, inducing charge state variations of the involved oxygen vacancies, meanwhile the defects associated to the blue and green band are less influenced. Another trend is the slight decrease of the FWHM with lithium incorporation for the green, orange and even to lesser extent for the violet band, meaning that the Li incorporation does not induce a considerable degree of disorder in the tin oxide lattice affecting these emission bands. On the contrary the most sensitive band regarding the FWHM evolution is the blue band, which could be related to the positive charge of the proposed defect, which could interact strongly with the Li⁺ ions.



Figure S3. Evolution with Li content of the a) peak energy position, b) FWHM and c) the relative intensity of the emission band.

References

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