SUPPLEMENTARY INFORMATION

Figure SI-1: Transmission electron micrographs (a-c) and sizing histograms (d-f) of Sn-doped In_2O_3 nanocrystals capped with different ligands: (a,b) oleylamine, (d,e) BF_4^-, and (c,f) $(Nb_6O_{19})^{8-}$

Figure SI-2: Coupled Thermogravimetric and mass spectrometry analysis of the polyniobates and vanadates precursors performed under air (nitrogen in case of V4+) gas flow (25 mL/min) with a heating rate of 10°C/min. Gaseous phases are placed in the temperature region where were detected.

Figure SI-3: High resolution XPS of Nb 3d peak, from the top, of hexaniobate, annealed hexaniobate, decaniobate, and annealed decaniobate. All annealing was carried out at 400˚C in air. The data are shown in red and fitting results in blue. Black lines beneath each spectrum indicate residuals and data are offset for clarity.

Figure SI-4: (a) Hydrodynamic sizes (b) and zeta potential measured at different steps of the ex-situ ligand exchange process. ITO nanocrystals were capped with BF_4^- (in black), $[Nb_6O_{19}]^{8-}$ (in pink) and, $[Nb_{10}O_{28}]^{6-}$ (in blue).

Figure SI-5: Cross sectional low resolution HAADF imaging (a) and EDS mapping (b-f) of a Nb_2O_5-ITO nanocomposite film on a silicon substrate, prepared by ex-situ ligand exchange. Silicon (e) and oxygen (d) appear in the protection layer immediately on top of the composite, followed by Pt (f).

Figure SI-6: Transmission electron micrograph of $[Nb_6O_{19}]^{8-}$ capped ITO colloidal NCs. The NCs appear embedded within a continuous polyoxometalate matrix.

Figure SI-7: Fourier Transform Infrared (FTIR) spectra during the ex-situ ligand exchange of OLAM using $NOBF_4$/DMF and POMs. a) In black is shown the OLAM-capped ITO NC film prior to the exchange. In blue, are the same NCs after the exchange using $NOBF_4$/DMF. The C-H stretching bands from OLAM disappear while DMF and BF_4 bands appear confirming the effectiveness of the ligand exchange. b) Final decaniobate-ITO nanocomposite film is shown in pink together with the control sample prior exchange. The broad absorption band in both spectra is assigned to the surface plasmon resonance from free carriers in the ITO nanocrystals. In addition to that, waters of crystallization in the POM structure also contribute to the broad band.

Figure SI-8: EDS spectra of Nb_2O_5-ITO nanocomposite films obtained from a) the ex-situ and b) the in-situ ligand exchange approaches. In to Nb atomic ratios were 0.3:1 in a) and 3:1 in b). The no appearance of the Si substrate peak in a) is due to the film was much thicker than b).

Table SI-1: Surface composition of ITO nanocomposite films determined from XPS analysis

Table SI-2: Surface composition of vanadium oxide films determined from XPS analysis

Table SI-3: Surface composition of niobium oxide films determined from XPS analysis

Table SI-4: XPS peak fitting parameters of vanadium oxide films

Estimation of the NC volume fraction and the edge-to-edge interparticle spacing

The volume fraction of each component phase in the final metal oxide nanocomposite films was estimated from the metal atomic ratios measured by EDS and their bulk densities.

Distances between edges of the embedded nanocrystals in the films were estimated by assuming monodispersed spherical nanoparticles with regular spacing. This approximation leads to the following expression:

$\text{NC spacing}=2R((0.74/f_{NC})^{1/3}-1))$

, where R is the NC radius and f_{NC} the NC volume fraction

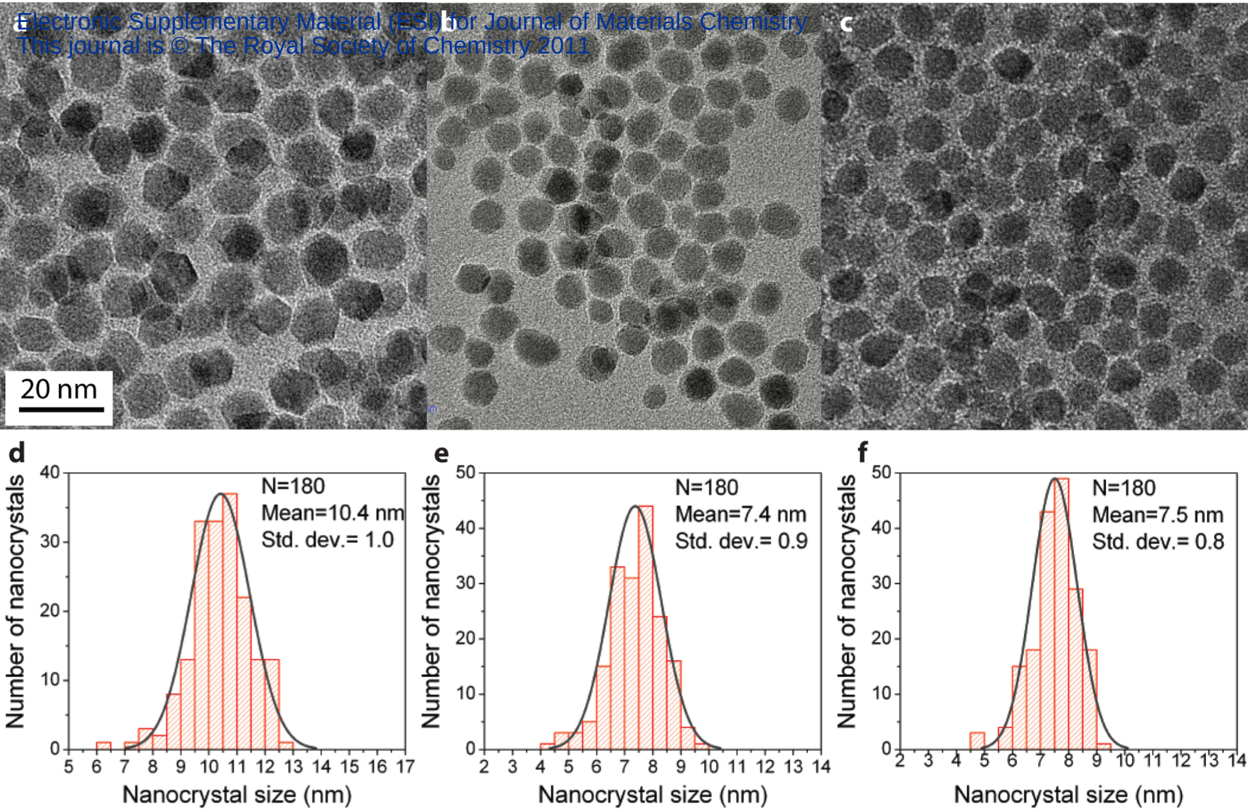
a
b
c
20 nm
d
N=180
Mean=10.4 nm
Std. dev.= 1.0
Number of nanocrystals
Nanocrystal size (nm)
e
N=180
Mean=7.4 nm
Std. dev.= 0.9
Number of nanocrystals
Nanocrystal size (nm)
f
N=180
Mean=7.5 nm
Std. dev.= 0.8
Number of nanocrystals
Nanocrystal size (nm)

Figure SI1.

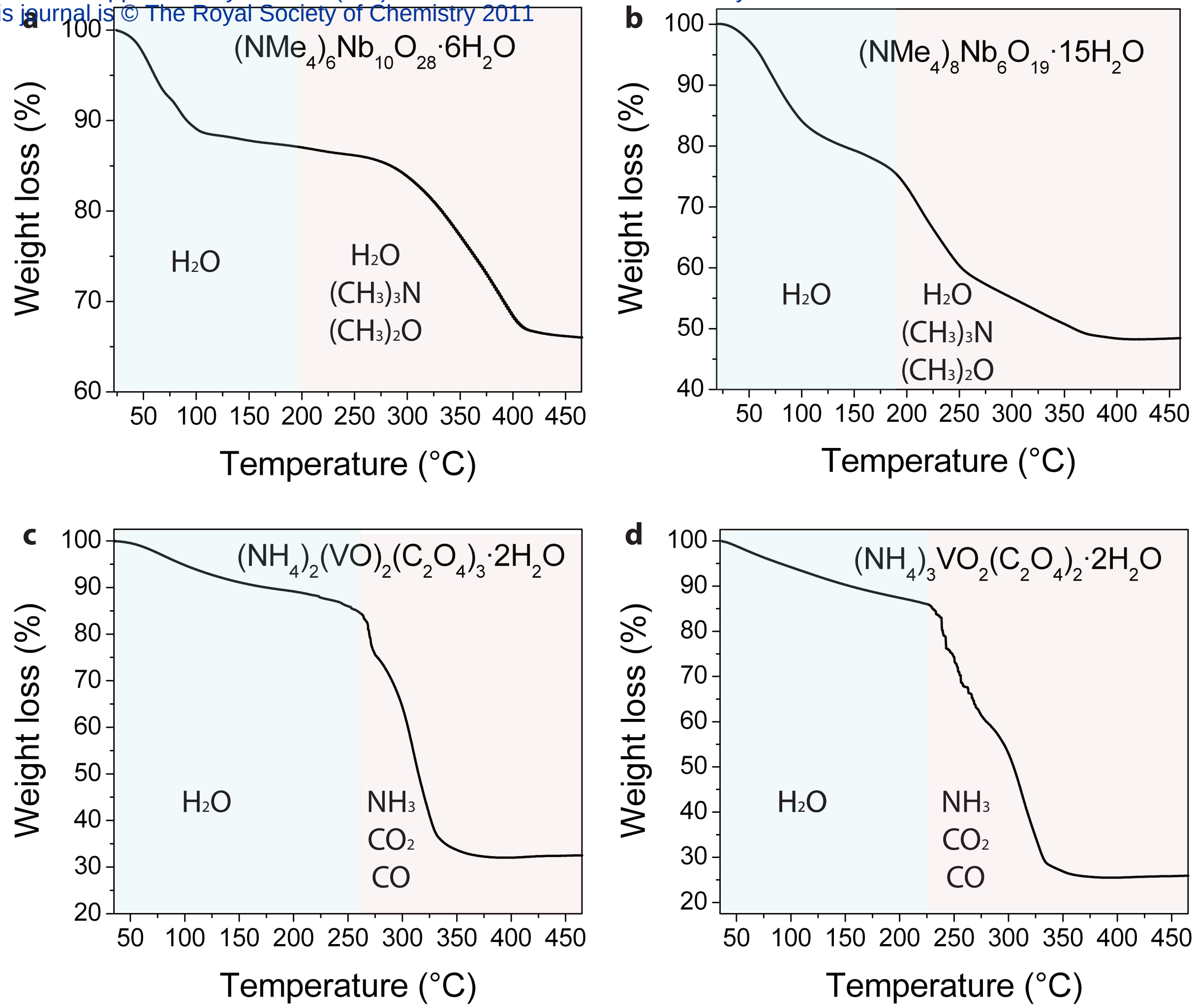
a
$(NMe_4)_6Nb_{10}O_{28}\cdot 6H_2O$
Weight loss (%)
Temperature (°C)
H_2O
H_2O
$(CH_3)_3N$
$(CH_3)_2O$
b
$(NMe_4)_8Nb_6O_{19}\cdot 15H_2O$
Weight loss (%)
Temperature (°C)
H_2O
H_2O
$(CH_3)_3N$
$(CH_3)_2O$
c
$(NH_4)_2(VO)_2(C_2O_4)_3\cdot 2H_2O$
Weight loss (%)
Temperature (°C)
H_2O
NH_3
CO_2
CO
d
$(NH_4)_3VO_2(C_2O_4)_2\cdot 2H_2O$
Weight loss (%)
Temperature (°C)
H_2O
NH_3
CO_2
CO

Figure SI2.

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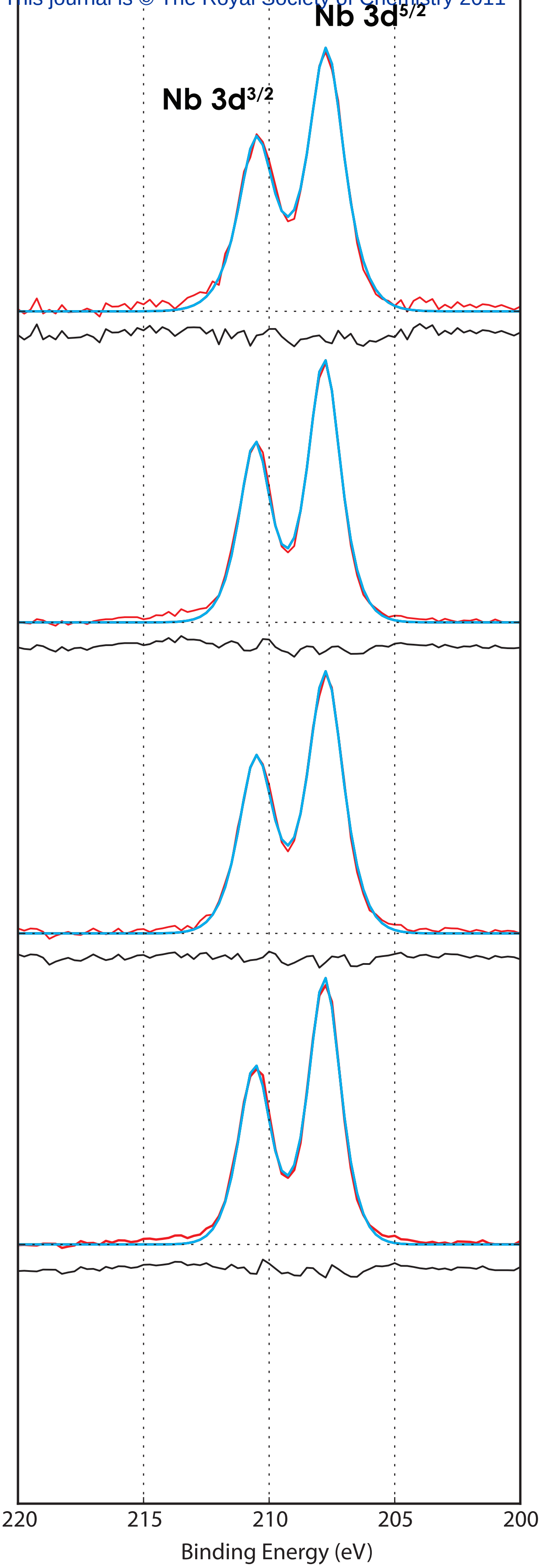
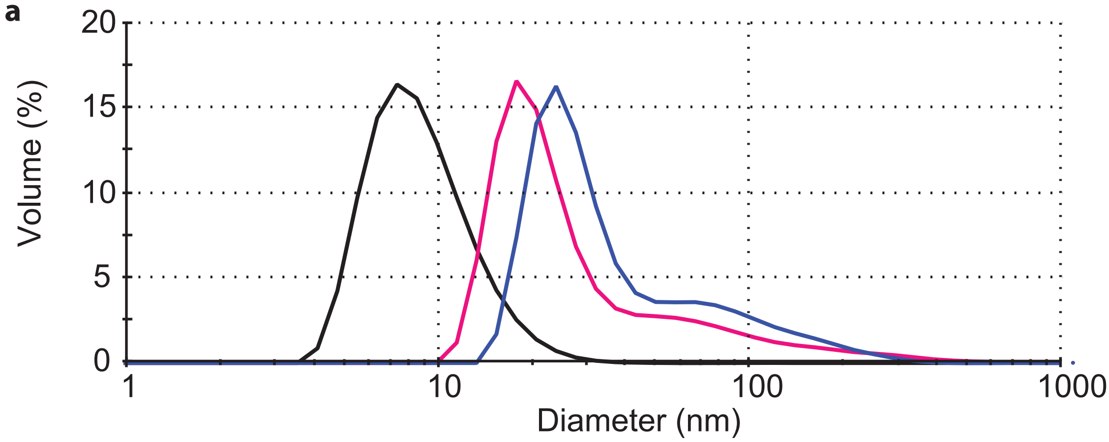


Figure SI3.


a
20
15
10
5
0
Volume (%)
1
10
100
1000
Diameter (nm)

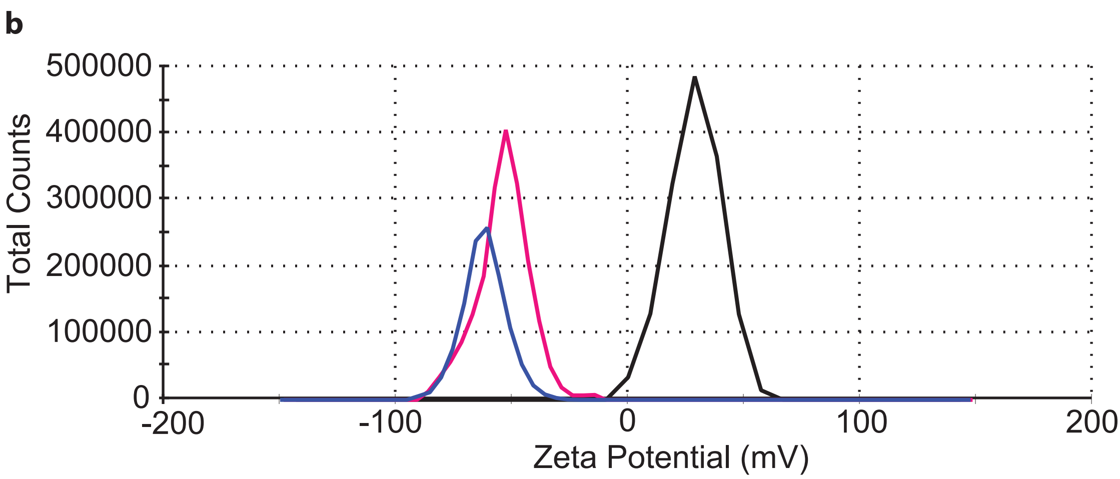

b
500000
400000
300000
200000
100000
0
Total Counts
-200
-100
0
100
200
Zeta Potential (mV)

Figure SI4.

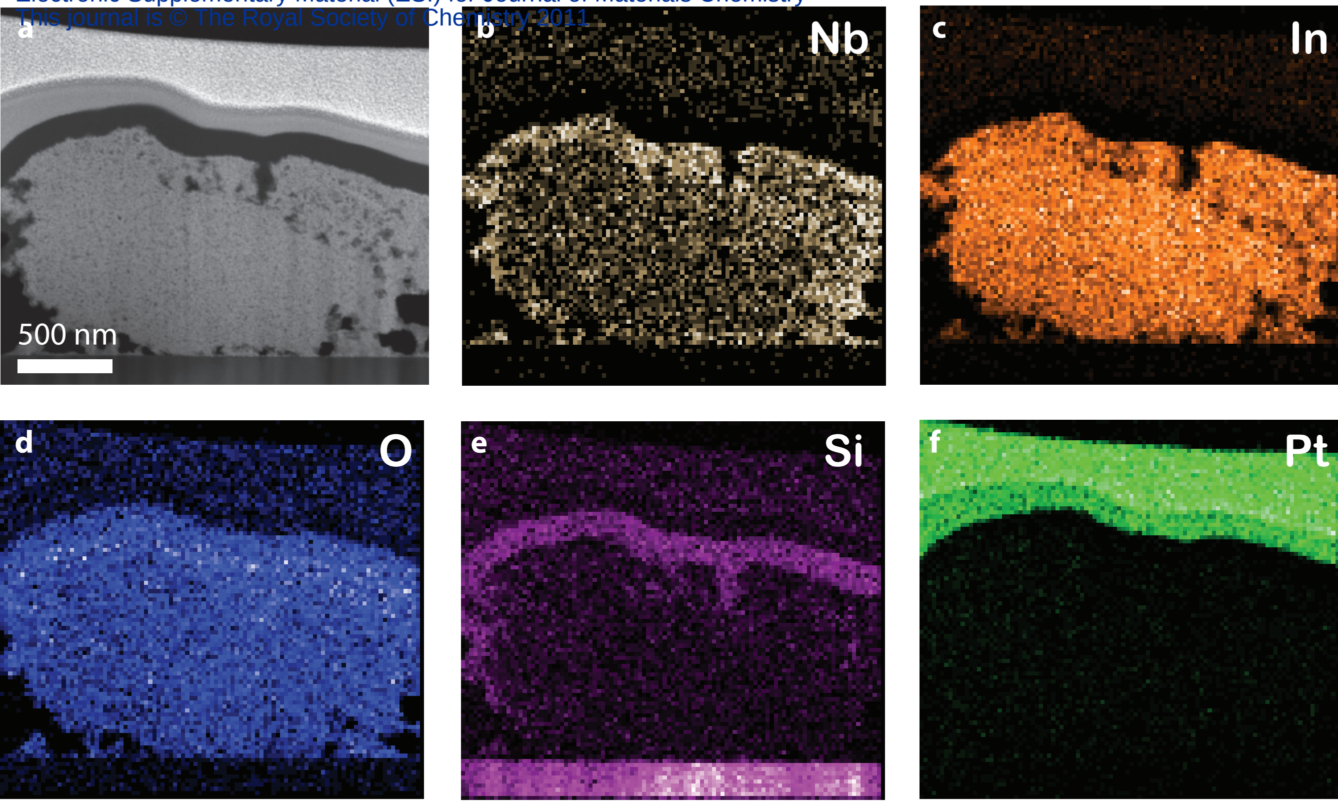


Figure SI5.

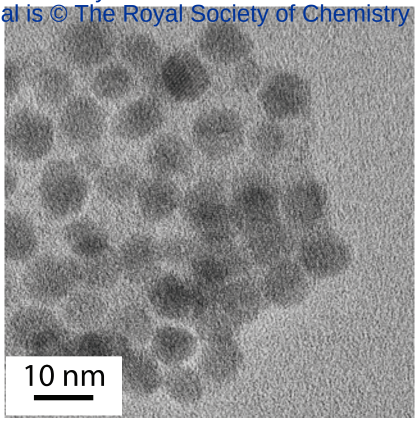
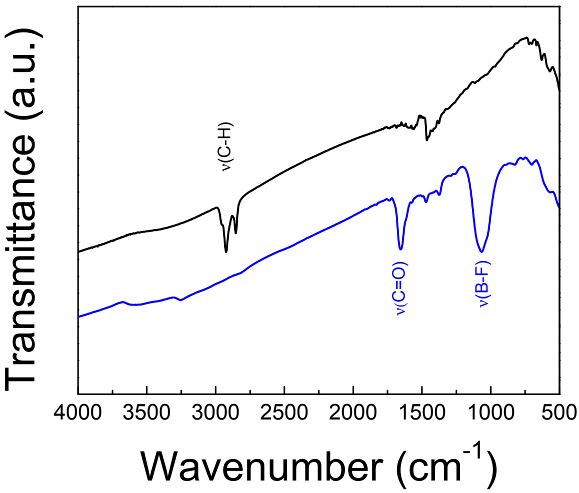


Figure SI6.

a



b

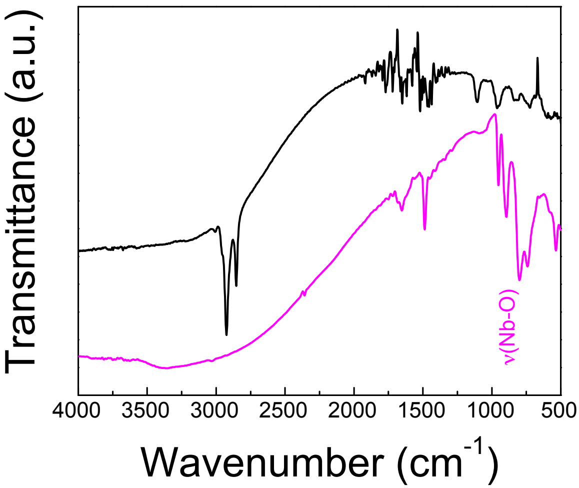


Figure SI 7.

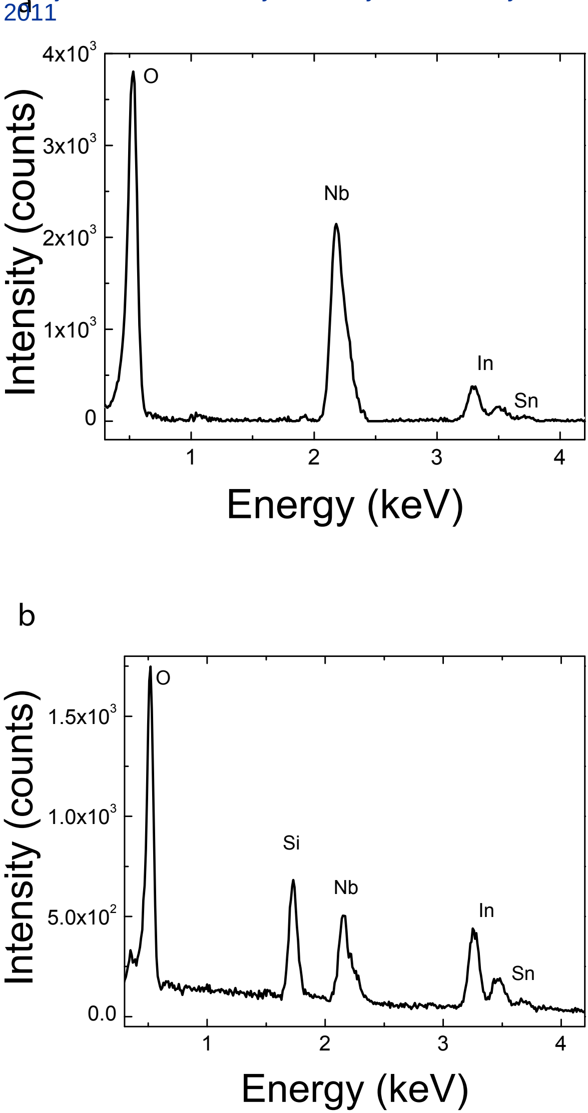

a
4x10^3
3x10^3
2x10^3
1x10^3
0
Intensity (counts)
O
Nb
In
Sn
1
2
3
4
Energy (keV)
b
1.5x10^3
1.0x10^3
5.0x10^2
0.0
Intensity (counts)
O
Si
Nb
In
Sn
1
2
3
4
Energy (keV)

Figure SI 8.

Table SI1

ITO Composites – XPS Surface Composition

Sample	Peak Name	Peak Position (eV)	Scaled Area	Atomic Composition
ITO-Nb10 Annealed	C 1s	285.2	28262	37%
	O 1s	530.3	16609	22%
	O 1s	532.0	14716	19%
	In 3d	444.9	13506	18%
	Sn 3d	486.8	1428	2%
	Nb 3d	207.7	1634	2%
		Total Area:	76154	
ITO-Nb6 Annealed	C 1s	285.3	27701	36%
	O 1s	530.3	19176	25%
	O 1s	532.1	14998	19%
	In 3d	445.0	13166	17%
	Sn 3d	486.9	1427	2%
	Nb 3d	207.7	1313	2%
		Total Area:	77781	
ITO-V(5+) Annealed	C 1s	285.4	33365	40%
	O 1s	531.9	20100	24%
	O 1s	530.3	14135	17%
	In 3d	445.0	13168	16%
	Sn 3d	486.9	1686	2%
	V 2p	516.4	1913	2%
		Total Area:	84367	

Table SI2

Vanadium Oxide – XPS Surface Composition

Sample	Peak Name	Peak Position (eV)	Scaled Area	Atomic Composition
V(5+) Nonannealed	C 1s	285.5	41663	47%
	O 1s	530.2	18446	21%
	O 1s	532.3	15515	17%
	V 2p	516.4	12728	14%
		Total Area:	88789	
V(5+) Annealed Air	C 1s	285.0	32046	35%
	O 1s	529.7	25344	28%
	O 1s	531.7	18666	20%
	V 2p	516.8	14700	16%
		Total Area:	91392	
V(4+) Nonannealed	C 1s	289.4	13084	25%
	C 1s	285.2	8673	17%
	O 1s	532.5	24245	47%
	O 1s	529.5	947	2%
	V 2p	516.0	4238	8%
		Total Area:	51487	
V(4+) Annealed Nitrogen	C 1s	285.2	35853	36%
	C 1s	285.2	2048	2%
	O 1s	529.9	24795	25%
	O 1s	531.8	18467	19%
	V 2p	516.3	17541	18%
		Total Area:	99334	

Table SI3

Niobium Oxide – XPS Surface Composition

Sample	Peak Name	Peak Position (eV)	Scaled Area	Atomic Composition
Nb10 Annealed	C 1s	285.4	14895	27%
	O 1s	530.6	15618	28%
	O 1s	531.7	14023	25%
	Nb 3d	207.8	11491	21%
		Total Area:	56026	
Nb10 Nonannealed	C 1s	287.1	40009	48%
	O 1s	533.2	11234	13%
	O 1s	531.0	21852	26%
	Nb 3d	207.7	11000	13%
		Total Area:	84094	
Nb6 Annealed	C 1s	285.5	22264	32%
	O 1s	530.7	19692	28%
	O 1s	531.9	14575	21%
	Nb 3d	207.8	12566	18%
		Total Area:	69097	
Nb6 Nonannealed	C 1s	286.7	57491	58%
	O 1s	533.8	21352	22%
	O 1s	531.1	14930	15%
	Nb 3d	207.7	4971	5%
		Total Area:	98745	

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Table SI4

Vanadium Oxide – Peak Fitting Parameters

Sample	Peak Name	Peak Position (eV)	Peak Width (eV)	Gaussian/Lorentzian
V(5+) Nonannealed	O 1s	532.6	2.9	0.51
	O 1s	530.2	2.1	0.54
	V 2p	516.5	3.0	0.81
V(5+) Annealed Air	O 1s	531.9	2.8	0.51
	O 1s	529.7	1.8	0.53
	V 2p	516.8	2.1	0.95
V(4+) Nonannealed	O 1s	532.5	2.2	0.55
	O 1s	529.0	3.1	0.52
	V 2p	517.0	3.3	0.89
	V 2p	514.4	2.9	0.34
V(4+) Annealed Nitrogen	O 1s	532.2	3.1	0.52
	O 1s	529.9	2.0	0.54
	V 2p	516.4	3.1	0.85

Table SI5

Niobium Oxide – Peak Fitting Parameters

Sample	Peak Name	Peak Position (eV)	Peak Width (eV)	Gaussian/Lorentzian
Nb6 Nonannealed	O 1s	533.8	2.2	0.52
	O 1s	531.1	2.7	0.53
Nb6 Annealed	O 1s	531.7	3.4	0.55
	O 1s	530.7	1.6	0.47
Nb10 Nonannealed	O 1s	533.3	2.6	0.53
	O 1s	531.0	1.9	0.55
Nb10 Annealed	O 1s	531.6	3.1	0.55
	O 1s	530.6	1.5	0.46