

Supplementary materials:

Interplay among Work Function, electronic structure and stoichiometry in nanostructured vanadium oxides films

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In table S1 are reported the oxygen partial pressure used to synthesize our samples.

Table S1: Stoichiometry of the NS films synthesized at different oxygen partial pressure in the Ar-O₂ carrier gas mixture.

Oxygen partial pressure [mbar]	x in VO _x
15 ± 5	0.53 ± 0.02
40 ± 5	1.5 ± 0.02
50 ± 5	1.6 ± 0.02
60 ± 5	2.2 ± 0.02
70 ± 5	2.45 ± 0.02

In table S2 are reported the fitting criteria (based on previous literature work ¹) we used to reproduce the core level line shape.

The Mg K α radiation used to record XPS spectra was not monochromatic so in the BE range 535-512 eV two oxygen satellites are present in the V2p_{1/2} region generated by the MgK α_3 and MgK α_4 radiation.

Table S2: Fitting criteria for O1s and V2p

Fit components	Energy difference
O1s -> V ⁵⁺ 2p _{3/2}	13±0.2 eV
O1s -> V ⁴⁺ 2p _{3/2}	14.2±0.2 eV
O1s -> V ³⁺ 2p _{3/2}	14.8±0.2 eV
O1s -> V ²⁺ 2p _{3/2}	17±0.2 eV
V2p _{3/2} -> V2p _{1/2}	7.2±0.2 eV
V ⁴⁺ 2p _{3/2} -> V ⁴⁺ 2p _{3/2} satellite	10.6±0.2 eV
V ³⁺ 2p _{3/2} -> V ³⁺ 2p _{3/2} satellite	11.6±0.2 eV
O1s -> O1s K α_3 satellite	8.5±0.1 eV
O1s -> O1s K α_4 satellite	10.1±0.1 eV

For all the spectra the intensity ratio of the V2p_{3/2} and V2p_{1/2} fit components is fixed:

$$I(V2p_{1/2})/I(V2p_{3/2})=0.5$$

The Background has been modelled using a Shirley curve.

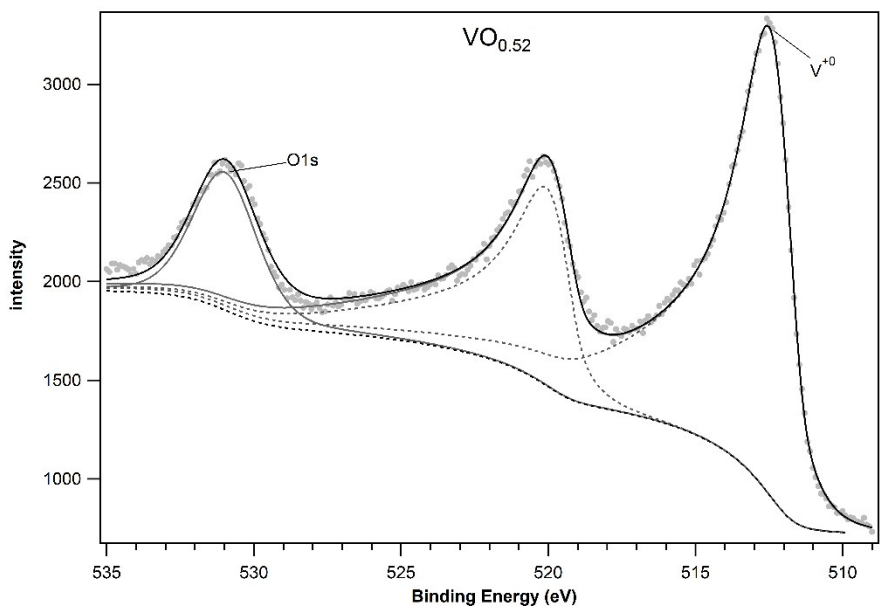


Figure S1: O1s and V2p XPS spectra (dot) of $\text{VO}_{0.52}$ and fit curve (continuous black line). A label highlights the component of the different vanadium species.

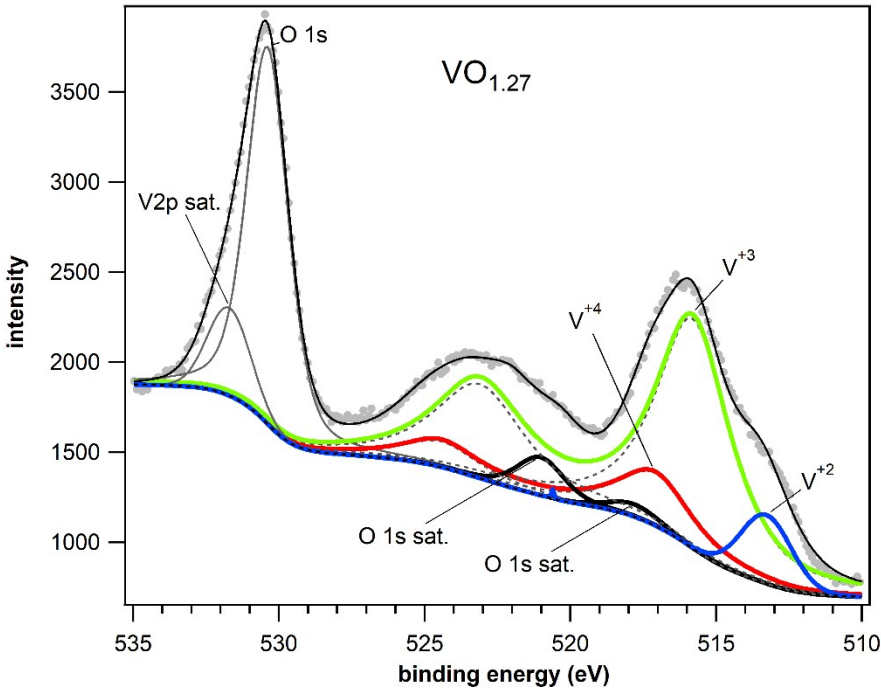


Figure S2: O1s and V2p XPS spectra (dot) of $\text{VO}_{1.27}$ and fit curve (continuous black line). A label highlights the component of the different vanadium species

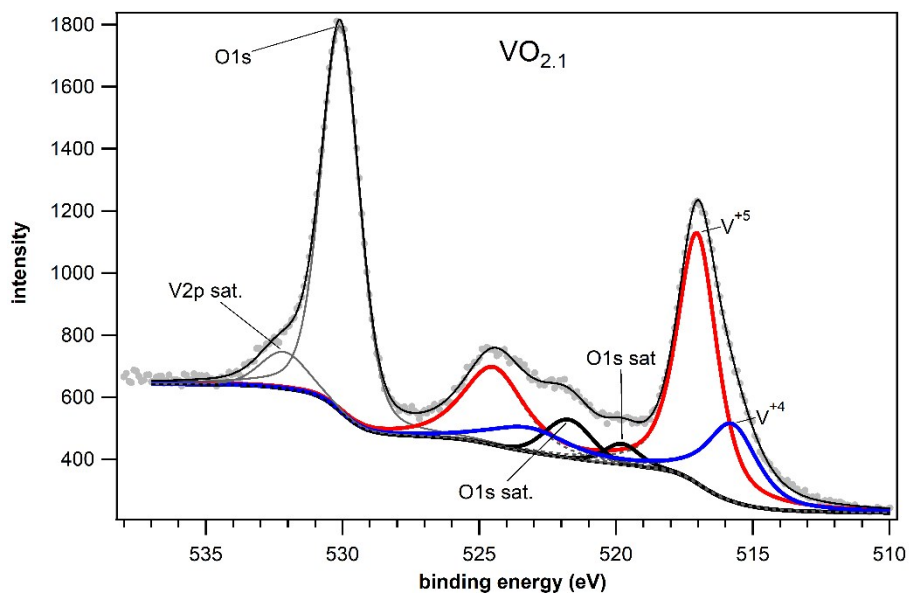


Figure S3: O1s and V2p XPS spectra (dot) of VO_{2.1} and fit curve (continuous black line). A label highlights the components of the different vanadium species

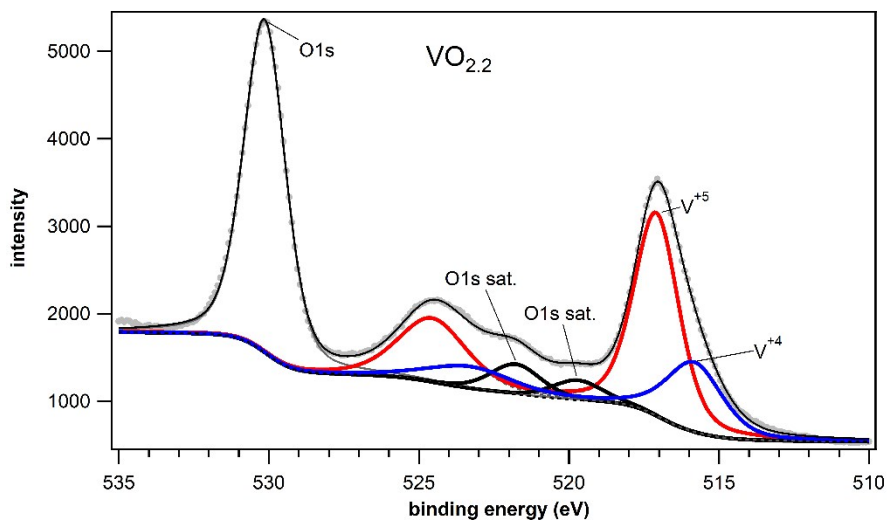


Figure S4: O1s and V2p XPS spectra (dot) of VO_{2.2} and fit curve (continuous black line). A label highlights the components of the different vanadium species

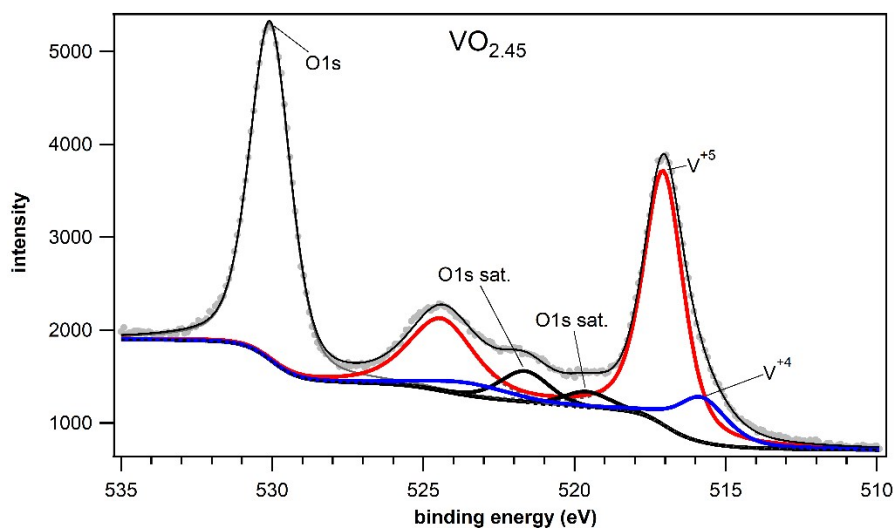


Figure S5: O1s and V2p XPS spectra (dot) of $\text{VO}_{2.1}$ and fit curve (continuous black line). A label highlights the components of the different vanadium species

Auger $L_3M_{2,3}M_{4,5}$ spectroscopy

The complete set of Auger spectra used to extrapolate the fraction of unpaired 3d electron is reported in fig S6.

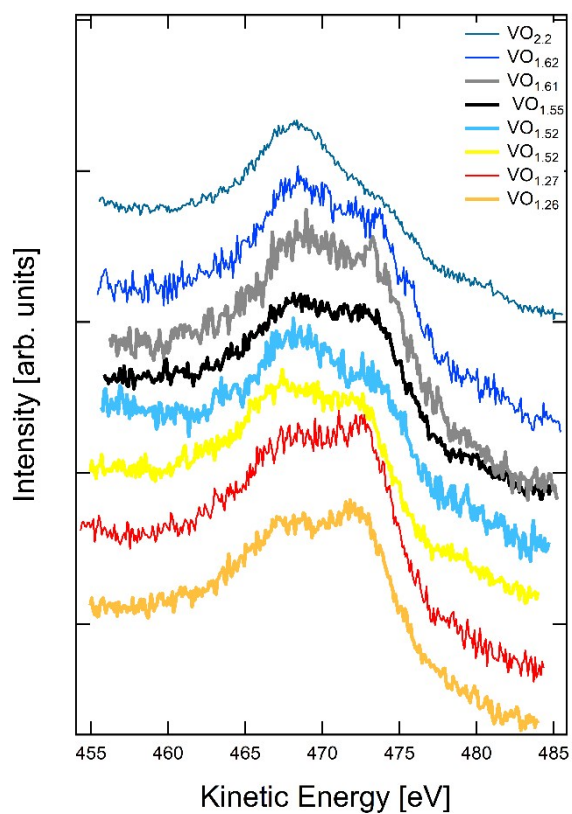


Figure S6: Auger V $L_3M_{2,3}M_{4,5}$ spectra for different oxidation state (reported in the legend).

The criteria used to fit the Auger $L_3M_{2,3}M_{4,5}$ spectra are reported in table S3

Table S3: Fit criteria of the Auger spectra.

Fit components	Energy difference
U \rightarrow V	5.5 ± 0.2 eV
U \rightarrow OKL ₁ L ₁	6.2 ± 0.4 eV

A representative fit example is reported in fig.S7.

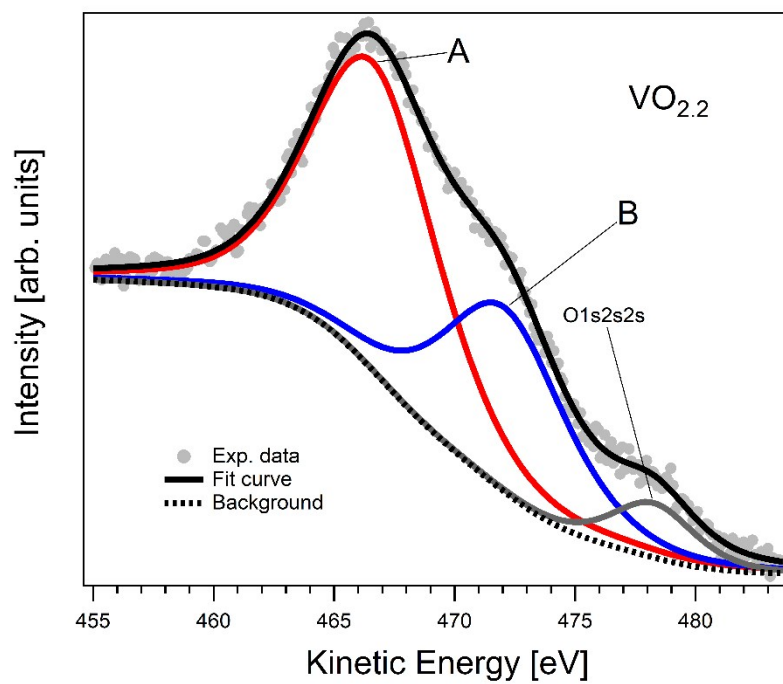


Figure S7: Auger V $L_3M_{2,3}M_{4,5}$ spectrum and fit components of $VO_{2.2}$

Valence band PES

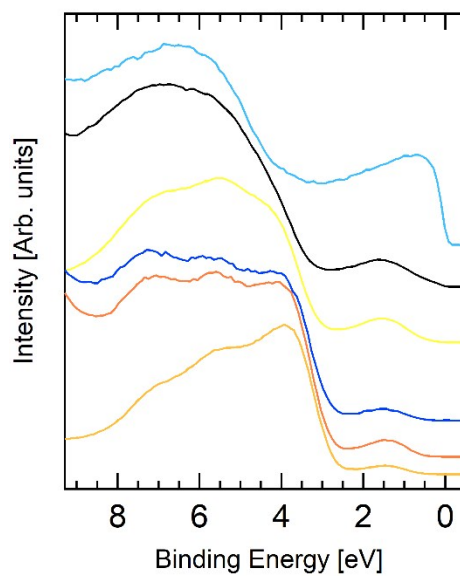


Figure S8: Full VB spectra for different vanadium oxides. From top to bottom: $VO_{0.53}$, $VO_{1.27}$, $VO_{1.60}$, $VO_{2.10}$, $VO_{2.20}$ and $VO_{2.45}$

The whole VB spectral intensity (O 2p + V 3d) can be decomposed as the sum of the partial intensities originating the A, B and C features, the contribution from unpaired V 3d electrons, and the inelastic background. We write this sum as:

$$I_{O2p} + I_{V3d} = I_A + I_B + I_C + I_{V3d}^u + Bg$$

where $I_{O2p} + I_{V3d}$ is the numerical integration of the VB spectra in BE range from 0 to 10 eV, $I_{A/B/C}$ is the intensity of produced by the feature A, B, and C, I_{V3d}^u is the signal coming from unpaired 3d electrons and Bg is the inelastic background.

As previously pointed out, each A, B and C features may represent a multiple orbital contribution:

$$I_{O2p} + I_{V3d} = I_{V4s} + I_{O2p}^A + I_{V3d}^B + I_{O2p}^B + I_{O2p}^C + I_{V3d}^u + Bg$$

here I_{V4s} is the contribution given from V 4s electrons to the overall intensity of the A feature and I_{V3d}^B is the intensity contribution supplied by V 3d electrons to B peak. $I_{O2p}^A + I_{O2p}^B + I_{O2p}^C = I_{O2p}^t$ is the total signal generated by O 2p electrons in the A, B and C features. Considering $I_{V3d}^B + I_{V3d}^u = I_{V3d}^t$ is the total signal associated to V 3d electrons we may write:

$$I_{O2p} + I_{V3d} = I_{V3d}^t \left(1 + \frac{I_{O2p}^t}{I_{V3d}^t} + \frac{I_{V4s}}{I_{V3d}^t} + \frac{Bg}{I_{V3d}^t} \right)$$

Where the ratio $\frac{I_{O2p}^t}{I_{V3d}^t}$ is the ratio of the intensity generated by the total amount of O 2p and V 3d electrons. Assuming a constant efficiency of the analyser in the BE range of our interest, we can write:²

$$I_{O2p}^t \propto \sigma_{O2p} n_O \quad \text{and} \quad I_{V3d}^t \propto \sigma_{V3d} n_V$$

where σ_{O2p} and σ_{V3d} are the cross-sections of O 2p and V 3d electrons, respectively and n_O and n_V

are the atomic concentration of vanadium and oxygen in the sample. $\frac{I_{O2p}^t}{I_{V3d}^t}$ can be written as:

$$\frac{I_{O2p}^t}{I_{V3d}^t} = \frac{\sigma_{O2p}}{\sigma_{V3d}} x$$

in which $x = \frac{n_O}{n_V}$ is the stoichiometric ratio. The term $I_{O2p} + I_{V3d}$ becomes:

$$I_{O2p} + I_{V3d} = I_{V3d}^t \left(1 + \frac{\sigma_{O2p}}{\sigma_{V3d}} x + \frac{I_{V4s}}{I_{V3d}^t} + \frac{Bg}{I_{V3d}^t} \right)$$

the ratio $\frac{I_{V4s}}{I_{V3d}^t}$ is a numerical constant since:

$$\frac{I_{V4s}}{I_{V3d}^t} = \frac{\sigma_{V4s} 4s \text{ electrons}}{\sigma_{V3d} 3d \text{ electrons}} = \frac{\sigma_{V4s} 2}{\sigma_{V3d} 3} = 0.02104 = K_{sd}$$

σ_{V4s} is the cross-section of V 4s electrons. Assuming a negligible background, in the V 3d region of the VB spectra the only contribution comes from unpaired 3d electrons, therefore we can write the outer-valence branching ratio as:

$$BR = \frac{I_{V3d}}{I_{O2p} + I_{V3d}} = \frac{P_{3d}}{\left(1 + K_{sd} + \frac{\sigma_{O2p}}{\sigma_{V3d}} x + \frac{Bg}{I_{V3d}^t} \right)}$$

(1)

$P_{3d} = \frac{I_{V3d}^u}{I_{V3d}^t}$ indicates the percentage of unpaired electrons in the film which we experimentally

measured in section 3.2 through Auger spectroscopy.

Figure 5: BR as a function of the stoichiometric ratio. The red curve is the fit obtained using the eq. 3 including the 3d-2p hybridization term; the blue dotted curve is obtained considering ionic model of the valence band.

$$P_{3d}(x) = 1 - 0,32x \quad (2)$$

Therefore in the equation 1 the only unknown remaining variable is $\frac{Bg}{I_{V3d}^t}$. If we assume a linear dependence from the stoichiometry, of the form $ax + b$ we may write the new equation for the BR:

$$BR = \frac{I_{V3d}}{I_{O2p} + I_{V3d}} = \frac{1 - 0,32x}{\left(\frac{\sigma_{O2p}}{\sigma_{V3d}} + a\right)x + 1 + K_{sd} + b}$$

TEM images for VO_{2.2}

TEM images with different magnification are reported. The aggregation of individual nanoparticles in fractal nanostructures can be seen in figure S10, nevertheless in figure S11 can be observed absence of coalescence.

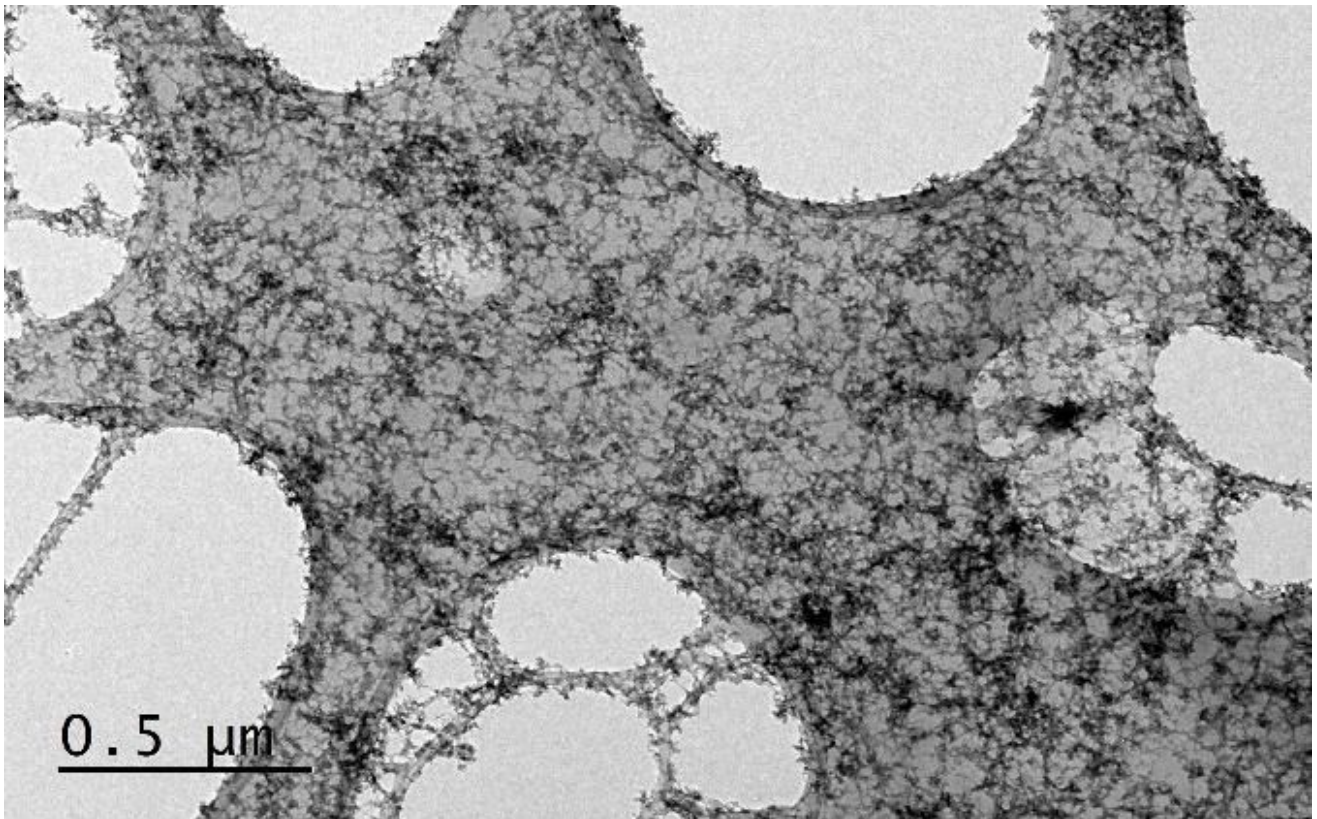


Figure S9: Dendritic shape agglomerate formed during the deposition process.

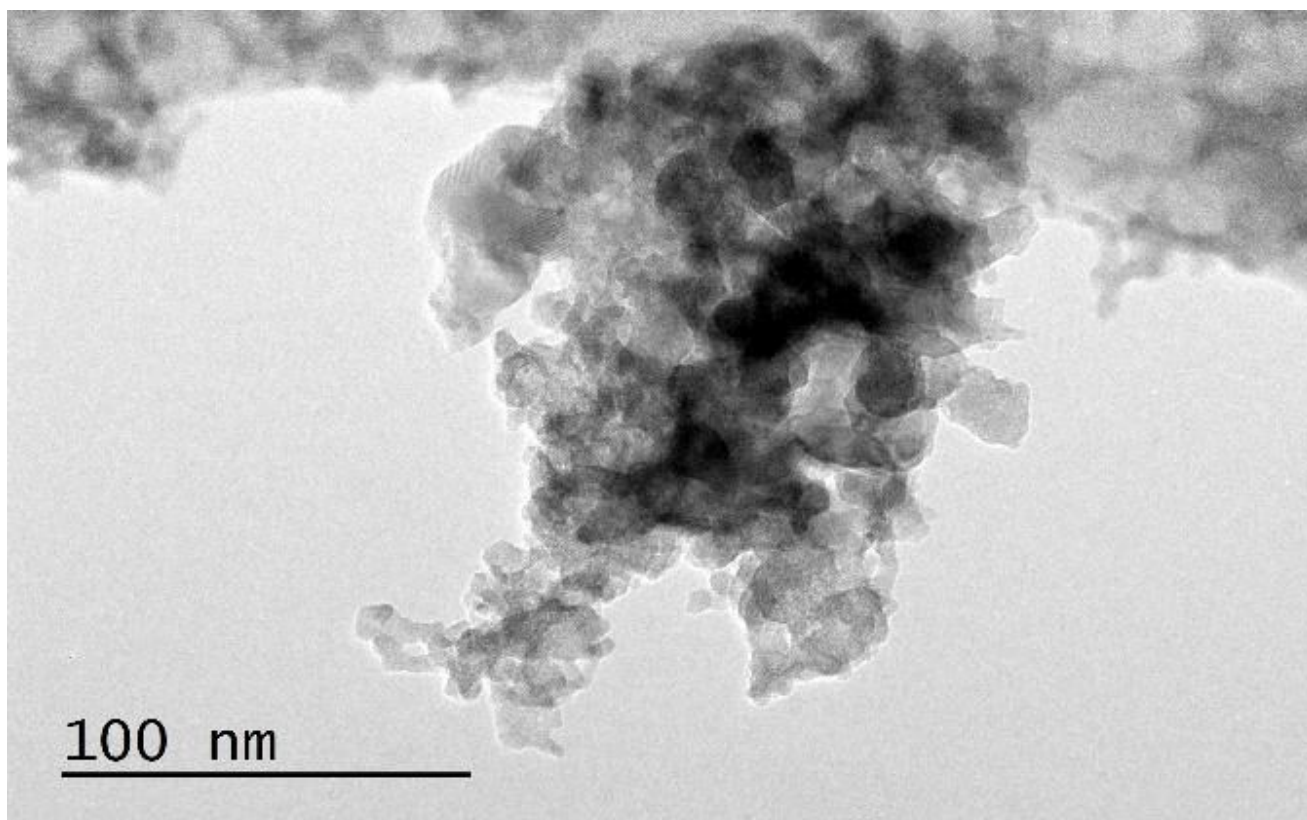


Figure S10: Fractal aggregation of individual nanoparticles.

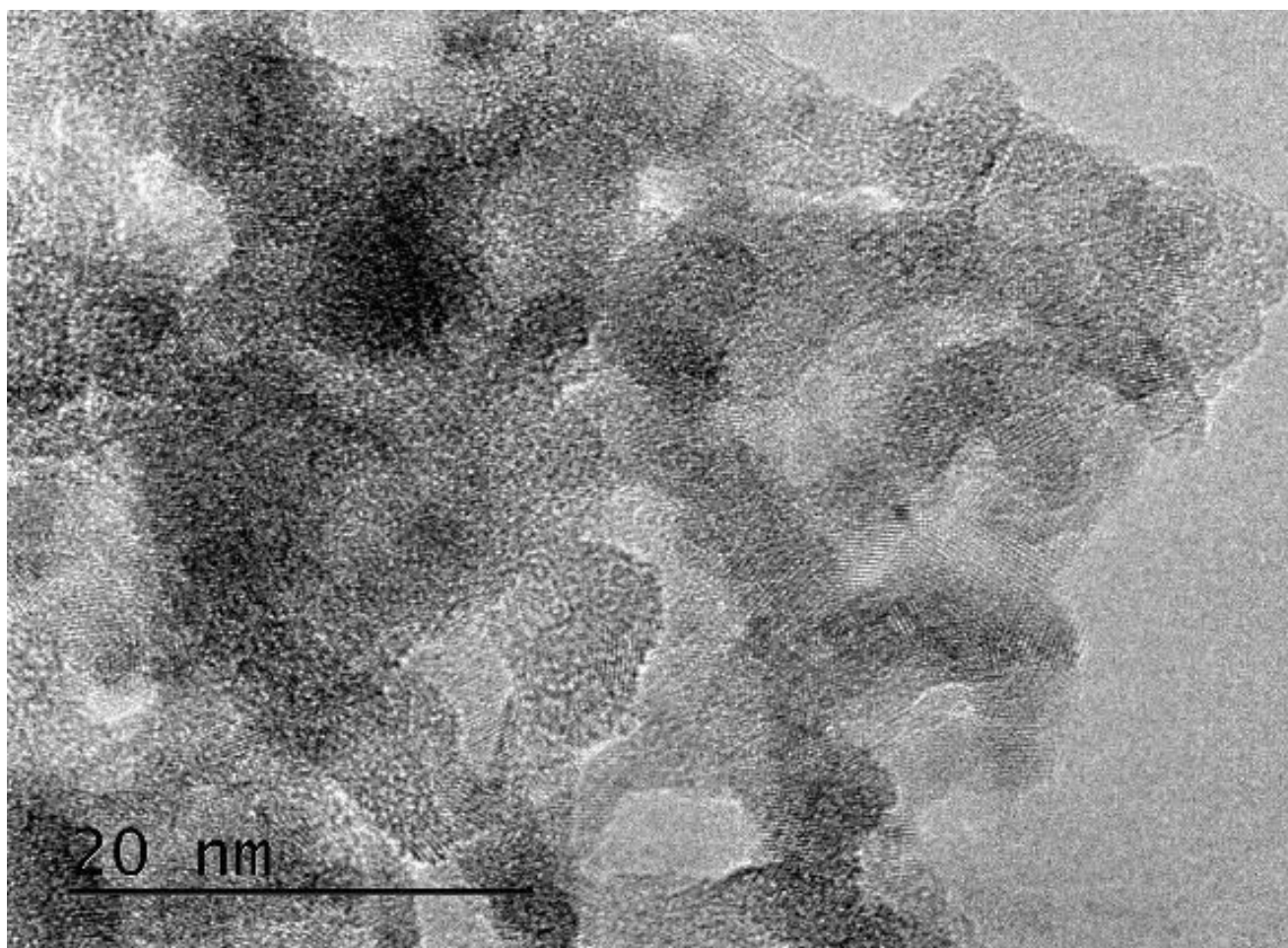
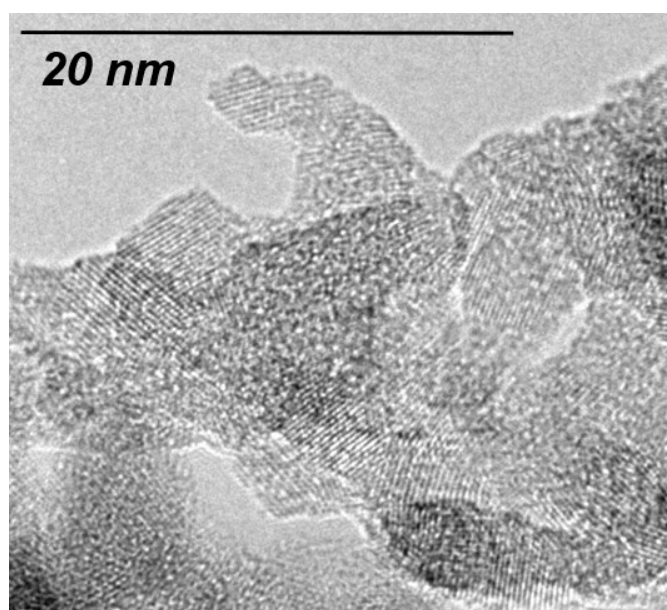


Figure S11: Assembled nanoparticles. The observation of atomic planes with different orientation



confirms that the nanostructured films grow without coalescence.

Figure S12: High magnification TEM images.

Structural properties.

The nanostructured films structure has been probed using XANES spectroscopy at the O K edge as reported in Figure S12.

In the crystalline VO₂ film the t_{2g}* and e_g* peak are well separated, which is the fingerprint of an ordered atomic structure. On the other hand, the nanostructured film exhibits two broad and overlapping slightly shifted in energy, pointing out a disordered structure heavily affected by Jahn – Teller distortion.³ This result can be generalized to the whole stoichiometry range considering that SCBD is low temperature synthesis method that favor the quenching of disordered structures.

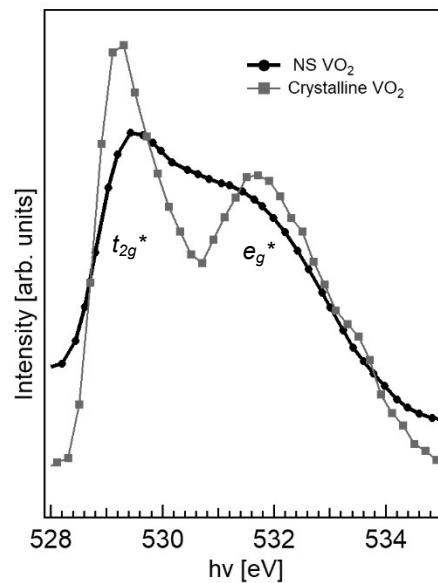


Figure S13: Comparison between the O K edge of the nanostructured VO₂ sample and a crystalline sample in the energy region 528-535 eV.

References

1. Silversmit, G., Depla, D., Poelman, H., Marin, G. B. & De Gryse, R. Determination of the V2p XPS binding energies for different vanadium oxidation states (V5+ to V0+). *J. Electron Spectros. Relat. Phenomena* **135**, 167–175 (2004).
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3. Ruzmetov, D., Senanayake, S. D. & Ramanathan, S. X-ray absorption spectroscopy of vanadium dioxide thin films across the phase-transition boundary. *Phys. Rev. B - Condens. Matter Mater. Phys.* (2007). doi:10.1103/PhysRevB.75.195102