$[{\rm VOCl}_2({\rm CH}_2({\rm COOEt}_2)\}_4]$ as a molecular precursor for thermochromic monoclinic VO_2 thin films and nanoparticles- ESI

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AACVD Schematic



Scheme S1: Schematic diagram of the aerosol assisted chemical vapour deposition (AACVD) apparatus.

Additional TEM characterisation



Figure S1: TEM images of nanoparticle samples: a) and b) Sample 2 showed evidence of vanadium oxide "spines" in hollow tube-like configurations. Sample 3 (c)) showed that in a greater oleic acid:oleylamine ratio, particle formation was seen. In an oleic acid environment, anisotropic particles were observed, as in image d).



Figure S2: TEM images of nanoparticle samples: a) Sample 4, b) and c) show the effect of oleyamine, which favoured rod and spine growth. The addition of 1,4-tetradecanediol with the "6,6" blend of oleic acid and oleylamine promoted particle growth analogous to sample 3 (figure ESIxx, d)).



Figure S3: TEM images of sample 6 post anneal. a) shows a *d*-spacing of 0.327 nm, corresponding to the <111> plane of vanadium oxide (V₄O₉, ICSD 15041).



Figure S4: Variable temperature UV/Vis/NIR spectrum of the vanadium oxide thin film deposited at 600 °C, showing the absence of a thermochromic switch.



Figure S5: (Top): XRD pattern of vanadium oxide thin film deposited at 600 °C, showing poor crystallinity and phase purity. (Bottom): VO₂ (M) ICSD standard pattern number 34033.



Figure S6: Hysteresis loop data for sample W-VO₂ deposited at 550 °C by AACVD. The incorporation of tungsten into the VO₂ lattice led to a reduction of the MST phase transition temperature to *ca*. 45 °C.

Additional SEM characterisation



Figure S7: Side-on SEM images of thermochromic VO₂ (M) thin films deposited onto glass substrates by AACVD at: a) 540 °C, b) 550 °C and c) 560 °C. d) is the W-doped VO₂ thin film deposited at 550 °C. Film thicknesses are as follows: a) $1.8 \pm 0.2 \mu$ m, b) $2.1 \pm 0.6 \mu$ m, c) $4.1 \pm 1.6 \mu$ m and d) $2.8 \pm 0.5 \mu$ m.

EDS spectral data

Sample number	V / at.%	O / at.%
1	26.2 (26.4)	73.8 (73.6)
2	9.66	90.3
3	1.82	98.2
4	0.180	99.8
5	29.0	71.1
6	1.91 (26.2)	98.1 (73.8)
8	10.2	89.8

Table S1: EDS at. % ratios of vanadium to oxygen in nanomaterial samples. Bracketed quantities are thosein the annealed spectra.