Supplementary Information

Modulating the Hysteresis of an Electronic Transition: Launching Alternative Transformation Pathways in the Metal—Insulator Transition of Vanadium(IV) Oxide

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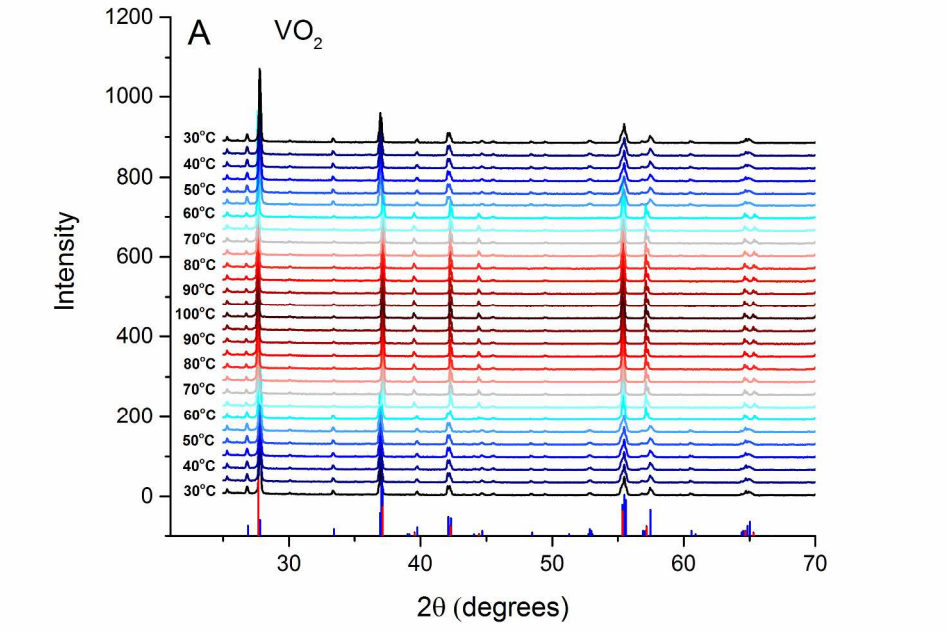

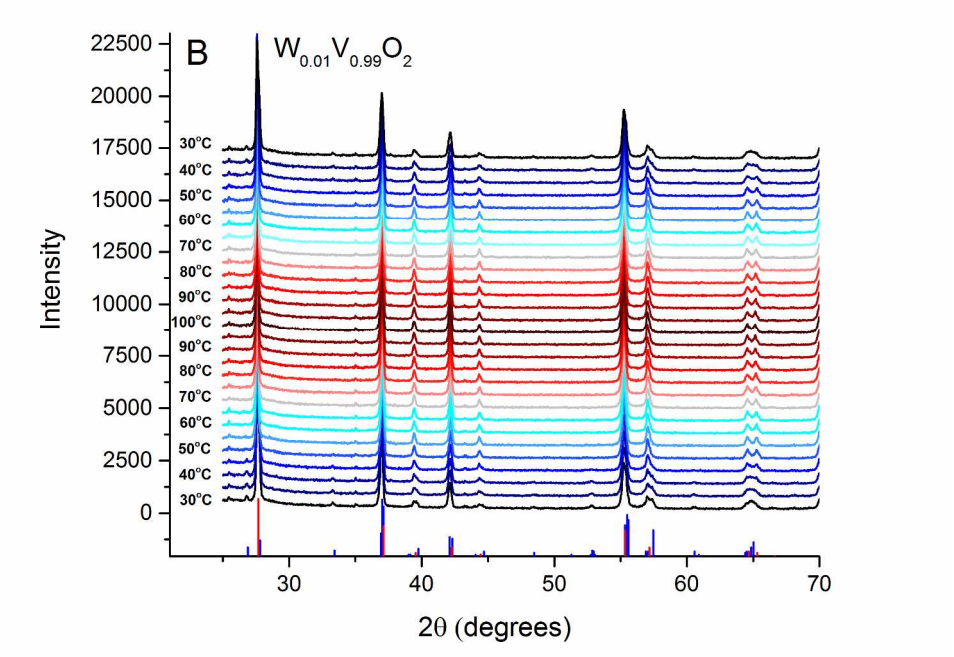

Figure S1. Extended powder XRD patterns acquired in the 2ϑ range from 25—70° for (A) undoped and (B) VO_2 incorporating 0.51 at.% W as a substitutional dopant.

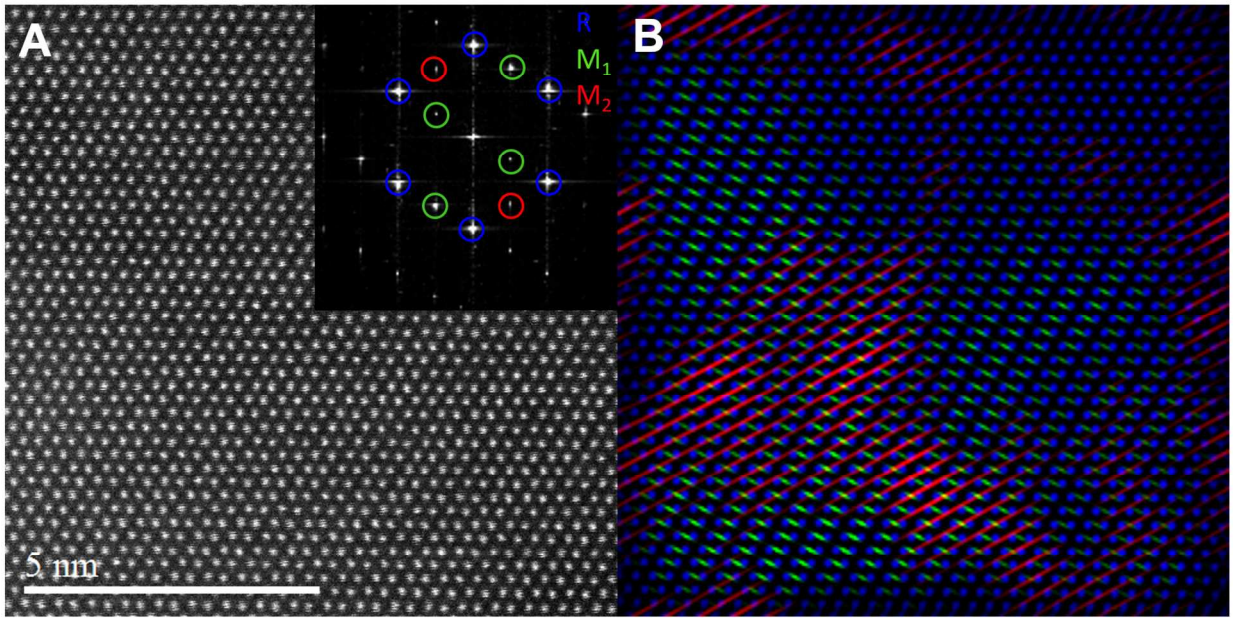

Figure S2. Atomic-resolution HAADF TEM image of a $W_xV_{1-x}O_2$ particle (with *x* of ca. 0.008) acquired at 25°C after warming from -180°C. A) TEM image and diffraction patterns with distinct diffraction spots indexed to R (blue), M_1 (green), and M_2 (blue) polymorphs. B) Composite map depicting the spatial distribution of the three phases.

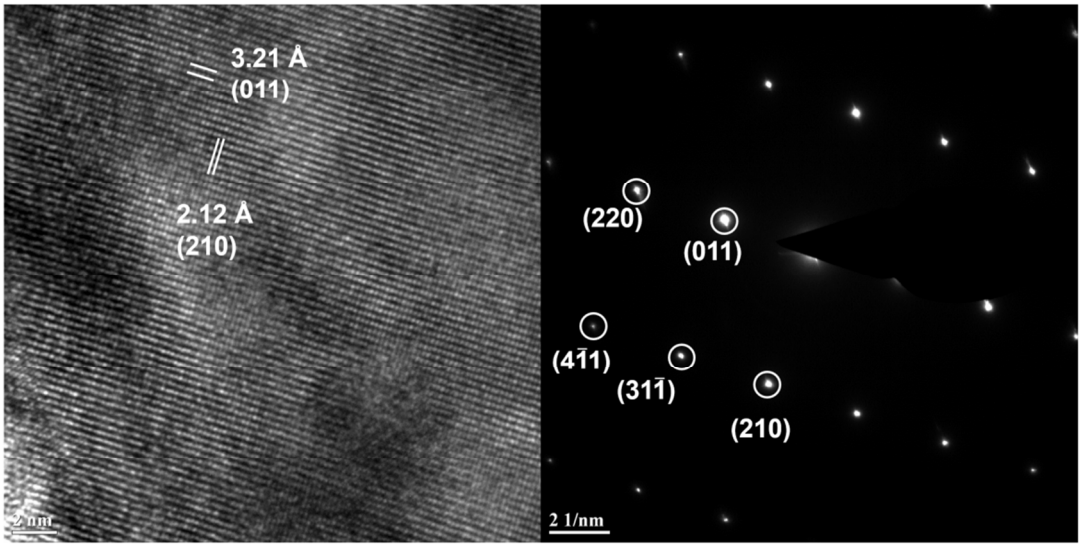

Figure S3. High-resolution TEM image (left) and selected area electron diffraction pattern (right) acquired for undoped VO_2 prepared by acetone reduction of V_2O_5. The diffraction pattern and interplanar separations correspond solely to the M_1 phase of VO_2.

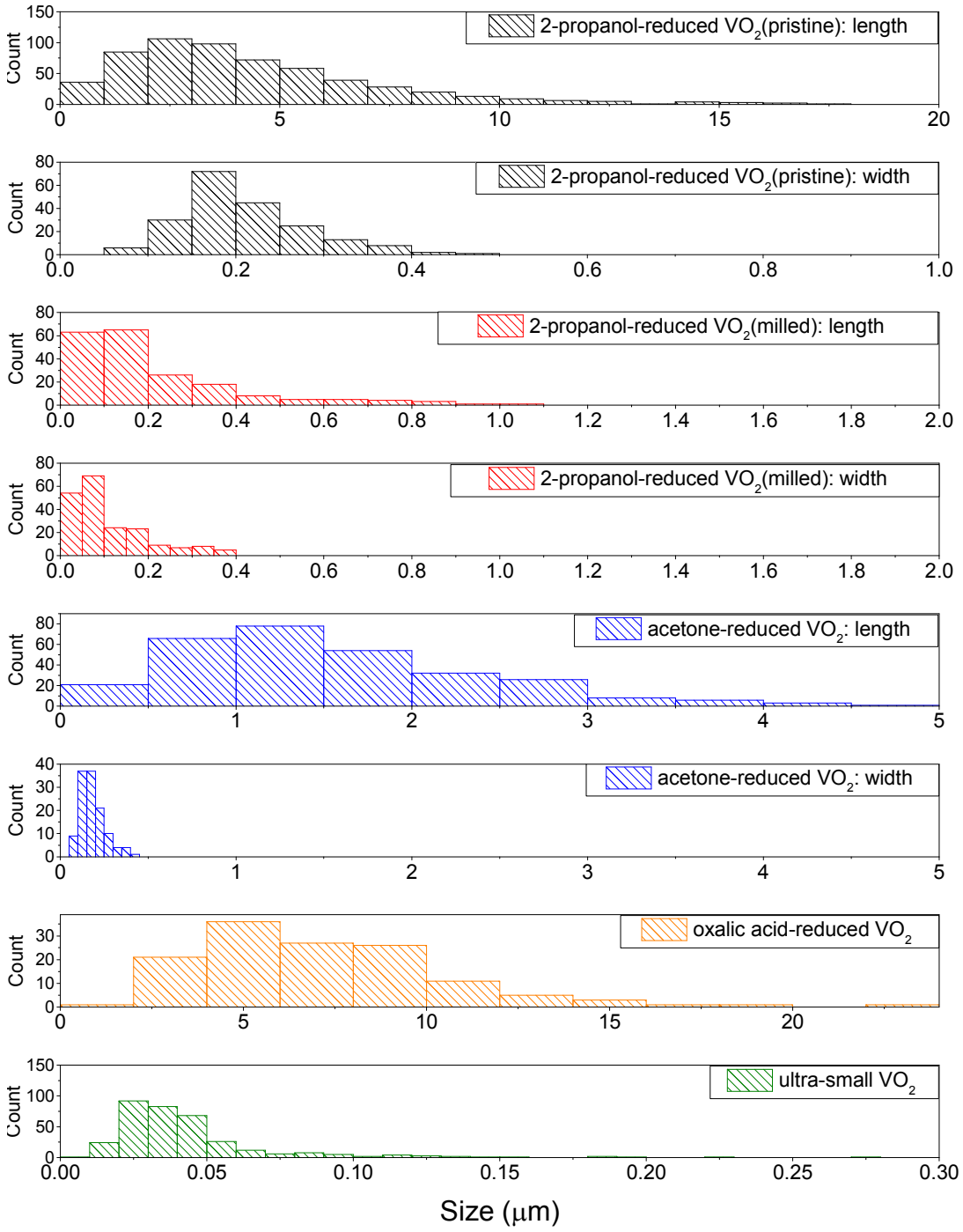

Figure S4: Size distribution histograms for four different sample preparations yielding different sized particles. Oxalic acid and ultra-small VO_2 yield star shaped and spherical particles respectively and thus a single value, the diameter, is shown as a measure of the size.

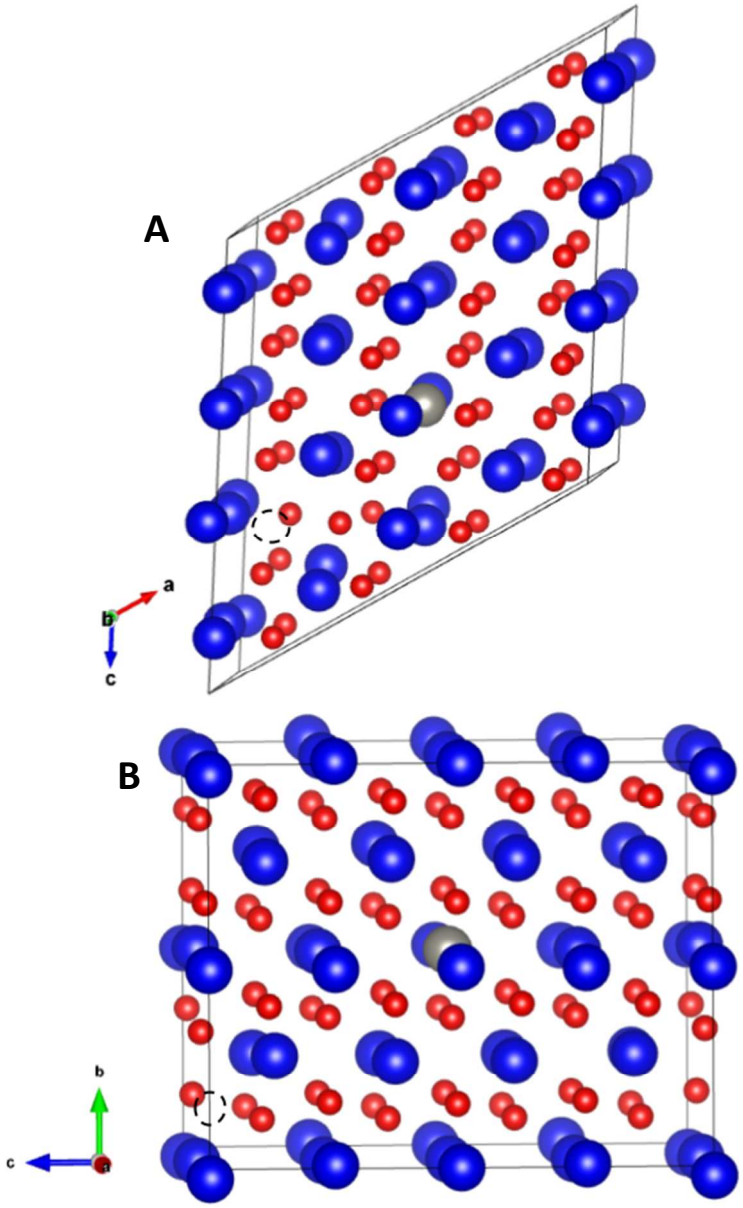

Figure S5: Structural representation of supercell used in defect calculations of doped A) M_1 and B) R polymorphs of VO_2. The oxygen vacancy is represented by a dashed circle, whereas the tungsten atom is depicted in silver. Vanadium atoms are depicted in blue and oxygen atoms in red. To test for a possible local effect, an oxygen vacancy was created at an adjacent site and far from tungsten as seen in Figure S3 in both rutile and monoclinic supercells. After introducing a vacancy, supercell structures were fully relaxed. The energy of the rutile cell did not change significantly, less than 6 meV, as a result of proximity of the oxygen vacancy to the tungsten atom.