Electronic Supplementary Material (ESI) for CrystEngComm

Hydrothermal synthesis and controlled growth of vanadium oxide nanocrystals

Electronic Supplementary Information

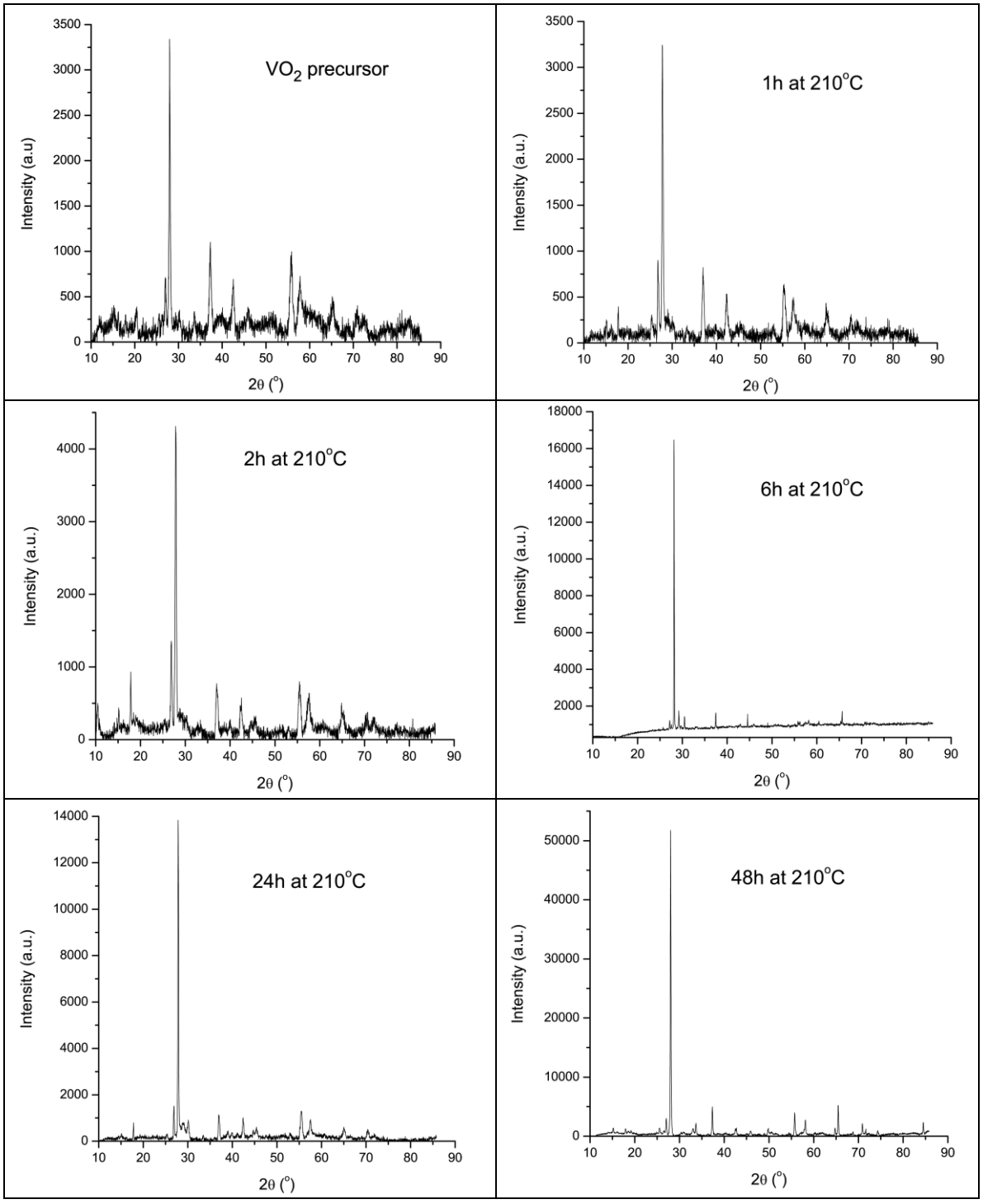

Figure S1. XRD spectra of products of ligand-free reactions of hydrothermal VO_2 (M) nanoribbon synthesis after different reaction times

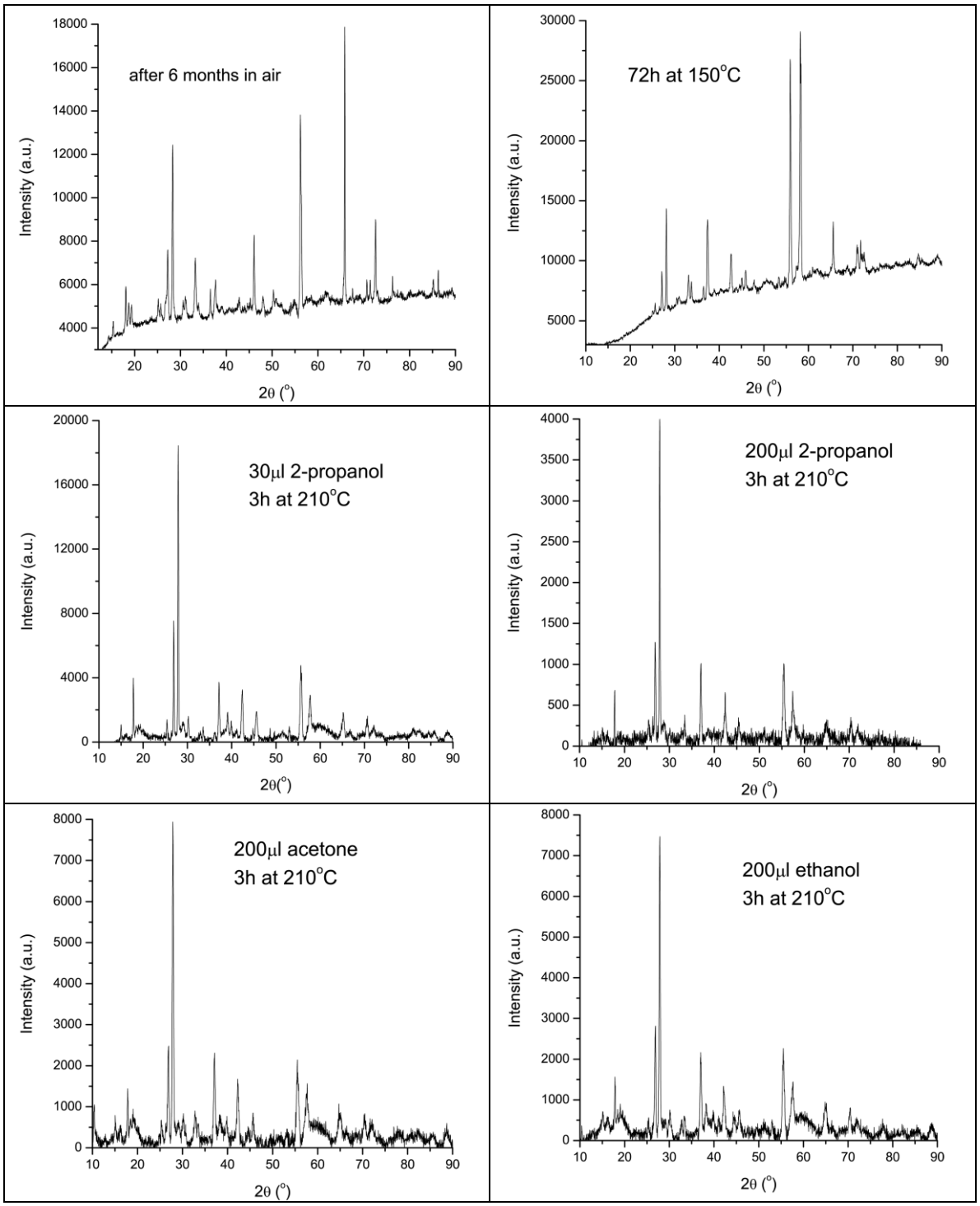

Figure S2. XRD of products of hydrothermal synthesis of VO_2 (M) nanocrystals synthesized under different reaction conditions and using different ligand molecules

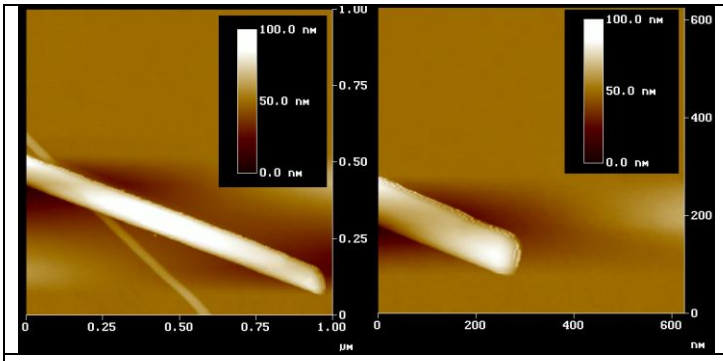

Figure S3. AFM images of VO_2 (M) nanoribbon bundles

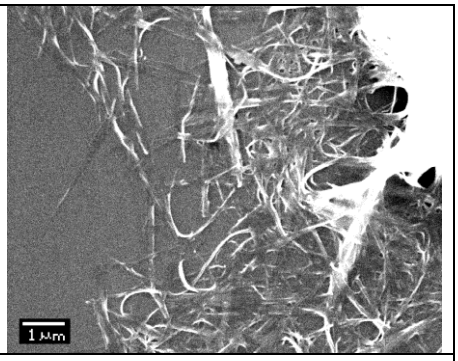

Fig. S4. SEM image of VO_2 (M) nanoribbons

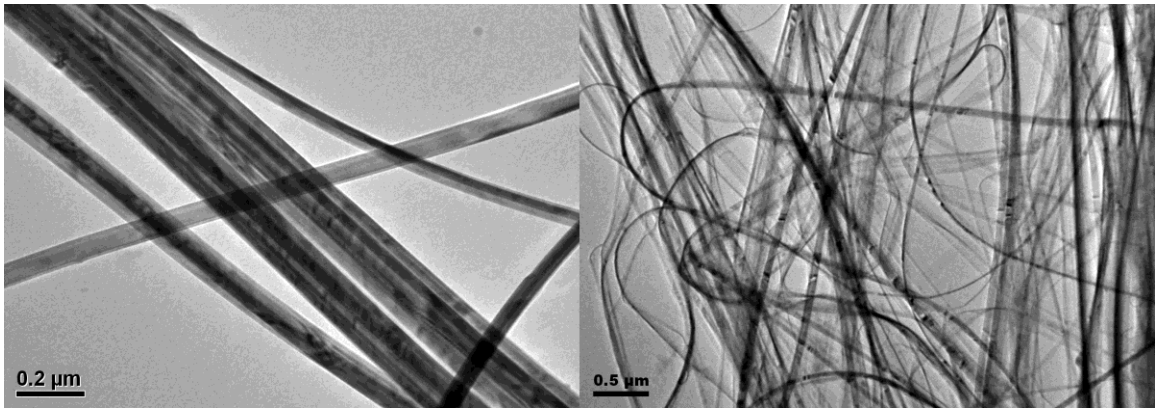

Figure S5. TEM images of VO_2 nanostructures produced in hydrothermal reaction with 2-propanol as a ligand (left: 30μl; right: 200μl)

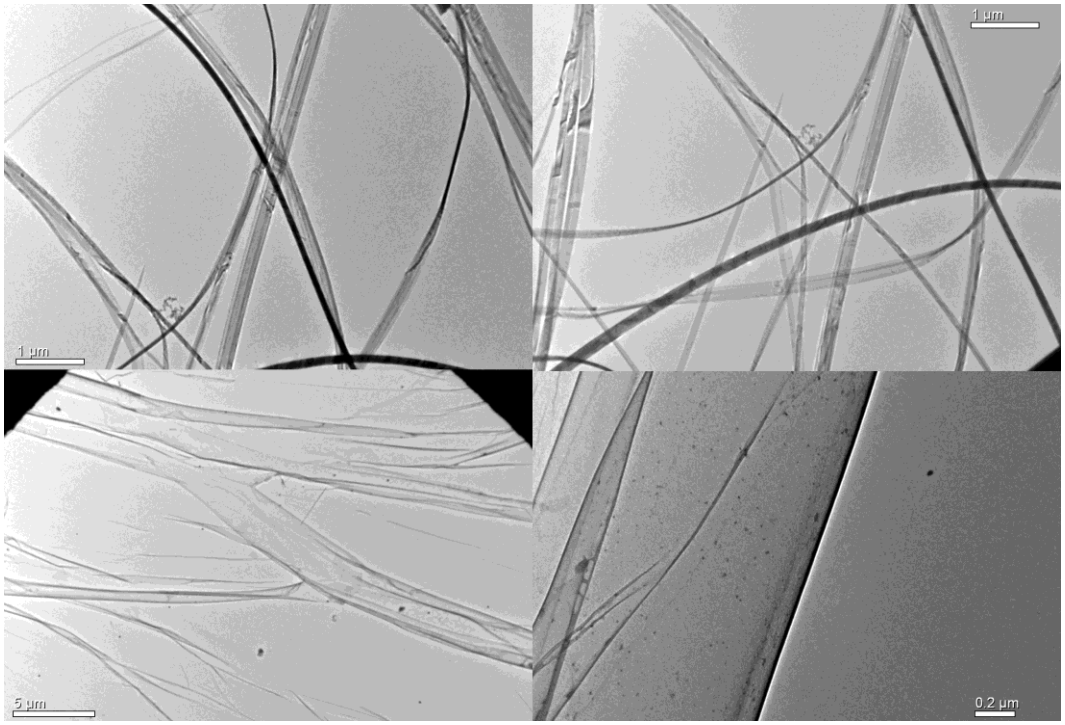

Figure S6. TEM images of VO_2 nanostructures produced in hydrothermal reaction with acetone as a ligand (top: 30µl; bottom: 200µl)

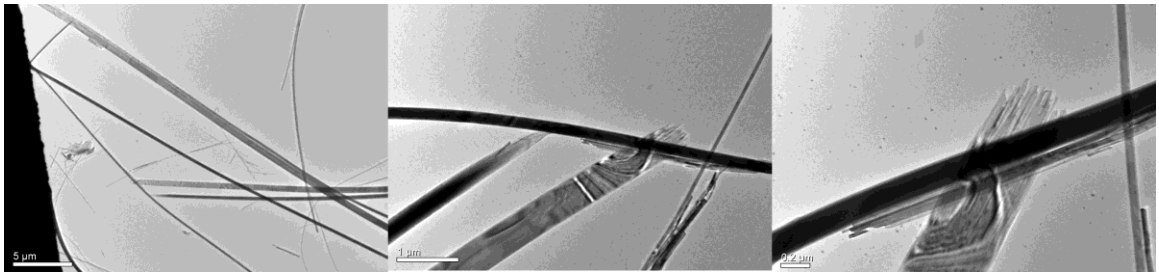

Figure S7. TEM images of VO_2 nanoribbons produced with ethanol as a ligand

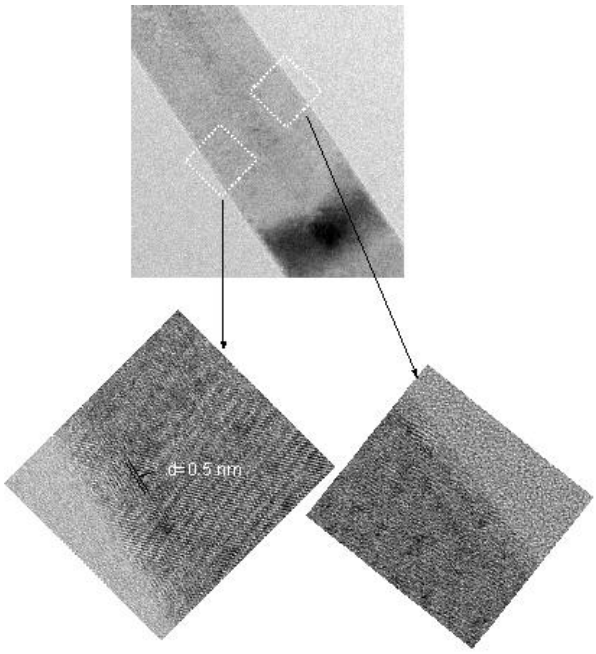

Figure S8. HRTEM image of VO_2 nanoribbon, showing V_3O_7 phase due to surface oxidation after exposure of the sample to air

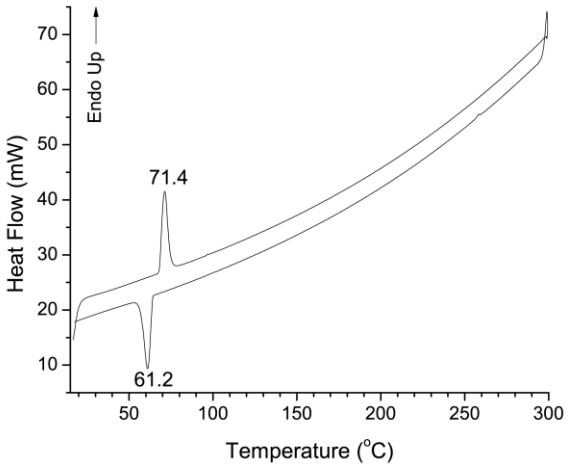

Figure S9. DSC scan of VO_2(M) nanoribbon sample showing reversible phase transition around 70°C

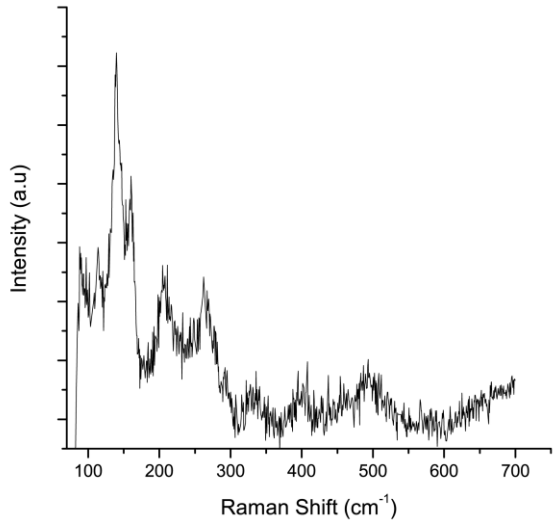

Figure S10. Raman spectrum of VO_2(M) nanoribbons

Surface oxidation in air

All nanocrystalline VO_2(M) exhibit surface oxidation when exposed to air. The surface layer seems to be limited to a monolayer on the surface of the nanocrystals, as there are no phase boundaries evident in HRTEM images. Moreover, both the samples synthesized in air and the samples synthesized in inert atmosphere and then exposed to air exhibit as VO_2(M) in XRD measurements. Neither the samples synthesized in air nor the samples synthesized in inert atmosphere and then exposed to air show any sign of significant oxidation due to prolonged

exposure to air over a period of six months (Figure S2, top left), unlike the commercial bulk powder VO_2 precursor, which oxidizes in air when exposed to light. However, surface oxidation means that the samples in HRTEM images exhibit structure of tetragonal V_3O_7, in spite being synthesized and handled in inert atmosphere, except during the sample loading procedure into the instrument. In addition, Raman spectra of these samples exhibit VO_2 peaks when synthesized and handled in inert atmosphere, but oxidize instantly in contact with air, exhibiting peaks characteristic of orthorhombic V_2O_5 phase. All the while, in XRD measurements these samples exhibit no observable secondary phase in addition to VO_2(M), while even those samples exposed to air exhibit a reversible phase transition around 70^{o}C (Figure S9). However, it was not possible at this point to determine the influence of surface oxidation on the phase transformation process. Therefore, the manuscript includes only those measurements where either it was possible to protect the samples from air or those where subsequent exposure to air made no difference.