Preliminary test on the influence of the laser pulsing frequency on the morphology of VO_2(M) films:

In order to investigate the influence of the laser pulses frequency on the morphology of the PLD-grown VO_2(M) films toward exploring the possibility of synthesizing VO_2(M) micro/nanowires, 4 laser pulsing frequencies were tested under the deposition conditions specified in the manuscript for a substrate temperature fixed at 650°C. The SEM results summarized in figure S1 show that the lowest laser pulses frequency (2 Hz) allows for the synthesis of elongated structures (rods). Therefore, 2 Hz was adopted for the further steps of the study.

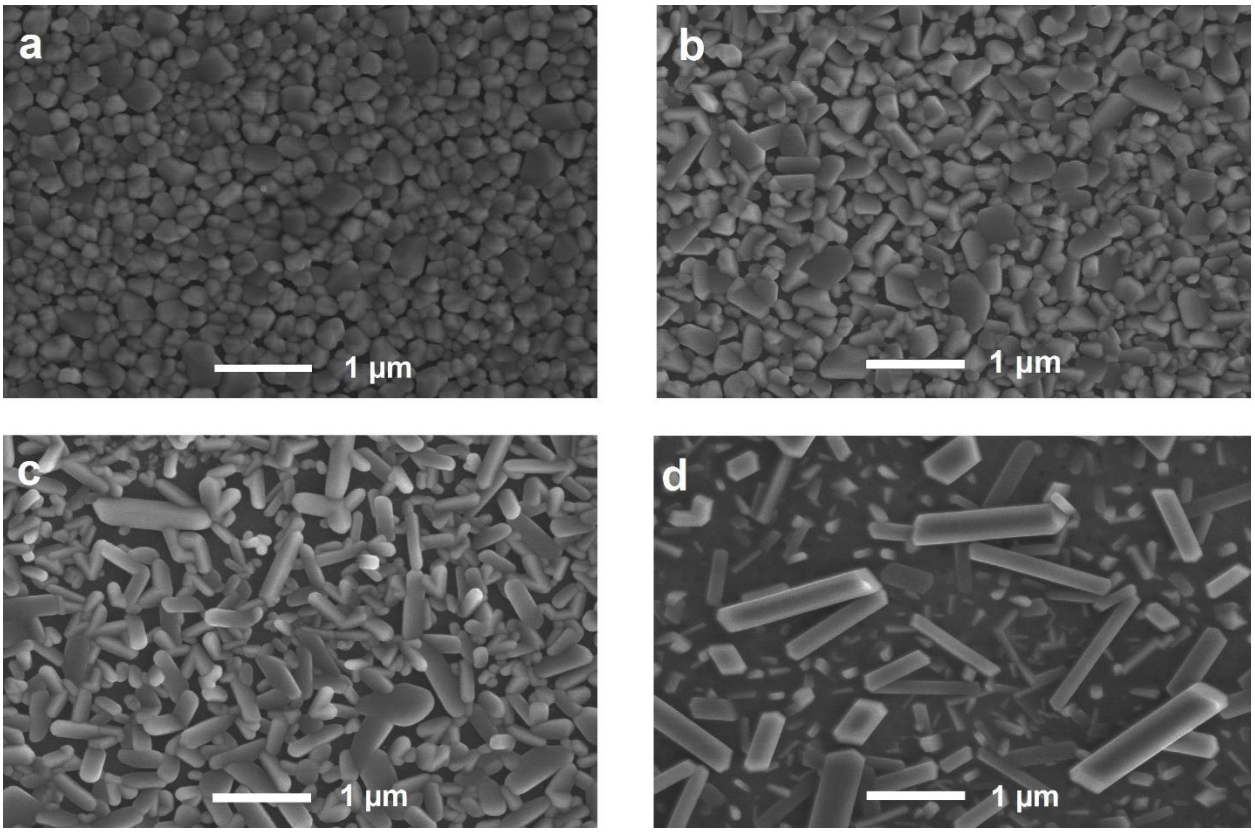

Figure S1. SEM images of the PLD VO_2(M) films grown at 650°C and different laser pulsing frequencies: (a) 20 Hz, (b) 14Hz, (c) 8 Hz and (d) 2 Hz

X-ray photoelectron spectroscopy (XPS) analysis:

XPS measurements were performed to investigate the valence state content of vanadium. As shown of Figure S2, the binding energy of the $V2p_{3/2}$ core level depends on the oxidation state of the V cation. The $V2p_{3/2}$ peak was thus used to determine the valence state content of vanadium in the VO_2 films using the CasaXPS software and a Shirley function to remove the background. The $V2p_{3/2}$ peak was deconvoluted into a combination of a V^{5+}, V^{4+} and V^{2+} Gaussian/Lorentzian peaks.

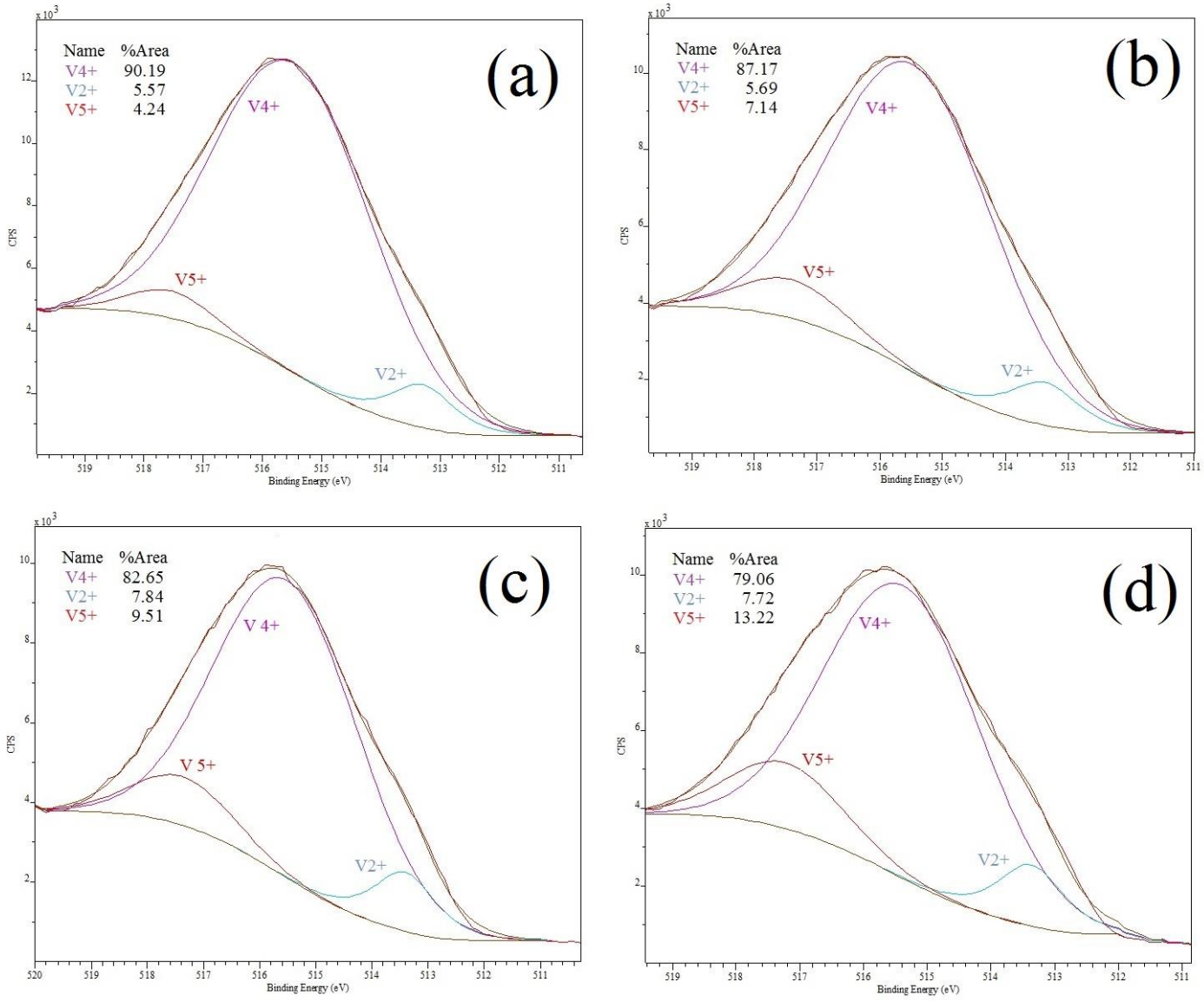

Figure S2. XPS spectra of the $V2p_{3/2}$ peak deconvoluted into V^{5+}, V^{4+} and V^{2+}: for the samples processed at different substrate temperatures: (a) 450°C, (b) 550°C, (c) 650°C and (d) 750°C