Supplementary Information

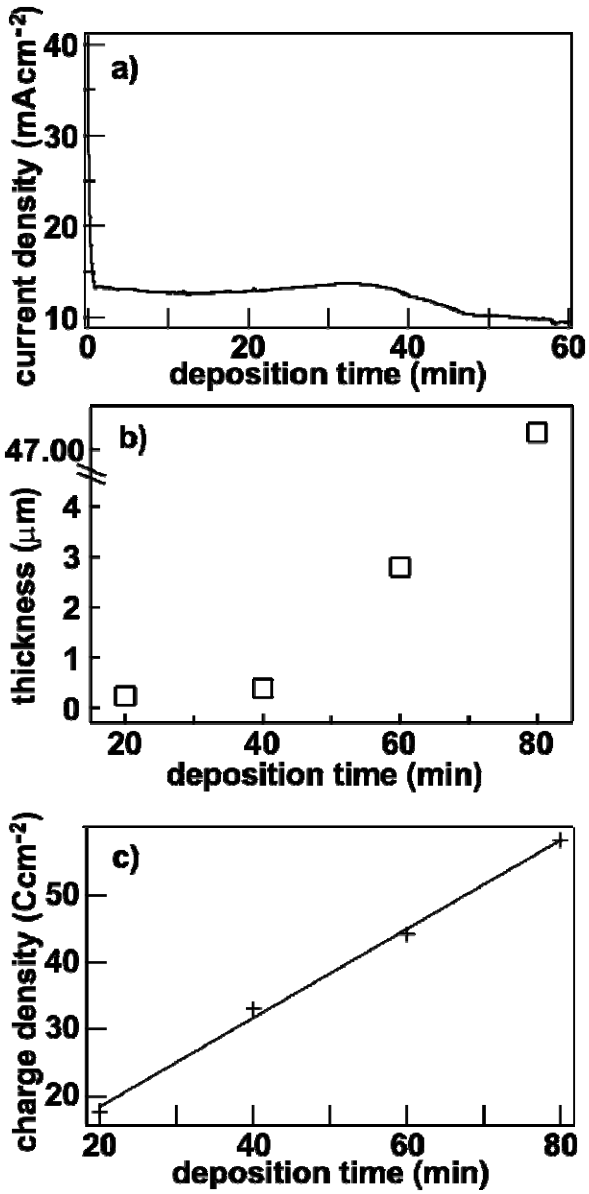

Fig. S1 Deposition of flat films. a) A typical current density *vs.* deposition time curve. b) The dependence of film thickness after heat-treatment at 120 °C on deposition time. c) The dependence of charge density passed on deposition time.

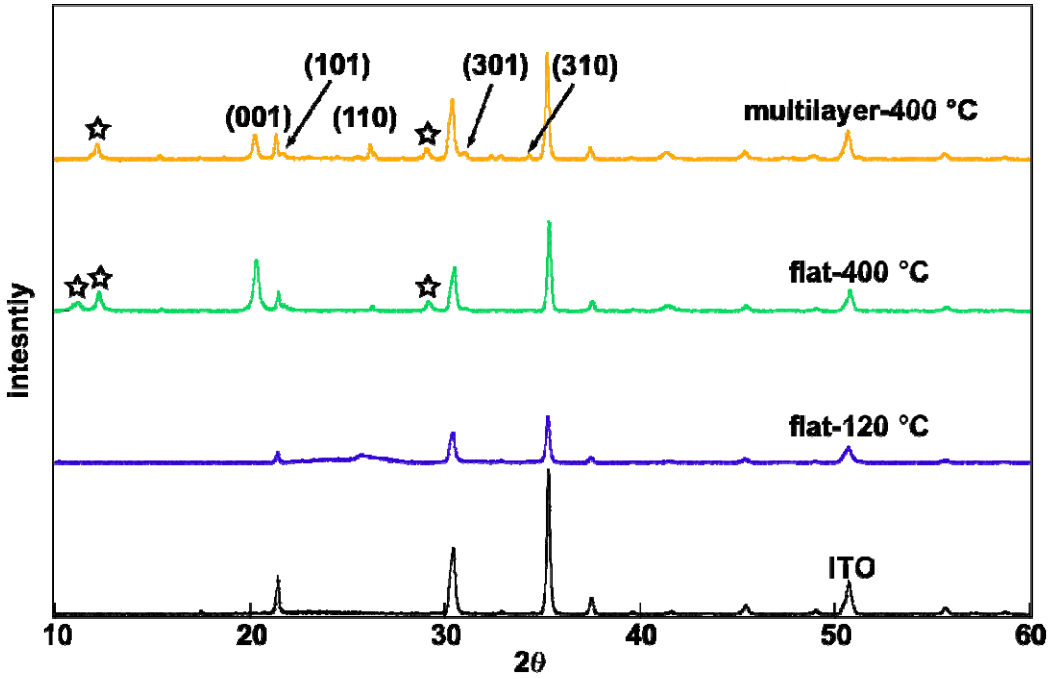

Fig. S2 Wide-angle XRD patterns of flat and multilayer macroporous films heat treated at 120 °C and 400 °C. Star denotes the diffraction peaks from NaV_6O_{15}.

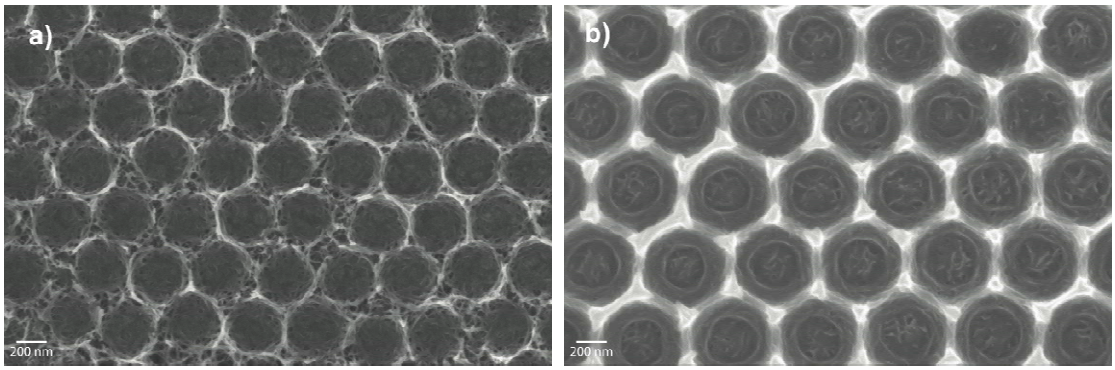

Fig. S3 SEM images of monolayer vanadium oxide films with different fractions of a template layer after heat treatment at 120 °C. a) 0.23 *D* thick monolayer film, b) 0.73 *D* thick monolayer film.

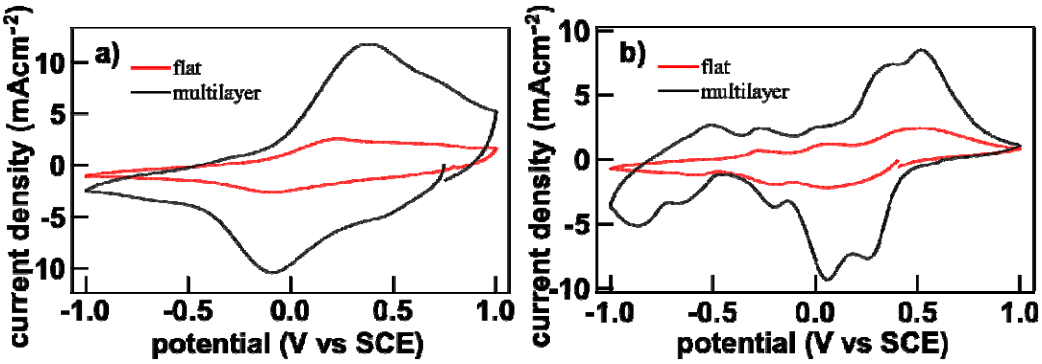

Fig. S4 Cyclic voltammograms of flat and multilayer macroporous films after heat treatment at a) 120 °C and b) 400 °C, respectively. These were recorded in a 1 M $LiClO_4$/propylene carbonate solution at a scan rate of 10 mVs^{-1}. The increase in the oxidative charge has been utilized to measure the increase in surface area of the multilayer compared to the flat film.

The redox peaks have been assigned to the progressive redox reactions[1,2]:

$$V_2O_5 + 1/2Li^+ + 1/2e^- \rightleftharpoons Li_{0.5}V_2O_5$$

$$Li_{0.5}V_2O_5 + 1/2Li^+ + 1/2e^- \rightleftharpoons LiV_2O_5$$

These redox reactions occur at slightly different potentials for different crystalline phases. Therefore with increased crystallinity at 400 °C, the broad peaks split and the peak currents are indicative of the relative electroactivity of the exposed crystal planes. Also it is apparent from the CVs that for the multilayer macroporous films heat treatment at 400 ^oC slightly decreases the surface area compared to the 120 ^oC as manifest in the corresponding slight decrease in current density.

References

1 A. Tranchant, R. Messina and J. Perichon, *J. Electroanal. Chem.*, 1980, **113**, 225.

2 M. Benmoussa, A. Outzourhit, A. Bennouna and E. L. Ameziane, *Thin Solid Films*, 2002, **405**, 11.