Electronic Supporting Information (ESI)

Vertically Aligned Mixed V_2O_5-TiO_2 Nanotube Arrays for Supercapacitor Applications

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Experimental section:

Ti-V alloy plates (Ti: V= 99.8: 0.2 at%, 97: 3 at% and 82: 18 at%, provided by Central Institute for New Materials and Processing Technology, University of Erlangen, Germany) and Titanium foils (0.1 mm, 99.6%, Advent Materials) were used as substrates. Samples of each material were ground and polished to a mirror finish before use, followed by sonicating in acetone, isopropanol and ethanol, respectively. After rinsing with deionized (DI) water and drying in nitrogen, substrates were anodized under self-organizing conditions to grow oxide nanotubes. Electrochemical anodization was carried out at room temperature in a solution of ethylene glycol (EG, Riedel-de Haën, 99.5%) with 0.2 M HF (40 vol%, Merck). The anodization was conducted at 120 V for 30 minutes to grow 4~5 μm long nanotubes using a high-voltage potentiostat PE 1530 (Philips) and a conventional two-electrode configuration with a platinum gauze as counter electrode. After anodization, the samples were soaked in ethanol for overnight and then washed with DI water followed by drying in a nitrogen stream.

Thermal treatments of the samples were carried out using a Rapid Thermal Annealer (Jipelec JetFirst 100) at different temperatures for 1 hour in air with a heating/cooling rate of 5 ^{o}C min^{-1}. A field-emission scanning electron microscope (Hitachi FE-SEM S4800) equipped with an Energy dispersive X-ray (EDX) analyser was used to investigate the morphologies and compositions of the samples. X-ray diffraction (XRD) analysis was performed by an X'pert Phillips PMD with a Panalytical X'celerator detector using graphite-monochromized CuKα radiation. The composition and the chemical state of the samples were characterized by using X-ray photoelectron spectroscopy (XPS, PHI 5600, Perkin Elmer).

Electrochemical properties and capacitance measurements were carried out in a classical three electrode set-up: For this, the nanotubes on the metal substrates were used as working electrode; a platinum plate served as a counter electrode; and a Ag/AgCl (3 M KCl) electrode in a Haber-Luggin capillary served as a reference electrode. The electrochemical properties and capacitance measurements of the samples were studied by cyclic voltammetry (CV) and galvanostatic charge/discharge (chronopotentiometry) on an Autolab PGSTAT 30 Potentiostat/Galvanostat (Ecochemie, The Netherlands). The specific capacitance (C_{sp}) can be estimated from the charge/discharge curves according to the following equation:

$$C_{\mathrm{sp}} = \frac{I \times t}{\Delta V \times \mathrm{m}} \qquad (1)$$

where I is the current density during charge/discharge process, t is the charge/discharge duration in each segment, ΔV is the potential window (i.e., 0.80 V), and m is the estimated weight of nanotubes. For long term stability measurement, the specific capacitance is also estimated from the CV curves according to the following equation:

$$C_{\mathrm{sp}} = (Q_{+} + |Q_{-}|)/(2m\Delta V) \tag{2}$$

where Q_+ and Q_- is the integrated charges of anodic and cathodic respectively, the m is the estimated weight of nanotubes, ΔV is the potential window (0.80 V vs. Ag/AgCl). The normalized specific capacitance is then the measured capacitance divided by the capacitance of the first cycle. Furthermore the energy density can be calculated from the equation:

$$E = \frac{1}{2} C_{\mathrm{sp}} (\Delta V)^2 \tag{3}$$

where C_{sp} is the specific capacitance, ΔV is the potential window (0.80 V vs. Ag/AgCl).

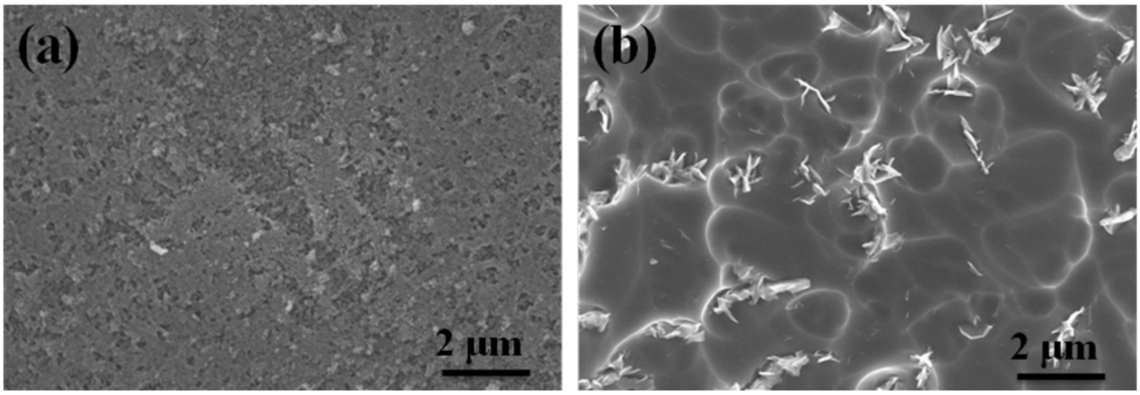

Figure S1. (a) Surface morphology of samples of a Ti40V alloy; (b) and Ti60V alloy after anodization.

It is clear that on these Ti-V alloys with high vanadium contents no nanotubes can be grown, just plain etching of the samples occurs.

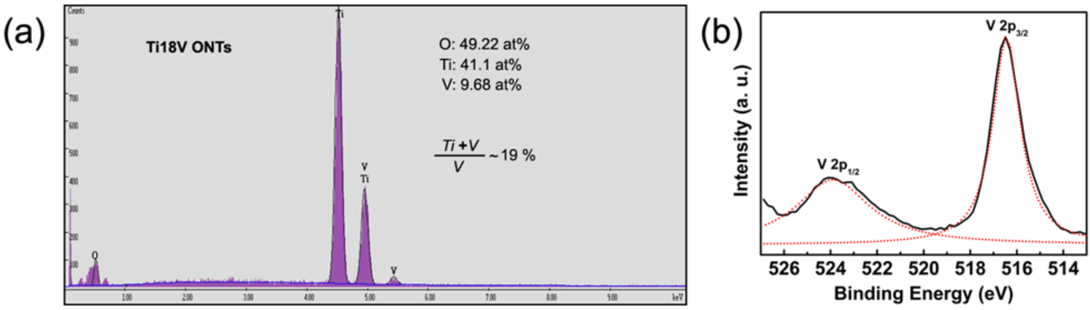

Figure S2. (a) EDX spectrum of the Ti18V oxide nanotubes; (b) V2p XPS spectrum of the Ti18V oxide nanotubes.

EDX result shows that even the composition of the Ti-V oxide nanotubes with the highest vanadium content, i.e. Ti18V, in our work is in good agreement with the nominal composition of the alloy. This indicates that the composition of the Ti-V oxide nanotubes have not changed during the anodization process in the electrolyte. And the V2p XPS spectrum presents the main peaks at 516.48 and 523.91 eV, which agree well with the binding energy of V^{5+} in V_2O_5.[1]

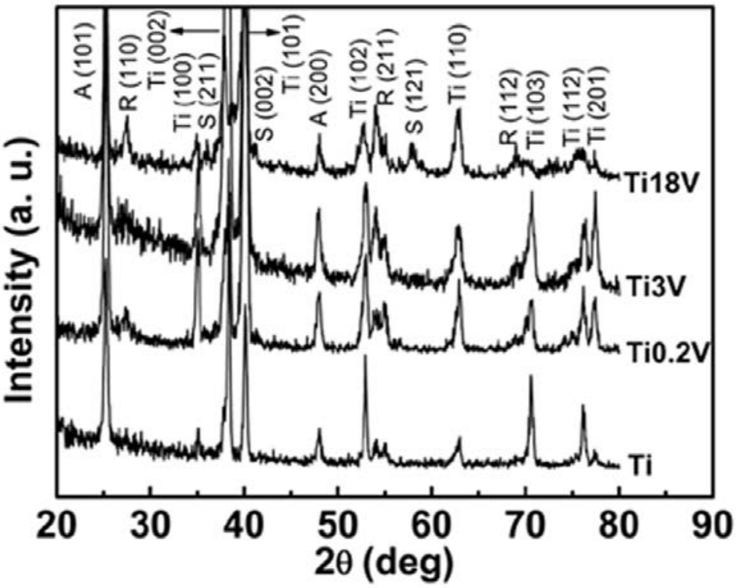

Figure S3. XRD patterns of the Ti, Ti0.2V, Ti3V and Ti18V oxide nanotubes after annealing at 400 °C for 1 hour (A: anatase phase of TiO_2, R: rutile phase of TiO_2, S: shcherbinaite phase of V_2O_5).

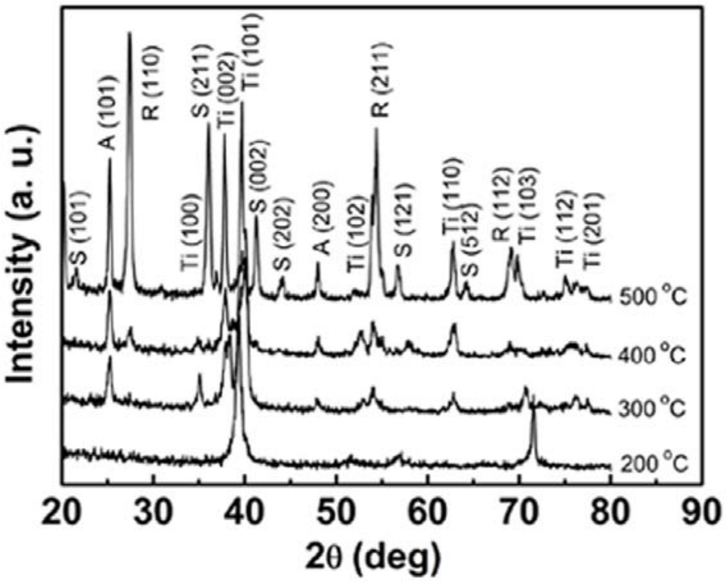

Figure S4. XRD patterns of the samples after annealing at different temperatures for 1 hour (A: anatase phase of TiO_2, R: rutile phase of TiO_2, S: shcherbinaite phase of V_2O_5).

The XRD patterns show that crystallization of the TiO_2 to anatase phase along with shcherbinaite V_2O_5 occurs at 300 ^{o}C. If the annealing temperature is elevated to 400 ^{o}C, rutile starts appearing. When annealed at 500 ^{o}C, well-crystalline shcherbinaite V_2O_5 together with large amount of rutile TiO_2 are formed in the oxide nanotubes.

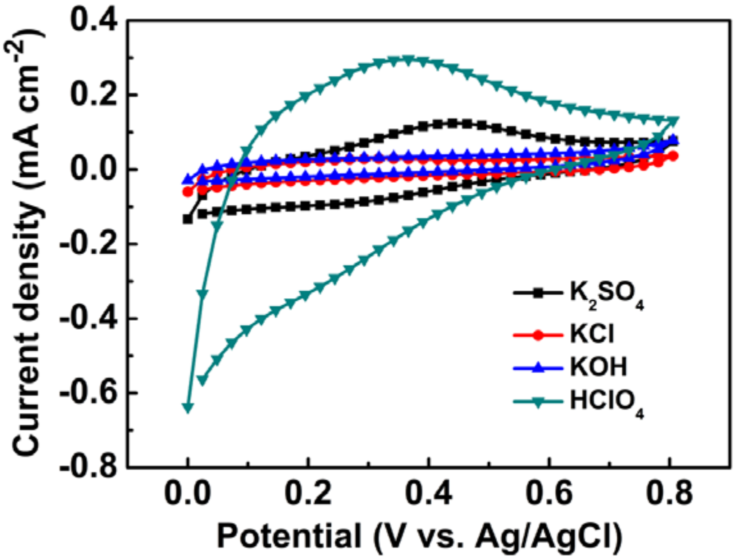

Figure S5. Cyclic voltammograms of the Ti18V oxide nanotubes performed over a voltage window between 0 and 0.8 V in different electrolytes, i.e. 0.1 M K_2SO_4, 2 M KCl, 1 M KOH and 0.1 M $HClO_4$, with scan rate of 50 mV s^{-1}.

It is evident from Figure S4 that the Ti18V oxide nanotubes show the highest current density in our experiments due to the much easier transportation of H^+ ion in the nanotube structure.[2]

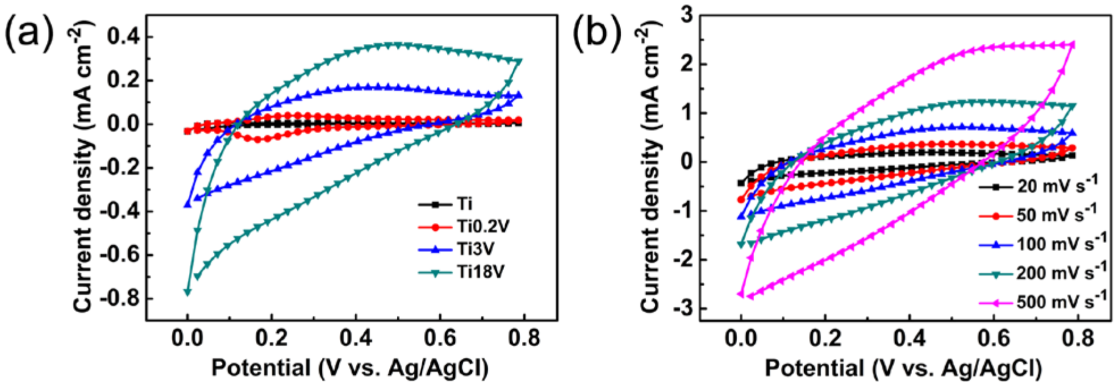

Figure S6. (a) Cyclic voltammograms of the Ti and Ti-V oxide nanotubes after annealing at 300 °C in air for 1 hour performed over a voltage window between 0 and 0.8 V in 0.1 M $HClO_4$ electrolyte with scan rate of 50 mV s^{-1}; (b) Cyclic voltammograms of the Ti18V oxide nanotubes with different scan rates from 20 to 500 mV s^{-1}.

The CV curves of the Ti and Ti-V oxide nanotubes annealed at 300 °C also show similar behavior together with much higher current densities compared with the nanotubes annealed at 400 °C. The scan rate dependence of the current density indicates a diffusion controlled process.

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2 D. M. Guldi, G. M. A. Rahman, V. Sgobba, N. A. Kotov, D. Bonifazi, M. Prato, *J. Am. Chem Soc.*, 2006, **128**, 2315; A. H. Liu, D. L. Li, I. Honma, H. S. Zhou, *Electrochem. Commun.*, 2006, **8**, 206; Z. Fan, J. Yan, L. Zhi, Q. Zhang, T. Wei, J. Feng, M. Zhang, W. Qian, F. Wei, *Adv. Mater.*, 2010, **22**, 3723.