

Figure S1. Measured Raman spectra of (a) compact  $\text{TiO}_{2-x}$  layer and (b) self-organized  $\text{TiO}_{2-x}$  NTs.

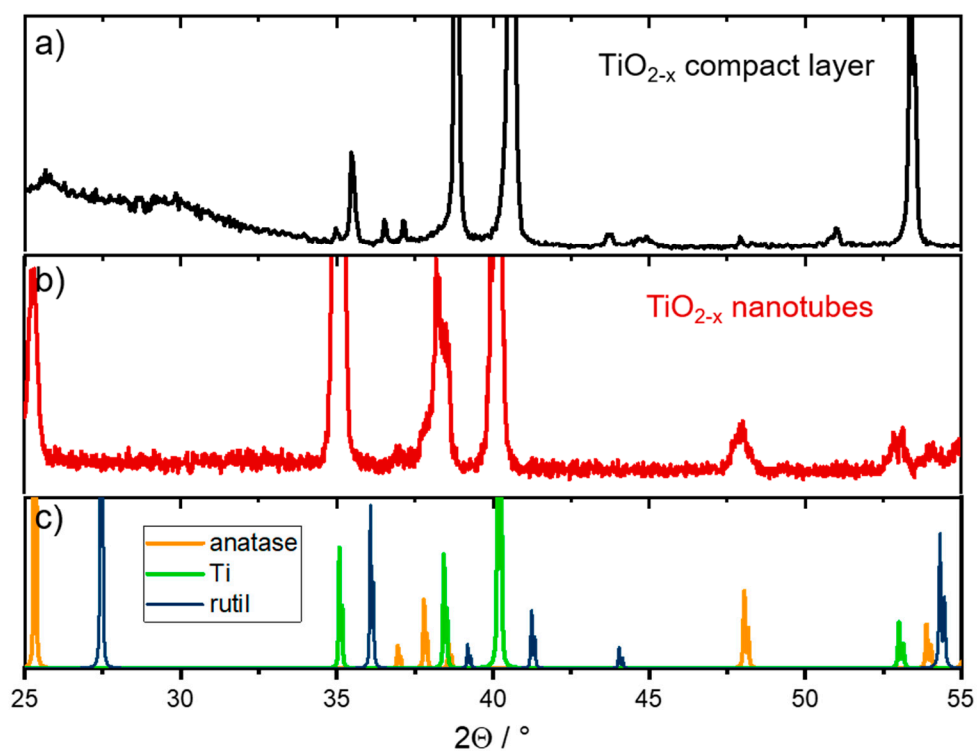
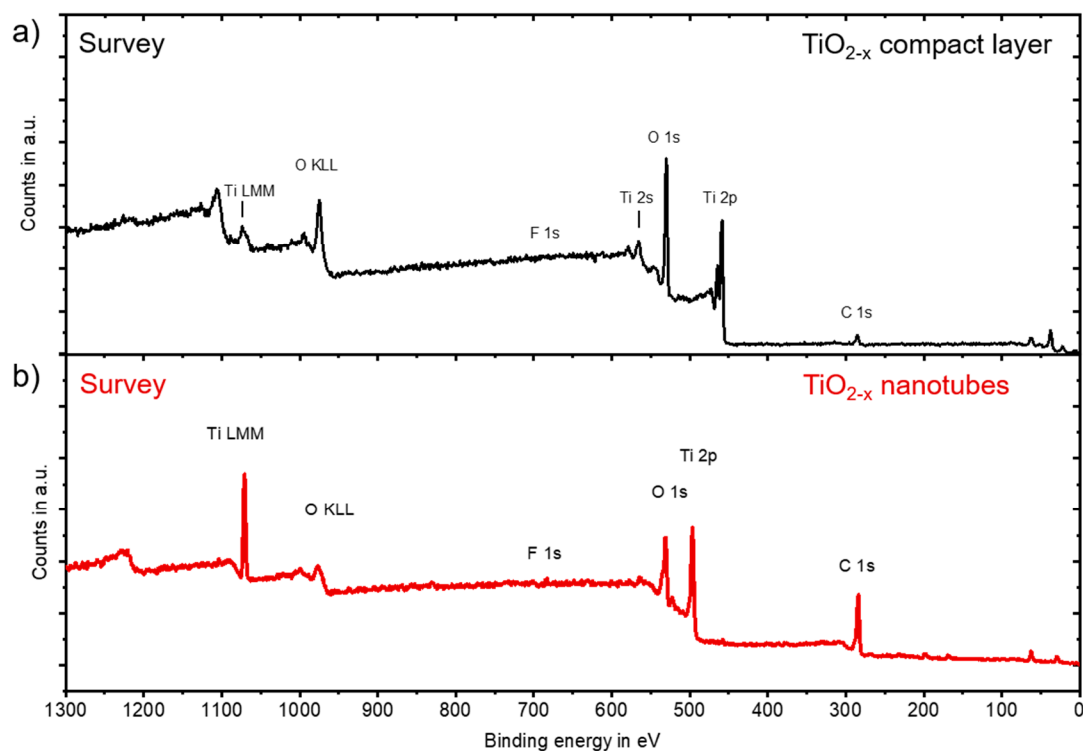
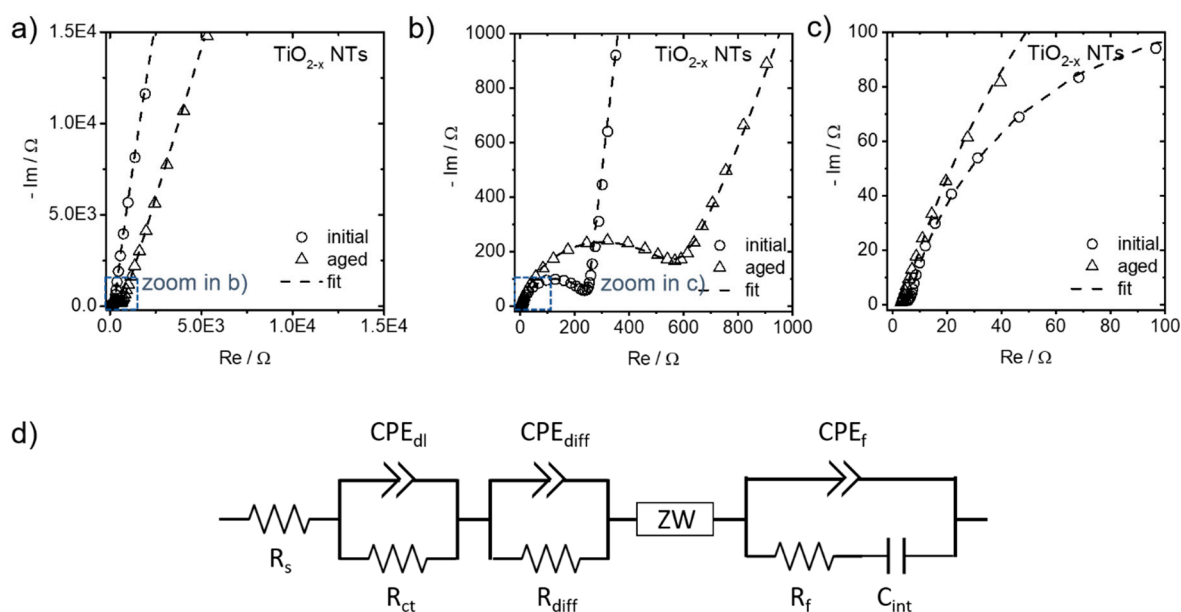


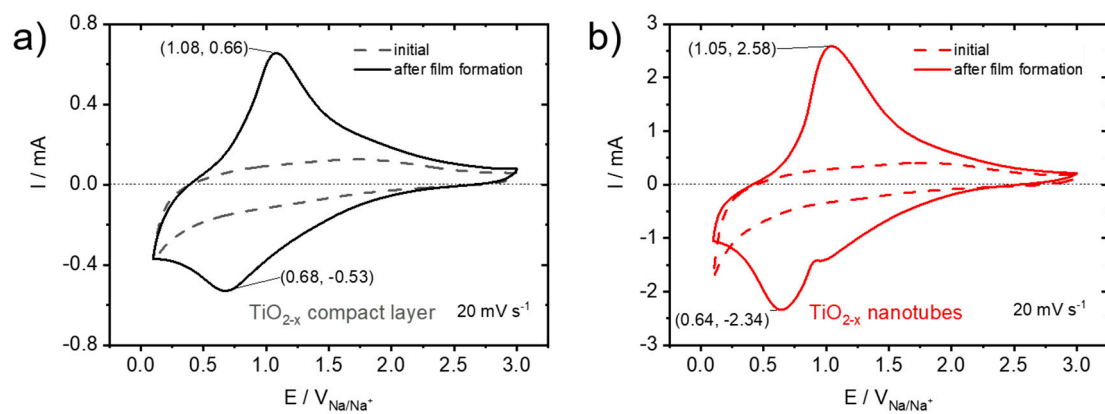
Figure S2. Measured XRD patterns of (a) compact  $\text{TiO}_{2-x}$  layer and (b) self-organized  $\text{TiO}_{2-x}$  NTs. (c) Reference data for Ti metal, anatase and rutile.



**Figure S3.** Measured XPS survey spectra of (a) compact  $\text{TiO}_{2-x}$  layer and (b) self-organized  $\text{TiO}_{2-x}$  NTs.



**Figure S4.** Electrochemical impedance spectroscopy (EIS). Nyquist plots of anatase  $\text{TiO}_{2-x}$  NTs before (initial) and after (aged) film formation by 230 galvanostatic sodiation/desodiation cycles, plotted from 100 kHz to 7.4 mHz in three different magnifications (a–c). (d) Equivalent electric circuit used for fitting the EIS data.  $R_s$ : solution resistance,  $R_{ct}$  interfacial Ti/TiO<sub>2</sub> NTs electron charge transfer resistance,  $C_{dl}$  and  $C_{dl}$ : corresponding capacitances, ZW: Warburg element for semi-infinite diffusion, (capacitances modelled with a CPE).



**Figure S5.** Electrochemical characterization and comparison. CV measurements for the initial (dashed line) and aged (solid line, after film formation) electrodes with (a) a compact  $\text{TiO}_{2-x}$  layer and (b) self-organized  $\text{TiO}_{2-x}$  NTs at a scan rate of  $20 \text{ mV s}^{-1}$ .