

## Supporting Information Available.

For the production of the  $\text{TiO}_2$  nanotubes, Ti foils (supplied by Sigma-Aldrich) were cut and cleaned by sonicating in acetone, isopropanol, and methanol, for 10 min each. The foils were then anodized by applying a constant voltage of 20 V during 2 hours using an EG&G PARSTAT 2273 potentiostat/galvanostat in a 1 M  $\text{H}_3\text{PO}_4$  + 1 M NaOH + 0.4 wt.% HF electrolyte at room temperature. A platinum foil counter electrode was used with the Ti foils as working electrodes.

For the sulphidation, the obtained  $\text{TiO}_2$  nanotubes (~80  $\mu\text{g}$ ) together with a sulphur pellet (~30 mg) were introduced into quartz ampoules (1 cm in internal diameter, 5 cm in length) which are sealed under vacuum (less than 1 Pa). The ampoules were placed at the center of a horizontal tube furnace (Carbolite CTF 12/75/700) and heated at 450 °C (above the 444 °C boiling point of sulphur) for 1 h, with a heating/cooling rate of 200 °C/min.

X-ray diffraction patterns were recorded (with a steptime of 10 s and step size of 0.02°) at room temperature using a Siemens D5000 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). EDS analyses (See Fig below) and scanning electron microscopy imaging were carried out with a Philips XL-30 FEG SEM.

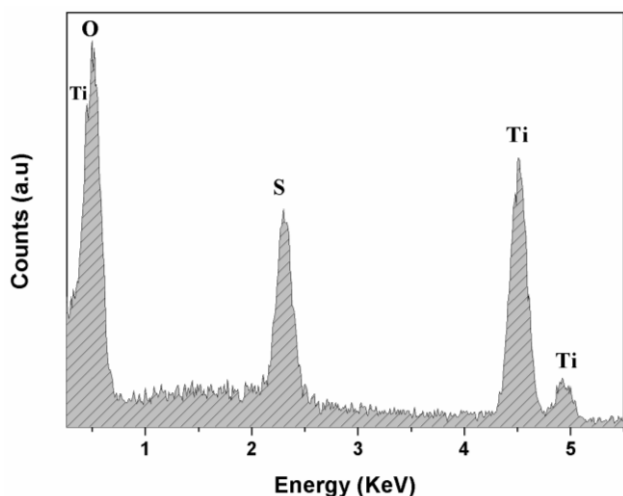


Fig. S1 EDS spectrum of the obtained  $\text{TiO}_x\text{S}_y$  nanotubes.

For the electrochemical measurements, two-electrode Swagelok-type cells were assembled [Li-metal/ $\text{LiPF}_6$  (EC:DEC)/ $\text{TiO}_x\text{S}_y$ ] in a glove-box filled with purified argon in which moisture and oxygen contents were less than 2 ppm. The galvanostatic experiments were then carried out with the prepared Li-metal/ $\text{LiPF}_6$  (EC:DEC)/ $\text{TiO}_x\text{S}_y$  cells using VersaSTAT3 potentiostat/galvanostat. The electrolyte supplied by Merck was embedded in a Whatman glass microfiber which acts as a separator. For the discharge/charge, a constant current density of 70  $\mu\text{Acm}^{-2}$  was applied to the assembled cells in the  $1.6 \leq U/V \leq 3.3$  voltage range. Additionally, cyclic voltammetry was carried out also with the

VersaSTAT3 potentiostat/galvanostat in the  $0.65 \leq U/V \leq 3.3$  voltage range at a scan rate of 0.1  $\text{mVs}^{-1}$ .

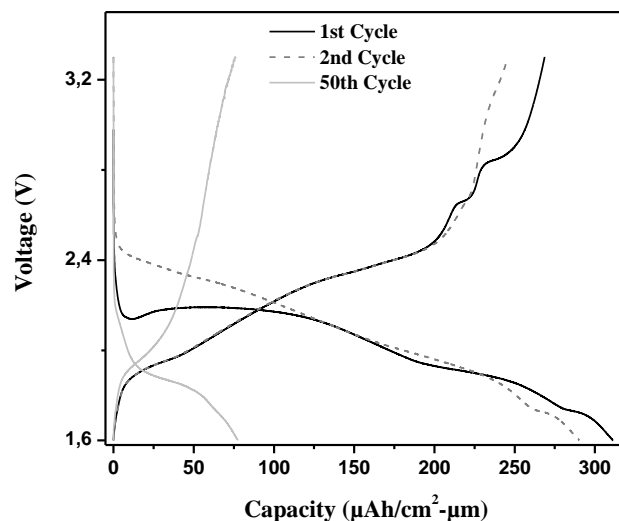


Fig. S2 Galvanostatic plot of voltage versus discharge capacity for the  $\text{TiO}_x\text{S}_y$  nanotubes. The sample was cycled in the  $1.6 \leq U/V \leq 3.3$  voltage range with a current density of 70  $\mu\text{Acm}^{-2}$ , using a two-electrode Swagelok cell [Li-metal/ $\text{LiPF}_6$  (EC:DEC)/ $\text{TiO}_x\text{S}_y$ ].

In order to verify the presence of sulphur in the electrolyte after cycling, a substantial amount of the electrolyte after charge/discharge experiment was collected onto a piece of silicon wafer, dried overnight at 70 °C, and analyzed by EDS.

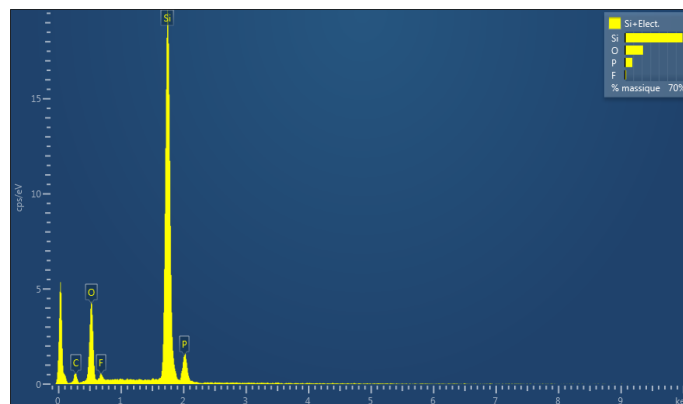


Fig. S3 EDS spectrum of used electrolyte dried on a Si wafer