## **Supporting Information**

## NH<sub>3</sub> treatment of TiO<sub>2</sub> nanotubes: From N-doping to semimetallic conductivity

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**Fig. S1** shows a typical SEM morphology of a 'classic' nanotube layer after an  $NH_3$ treatment at elevated temperature >800° C. These 'classic' tubes (produced in a EG electrolyte) are of a double wall structure (see Fig. S2, left) – this double layer structure makes the tube more prone to sintering and collapse than the single wall tubes (Fig. 1 and Fig. S2, right).



**Fig. S2** 'Double wall' vs. 'single wall' tubes. (a-d) TEM images for double wall (a,c) and single wall (b,d) morphology of  $TiO_2$  nanotubes. SEM top-view images of  $TiO_2$  nanotubes after fracture close to the bottom of tubes for the double wall (e) and single wall (f) nanotubes. TEM images of the double wall (g) and single wall (h)  $TiO_2$  nanotubes after annealing. The inset is an SEM top-view image of the double wall nanotubes, is taken from a fracture after annealing (Reproduced with permission [1]. Copyright 2013 Royal Society of Chemistry.).

## Methods:

Titanium foils (99.6% purity, Advent) with a thickness of 0.1mm were sonicated in ethanol for several minutes, followed by rinsing with deionised water and drying under a N<sub>2</sub> stream. TiO<sub>2</sub> nanotubes samples were prepared using the methodology as described by Mirabolghasemi et al. [1]. For this, a computer controlled power source (LAB/SM1600 by ET-Systems) was employed. After anodization, the samples were rinsed with deionised water and dried in a nitrogen stream. For the characterization of the sample morphology a field-emission scanning electron microscope Hitachi FE-SEM S4800 equipped with an Energy Dispersive X-ray Spectroscopy (EDX, EDAX/TSL Genesis 4000) was used.

The nitrogen doping of the TiO<sub>2</sub> layer was carried out by heating the samples at  $450^{\circ}$ C in a quartz tube under a continuous NH<sub>3</sub> flux (20 ml/min) for 120 min. The treated TiO<sub>2</sub>-nanotube layers were cooled down to room temperature under N<sub>2</sub> flow before contact with ambient air. For comparison, some TiO<sub>2</sub> nanotube layers were annealed in air at 450°C for 2 h to form an anatase crystal structure. The nitrogen reduced (modified samples) undergo a similar procedure but at higher starting temperature (900 °C) for only 10 minutes treatment time, followed by a second diffusion treatment at 500 °C in pure nitrogen for 30 min.

To examine the crystalline structure of the treated samples, XRD-measurements were performed using Cu K $\alpha$  radiation with an X`pert Philips MPD PW 3040 instrument.

The chemical composition of the samples was characterized by X-ray photoelectron spectroscopy (PHI 5600 XPS) using Al K $\alpha$  monochromated radiation. The spectra were corrected for spectral shifts using Ti2p at 459.1 eV.

For 2-point solid state measurements nanotube-tops were contacted by sputter evaporated Au dots through a mask (2mm in diameter). Using the two point approach was found to be in line with reported results from four point measurements [2].

The electrochemical experiments were carried out at room temperature in a cell with a three-electrode arrangement using an Autolab (PGSTAT 30) setup. The samples were contacted with a Cu back-plate (as working electrode) and then pressed against an O-ring opening in the wall of the cell, leaving an exposed area of 1 cm<sup>2</sup>. A Pt-gauze served as counter electrode and an Ag/AgCl electrode connected to a Haber-Luggin capillary was used as a reference electrode. For cyclic voltammetry, 5 mM Fe(CN)<sub>6</sub>-<sup>2/-</sup> <sup>3</sup> solution and 0.1 M NaCl as support with a sweep rate of 5 mV/s was used. Potentiostatic cyclovoltammetry (CV) was carried out in a potential window from +100mV to +300mV vs. Ag/AgCl reference electrode in aqueous 0.1M HCl (made from 37% HCL, Sigma-Aldrich) at a sweep-rate of 100mV/s.

Photocurrent spectra were taken in the range of 300 to 600 nm at an applied potential of 500 mV using a three electrode arrangement (Ag/AgCl, 3 M KCl, as reference and Pt as counter electrode) in an electrochemical cell equipped with a quartz glass window in 0.1 M sodium sulphate solution. The illumination setup consisted of an Oriel 6356 150 W Xe arc lamp as a light source and an Oriel XCornerstone 7400 1/8 monochromator. The data was obtained from photo transients with 10 seconds light exposure and with a step size of 20 nm.

## **References:**

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