Supporting Information

**Nb doped TiO$_2$ nanotubes for enhanced photoelectrochemical water-splitting**

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Self organized TiO$_2$ nanotube layers were grown by anodization the Ti foil (99.6% purity, Advent Materials, UK) of 0.12 mm thickness. The Nb doped TiO$_2$ nanotubes were prepared by anodizing Ti-Nb alloys with concentrations 0.02 at%, 0.05 at%, 0.1 at% , 0.2 at% and 0.5 at% of Nb (Helmholtz-Zentrum Geesthacht (Geesthacht Germany)). Prior to anodization, the alloys were mechanically ground, lapped, and finally polished using colloidal silica suspension. Prior to anodization all the substrates were sonicated with acetone and ethanol and then rinsed with D.I water and dried in a nitrogen stream. Anodization was carried out in a two electrode arrangement consisting of Ti foil or the Ti-Nb alloys as working electrode and platinum sheet as a counter electrode with 50 V applied potential for different time duration to grow different thicknesses of nanotube layers. The electrolyte was ethylene glycol containing 0.1M NH$_4$F and 1M H$_2$O. After anodization the samples were immersed in ethanol for overnight and then dried in a nitrogen stream.

The as formed amorphous TiO$_2$ nanotube layers were annealed at 450 °C and 650 °C for 3 hr in air using a Rapid Thermal Annealer (Jipelec JetFirst100) with a heating and cooling rate of 30 °C/min to convert them into crystalline phases.

For morphological characterization of nanotube layers, a field emission scanning electron microscope (Hitachi FE-SEM S4800) was used. To determine the crystal structure of the nanotube layers, X-ray diffraction analysis (XRD, X’pert Philips PMD with a Panalytical X’celerator detector) with graphite monochromized CuK$_\alpha$ radiation (Wavelength 1.54056 Å) was used.
Compositional analysis was carried out with X-ray photo electron spectroscopy (PHI 5600, Perkin Elmer) using the O1s, Ti2p, C1s and Nb3d peaks and manufacturer provided sensitivity factors.

The photocatalytic water splitting efficiency was characterized using a three electrode system, consisting of the doped and undoped TiO2 nanotube layer as photoanode, Pt foil as cathode and Ag/AgCl (3M KCl) as reference electrode. All experiments were carried out under simulated AM 1.5 illumination condition at an intensity of 100mW/cm² (solarlight, 300 W Xe with optical filter, Solarlight). Bias to the electrochemical cell was applied using a potentiostat (Jaissle IMP 88 PC).
**Fig. S1**: Photocurrent transients as a function of the potential (vs. Ag/AgCl) for TiO$_2$ nanotube layers of different thickness annealed at 650 ºC (a) and 6µm thickness nanotube layer annealed at different temperatures (b).

Tubes for these experiments were grown under the electrochemical conditions provided in the experimental section. A typical morphology is shown in Fig.S2 (a-c).
**Fig S2:** Cross-sectional SEM images different thicknesses (~2μm, 7μm and 12μm) of TiO$_2$ nanotube layers doped with different concentrations of Nb, 0 at % (a-c), 0.1 at % (d-f), 0.2 at % (g-i) and 0.5 at % (j-k).
**Fig. S3:** Photocurrent transient of Ti0.1Nb nanotubes as a function of applied potential (vs. Ag/AgCl) for different annealing temperatures under AM 1.5 illumination.
**Fig. S4:** XRD pattern of TiO$_2$ nanotube layers doped with different concentrations of Nb (0 at% - 0.5 at%) annealed at 650 °C in air. (A- anatase, R- Rutile, and T-titanium)

**Fig. S5:** XPS spectra Nb3d peaks of undoped TiO$_2$ as well as doped with different concentration of Nb (0.2 at% and 0.5 at%), confirming the presence of niobate in the nanotube layers [39,40].
**Figure S6**

![Graph showing photocurrent spectra](image)

**Fig. S6**: Photocurrent spectra of Ti0.1Nb and TiNT annealed at 450 and 650 °C and visible photo response (inset).

**Figure S7**

![Graph showing water splitting stability](image)

**Fig. S7**: Water splitting stability of Ti0.1Nb nanotubes over 15 hours of AM 1.5 illumination in 1M KOH electrolyte.
Fig. S8: Photocurrent vs. the length of Nb-doped and non-doped TiO2 nanotubes annealed at 650 °C at the applied potential 500 mV (vs. Ag/Agcl).