

## Nb doping of TiO<sub>2</sub> nanotubes for an enhanced efficiency of dye-sensitized solar cells

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### **Experimental section:**

A series of single phase Ti-Nb alloys with niobium contents of 0.02-1.0 wt% was produced by vacuum arc melting (GKSS-Research Centre, Geesthacht, Germany). Samples were cut and polished with sandpaper, the final polishing step was with a suspension of 0.06 µm colloidal silica. In order to achieve self-organized nanotube layers the substrates were anodized in an ethylene glycol electrolyte containing 0.1 M NH<sub>4</sub>F and 1 M H<sub>2</sub>O at 50 V to reach a 2 µm thickness. For TiO<sub>2</sub>, anodization took 6 min; for increasing Nb content anodization time was adjusted to also reach 2 µm-layer. The experimental setup consisted of a typical three-electrode arrangement, with an Ag/AgCl (3 M KCl) reference electrode and Pt mesh as the counter electrode. To crystallize the oxide, samples were annealed 3h in air at 450°C and 650 °C using a Rapid Thermal Annealer (Jipelec JetFirst100).

A field emission scanning electron microscope (Hitachi FE-SEM S4800) was used for morphological characterization of the samples. XRD patterns were collected on a powder diffractometer (XGpert Philips PMD with a Panalytical XGcelerator detector) using graphite-monochromatized CuK $\alpha$  radiation ( $\lambda=1.54056 \text{ \AA}$ ). The chemical composition of the layer was investigated with X-ray photoelectron spectroscopy (XPS, PHI 5600 XPS spectrometer). For dye-sensitization, a Ru-based N719 dye (cis-bis (isothiocyanato) bis (2,2-bipyridyl 4,4-dicarboxylato) ruthenium(II) bis-tetrabutylammonium) (Solaronix SA, Switzerland) was used. The nanotube samples were immersed for 72 h at 40 °C in a 300  $\mu$ M solution of the N719 dye in a mixture of acetonitrile and tert-butyl alcohol (volume ratio: 1:1). After dye-sensitization, the samples were rinsed with acetonitrile to remove non-chemisorbed dye. To evaluate the photovoltaic performance, the sensitized tube layers were sandwiched together with a Pt coated fluorine-doped glass counter electrode (TCO22-15, Solaronix) using a polymer adhesive spacer (Surlyn, Dupont). An electrolyte (Iodolyte R50, Solaronix) was introduced into the space between the sandwiched cells. The current–voltage characteristics of the cells were measured under simulated AM 1.5 illumination provided by a solar simulator (300W Xe with optical filter, Solarlight) applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2420 digital source meter.

Intensity modulated photovoltage and photocurrent spectroscopy (IMVS and IMPS) measurements were carried out using an IM5d FRA (Zahner electric, Germany) with modulated light (10% modulation depth) from a high power green LED ( $\lambda=530 \text{ nm}$ ). The modulation frequency was adjusted between 0.1 Hz to 1000 Hz and the photocurrent or photovoltage of the cell was measured. The light intensity incident on the cell was measured using a calibrated Si photodiode. The time constants were obtained from complex real and imaginary photocurrent plots according to Ref. 17 and 18.

Table S1 Extracted photovoltaic characteristics for DSSCs fabricated using TiO<sub>2</sub> nanotube layers with and without Nb doping and treated at two different annealing conditions (450°C and 650°C). The doped layers contain different amounts of Nb.

	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	$FF$	$\eta$ (%)
<b>0.02 Nb-TiO<sub>2</sub>-450</b>	5.45	0.69	0.47	1.77
<b>0.05 Nb-TiO<sub>2</sub>-450</b>	5.66	0.70	0.52	2.06
<b>0.1 Nb-TiO<sub>2</sub>-650</b>	6.26	0.67	0.55	2.29
<b>TiO<sub>2</sub>-650</b>	0.56	0.63	0.31	0.11
<b>0.1 Nb-TiO<sub>2</sub>-450</b>	9.70	0.63	0.52	3.21
<b>TiO<sub>2</sub>-450</b>	7.07	0.63	0.52	2.40
<b>0.2 Nb-TiO<sub>2</sub>-450</b>	5.42	0.67	0.55	1.99
<b>0.5 Nb-TiO<sub>2</sub>-450</b>	7.74	0.64	0.45	2.22
<b>1.0 Nb-TiO<sub>2</sub>-450</b>	5.56	0.58	0.35	1.13

Figure S1

(a) Survey XPS spectrum obtained from the surface of 1.0 wt% Nb-doped TiO<sub>2</sub> NT film anodized in ethylene glycol electrolyte containing 0.1M NH<sub>4</sub>F and 1M H<sub>2</sub>O. XPS spectra of (b) for the Ti2p peak, (c) the Nb3d peaks and (d) O 1s peak from spectrum in (a) 1.0 wt% Nb-doped TiO<sub>2</sub> NT sample was measured because of detected limitation of XPS. A quantitative evaluation yields 1.4 wt% (0.47 wt%) Nb.

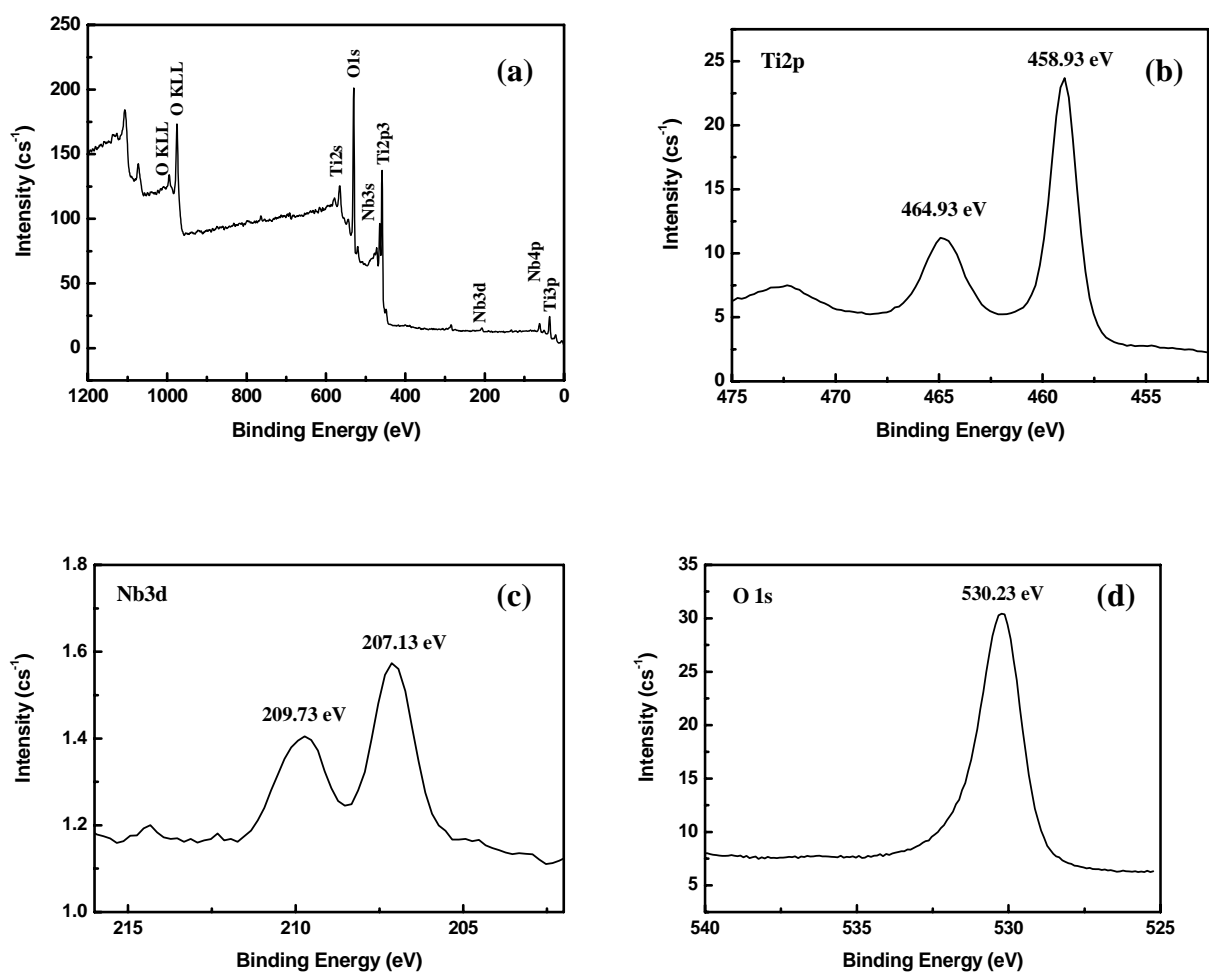


Figure S2

SEM images of Nb-doped TiO<sub>2</sub> NTs with different doping level (0.02, 0.05, 0.2, 0.5 and 1.0 wt%).

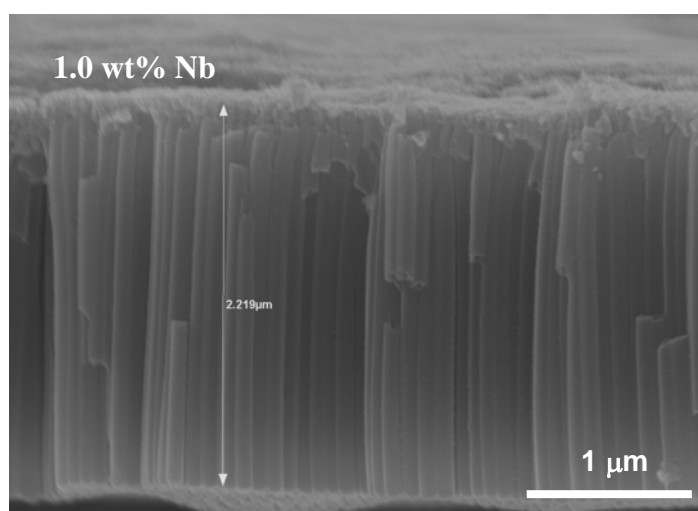
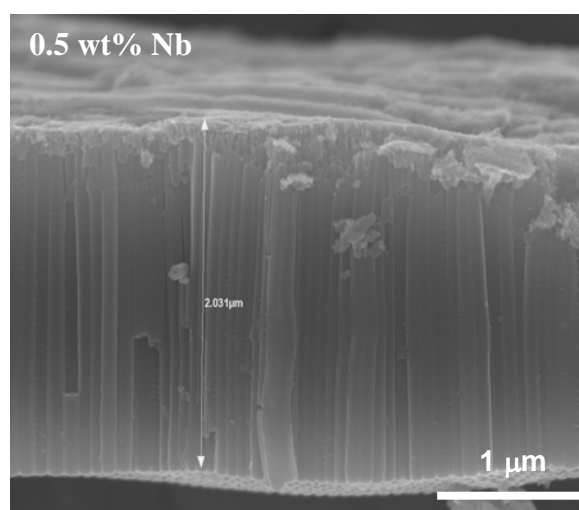
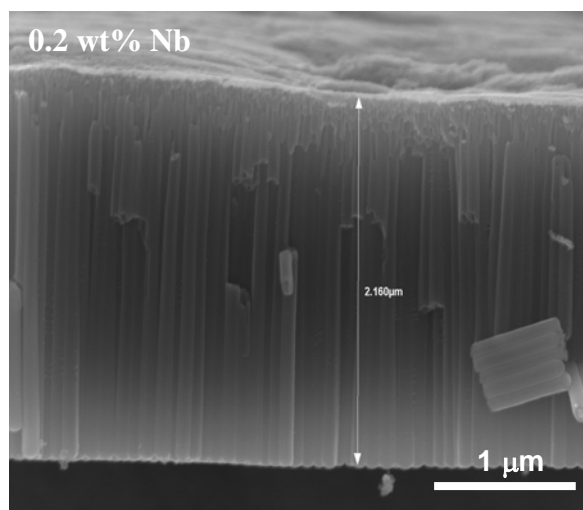
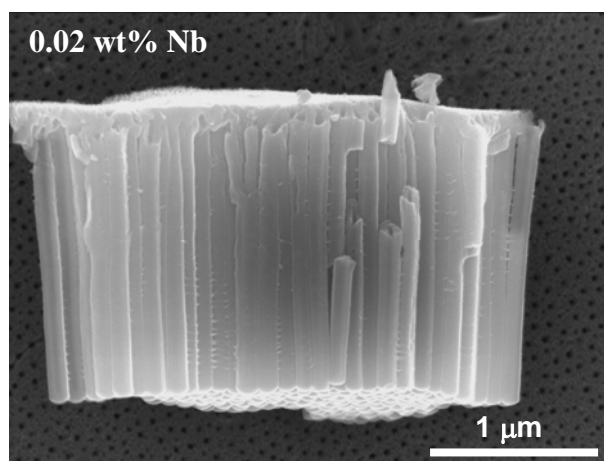
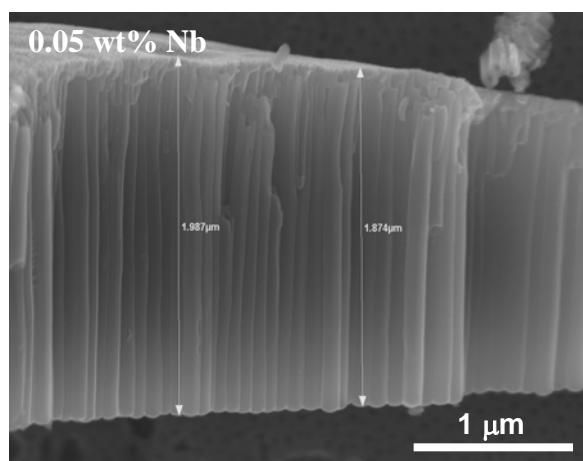
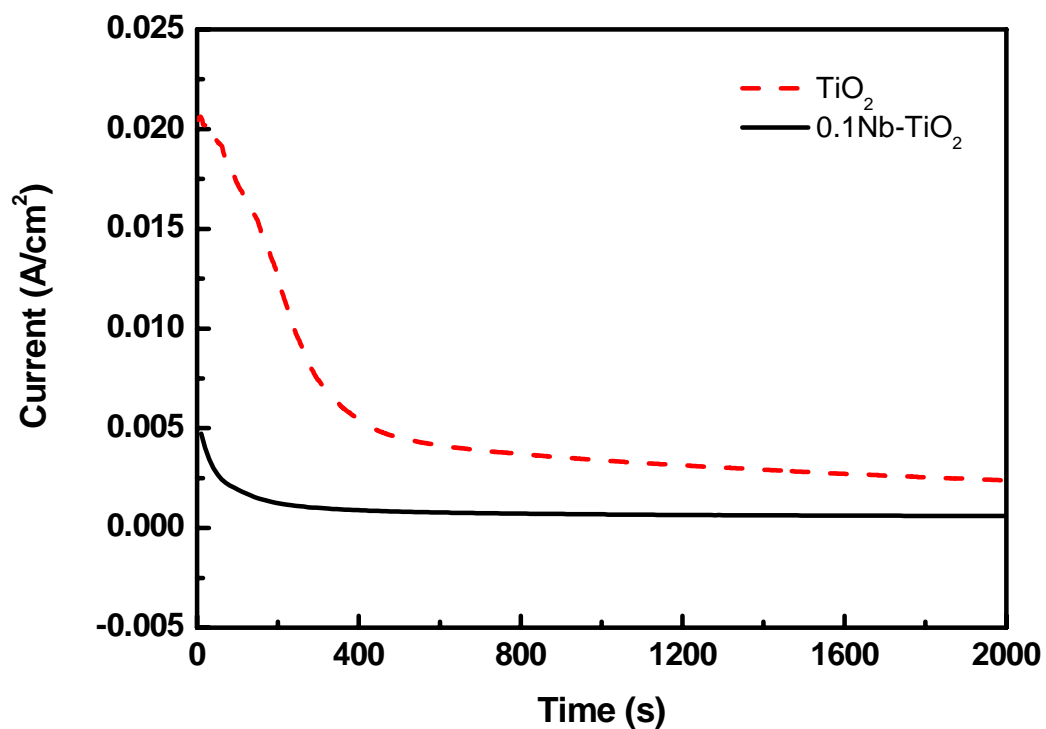


Figure S3

Current–time transients at 50 V during anodization of 0.1Nb-TiO<sub>2</sub> and pure TiO<sub>2</sub> in ethylene glycol electrolyte containing 0.1 M NH<sub>4</sub>F and 1 M H<sub>2</sub>O.



Clearly a strongly reduced current density is obtained for the Nb doped samples – this explained the lower growth rate of these nanotubes under potentiostatic conditions.