Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Electronic Supplementary Information for:

Electrosynthesis of gradient TiO_2 nanotubes and rapid screening using Scanning PhotoElectroChemical Microscopy

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I. Experimental details:

TiO_2 nanotubes synthesis:

Preparation of Ti electrodes:

Before the nanotubes growth, Ti foil (15x20mm; 50µm; MaTeck GmbH; 99.6%) were cleaned by ultrasonication during 15 minutes in successive bath of acetone, ethanol and water (milliQ) and then dried under nitrogen flux. In order to increase the final nanotubes order and their adhesion to the Ti substrate, a preanodization step was performed: the Ti foils were immersed in an electrolyte composed of ethylene glycol (Sigma-Aldrich; 99.8%), with $0.3\%_W$ NH_4F (Sigma-Aldrich; 98%) and $1\%_V$ ultrapure water. After an OCV of 3 minutes, the potential was increased to 45 V with a ramp of $1V.s^{-1}$ (with a BioLogic SP300 potentiostat) between the Ti foil and the counter electrode (Pt foil, MaTeck GmbH) separated by a distance of 3 cm. This potential was kept during 1.5 hours, after rinsing the electrode with milliQ water and drying it under nitrogen flux, the obtained nanotubes were peeled off using scotch tape.

Synthesis of TiO_2-NTs electrode with a constant NTs length:

The NTs growth is achieved by second anodization on the treated Ti foil, with the same conditions as the preanodization step, but with a controlled temperature of 25°C. The synthesis is stopped when the charge density, *Q*, passed during the anodization reach a certain value, which is proportional to the amount of TiO_2 formed.

Synthesis of TiO_2-NTs electrode with a gradient of NTs length along the h axis (VTLE):

The growth of nanotubes with a gradient of length over a single electrode was performed in the same conditions as the anodization, excepted by the addition of a peristaltic pump (Watson-Marlow 323), which slowly removes the electrolyte out of the cell during the synthesis time (typical electrolyte flow: 1 $mL.min^{-1}$). When the Ti electrode is not anymore in contact with the electrolyte, the anodization is stopped.

After the synthesis, both types of sample are washed several times with milliQ water and gently dried under nitrogen flux. Then the samples are annealed at 500°C during 4h (Annealsys AS1; heating and cooling ramp of 5°$C.min^{-1}$) in air atmosphere (air flow 100 $cm^3.min^{-1}$).

Characterization methods:

Photoelectrochemical measurements:

Cyclic voltammetry (CV) and External Quantum Efficiency measurements (EQE) were performed on several electrodes with different NTs length. The electrode is placed in a 3 electrodes cell composed of a platinum counter electrode and a Mercury Sulfate Electrode (MSE; +0.64 V vs. NHE) as reference electrode. The cell is filled with a basic electrolyte composed of 0.01M NaOH (AcrosOrganics ; $50\%_w$) and 0.1M Na_2SO_4 (VWR chemicals; 99.2%), which is deoxygenated by a constant N_2 flux bubbling in the solution (100 $cm^3.min^{-1}$).

For CV, the TiO_2-NTs sample is illumined with a Xe arc lamp (300 W; Newport) passing through an AM1.5G filter (Newport), the light intensity arriving on the cell surface is set to 100 $mW.cm^{-2}$. Cyclic voltammograms are performed with a BioLogic SP300 potentiostat at a scan rate of 10 $mV.s^{-1}$.

EQE are performed with the same cell as for CV. The TiO_2-NTs are then irradiated with selected wavelength from a Xe arc lamp (150 W Newport) passing through a Newport Oriel 1/8m Cornerstone monochromator. The photocurrent density J_{ph} (λ) is measured with the potentiostat and the light power density reaching the sample is controlled by a powermeter (918D Newport) placed behind a beam sampler. The EQE is measured with a 8 nm step from 800 nm to 280 nm with a constant applied potential of -0.3 V vs. MSE applied to the sample.

Scanning PhotoElectroChemical Microscope (SPECM):

The VTLE electrode was fixed horizontally on a glass slide and then a cell made in PDMS was built around the sample. The SPECM experiment was run in a three electrodes configuration. A platinum mesh was used as the counter electrode and an Ag/AgCl (NaCl 3 M) as the reference electrode. The VTLE was the working electrode and its potential was set at 0.6 V vs Ag/AgCl. The sample was irradiated through an optical fiber with a numerical aperture of 0.22 and a core diameter of 200 µm. The light source was a mercury-xenon lamp (LC8 from

Hamamatsu) providing a spectrum centered at 365 nm. The optical fiber was moved along xy axes at a scan rate of 400 µm.s^{-1}, with steps of 40 µm each 0.1 s. The distance, z, between the tip and the surface was constant (around 20 µm) during the measurement. When the UV source was turned on, the optical fiber illuminated locally the TiO_2 nanotubes, and the current was simultaneously recorded as a function of the optical fiber position. This current corresponds to the photoelectrochemical oxidation of water, which happens only below the light spot. With this system, a 2D image of TiO_2 nanotube gradient was obtained.

Scanning electron microscopy:

The samples were observed with a ZEISS Gemini SEM FEG, with a working distance of 3 mm, an extraction potential of 3.0 kV, and observed at a take of angle of 45°. This SEM allows tracking accurately the position along the axe *h* of the sample. The nanotubes dimensions were determined with ImageJ software using a statistical analysis realized on at least 10 nanotubes per measurement.

II. Images of VTLE sample:

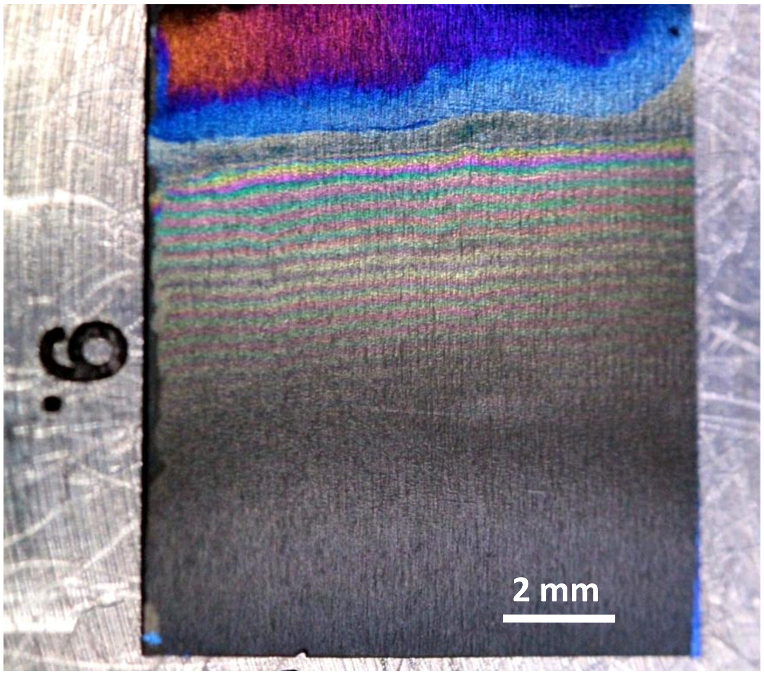

Figure S1: *Optical image of TiO_2-NTs VTLE sample.*

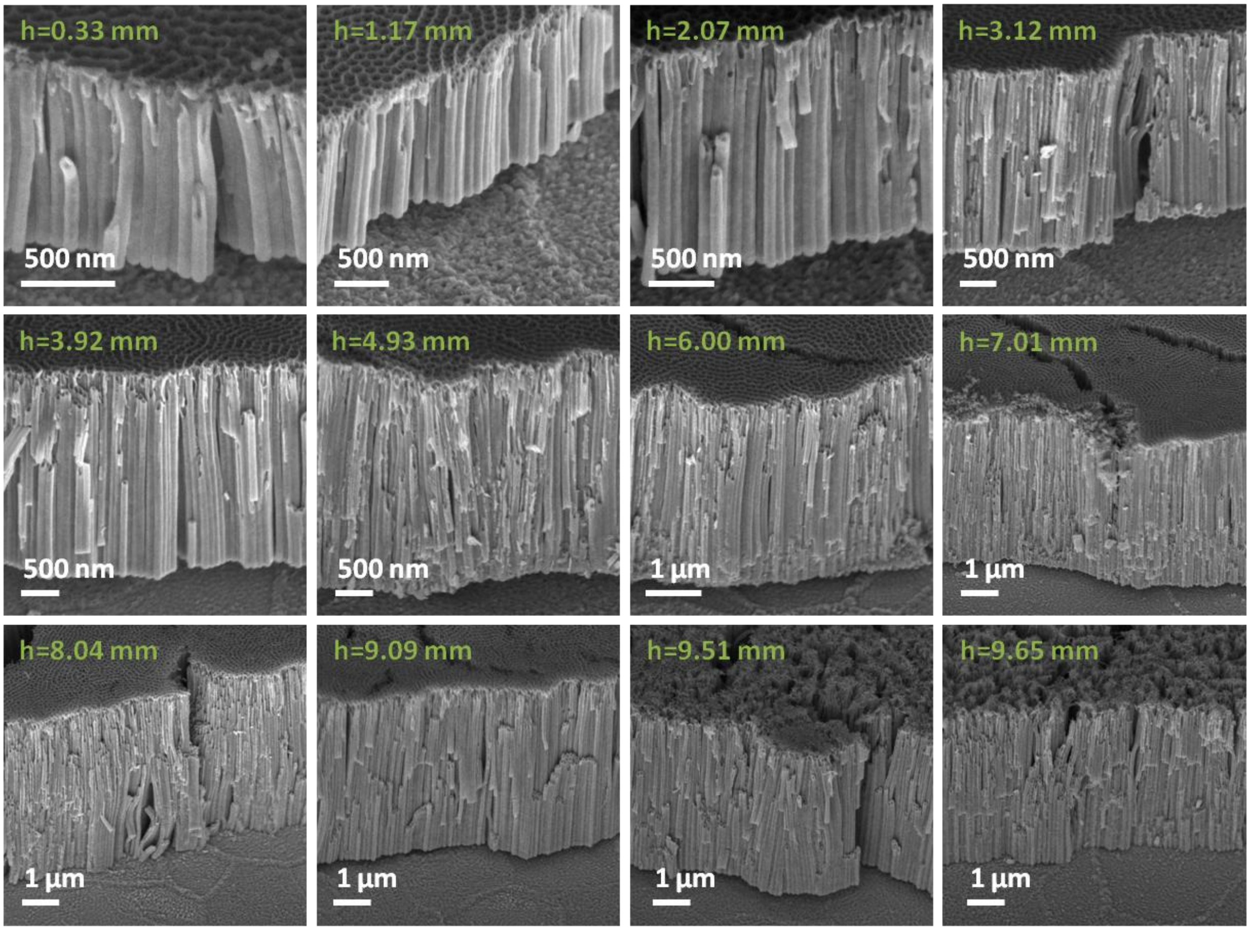

Figure S2: *whole set of SEM images of the TiO_2-NTs VTLE observed at different h positions with a tilt angle of 45°.*

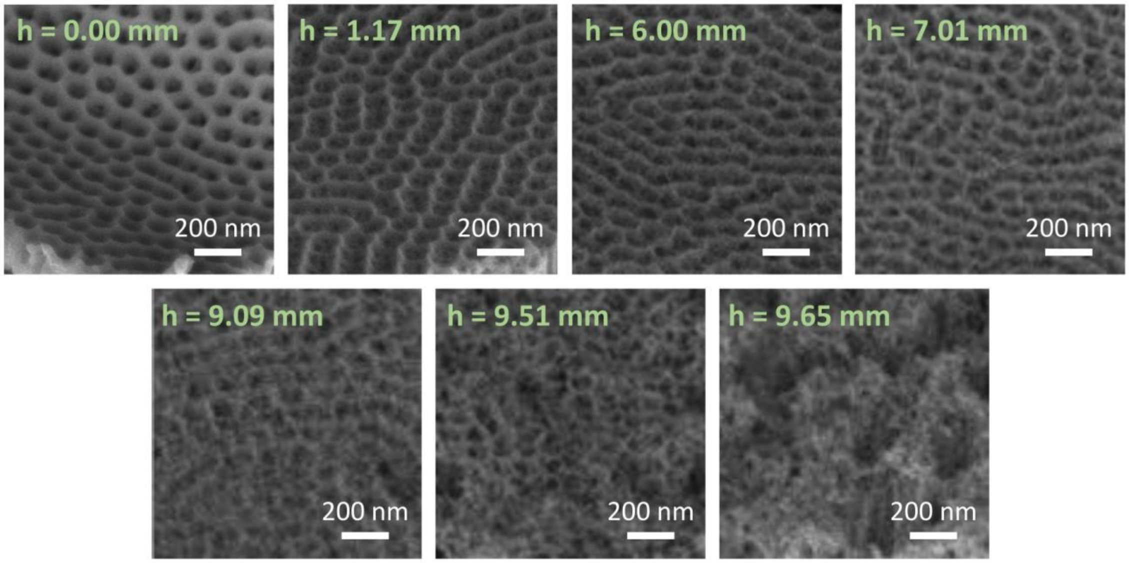

Figure S3: *SEM images of the top of TiO_2-NTs VTLE observed at different h positions with a tilt angle of 45°.*

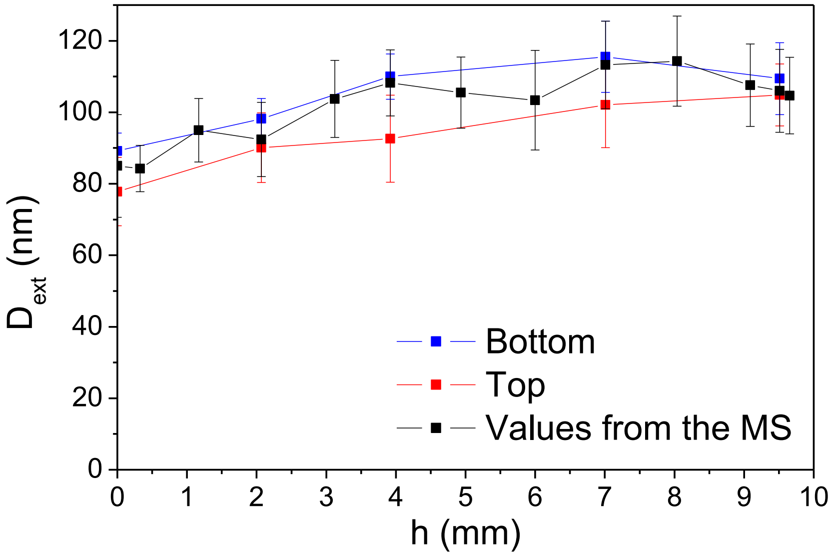

Figure S4: *External diameter of the TiO_2-NTs measured from SEM images at different h positions. The values from the MS as well as the values measured at the top and bottom of the NTs are reported here.*

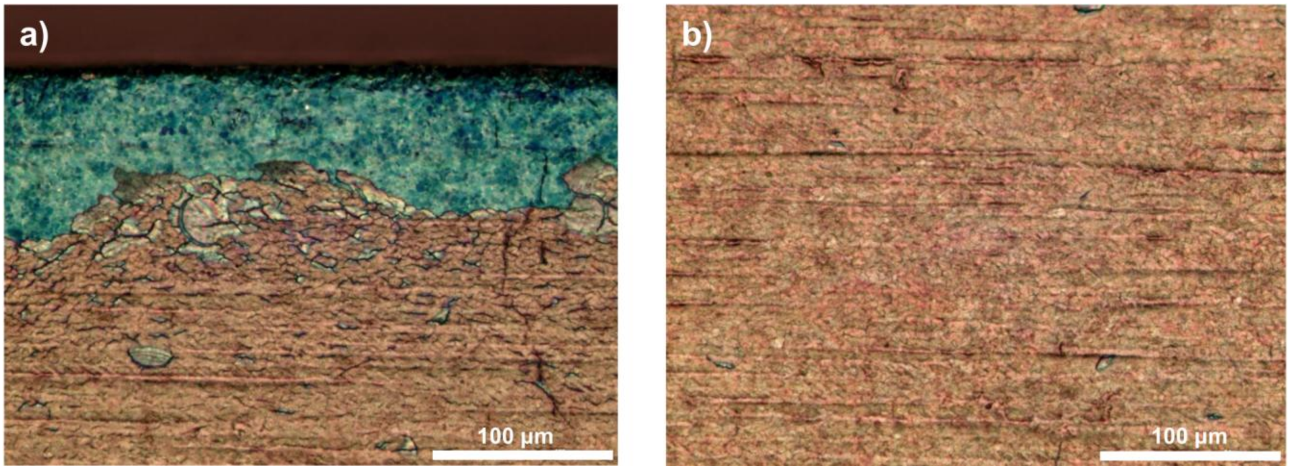

Figure S5: *optical images of the VLTE sample, a) on the side and b) in the middle of the sample. The visible horizontal lines are due to the rolling process of the Ti foils.*

III. Photo-electrochemical measurement of reference TiO_2-NTs sample:

Several electrodes with a constant NTs length were synthesized by controlling the charges density transferred during the anodization (3, 4, 5 and 7 $C.cm^{-2}$). Their lengths are 2390, 2730, 4020 and 5000 nm respectively. Cyclic voltammetry was performed on these electrodes (example in Figure S5) in the dark and under AM1.5 illumination (100 $mW.cm^{-2}$). The difference between the two curves give the photocurrent, J_{ph} represented in figure S6.a) for the 4 samples. The inset of figure S6.a) represents the photocurrent evolution with the length of the nanotubes. From these values of cyclic voltametry, the yield can be determined according to the following equation:

$$\eta = \frac{J_{ph} \times (1.23 - \Delta E)}{P_{AM1.5}}$$

Where ΔE is the difference between the applied potential and the open circuit current (OCV) under irradiation, and $P_{AM1.5}$ is the light power density reaching the cell.

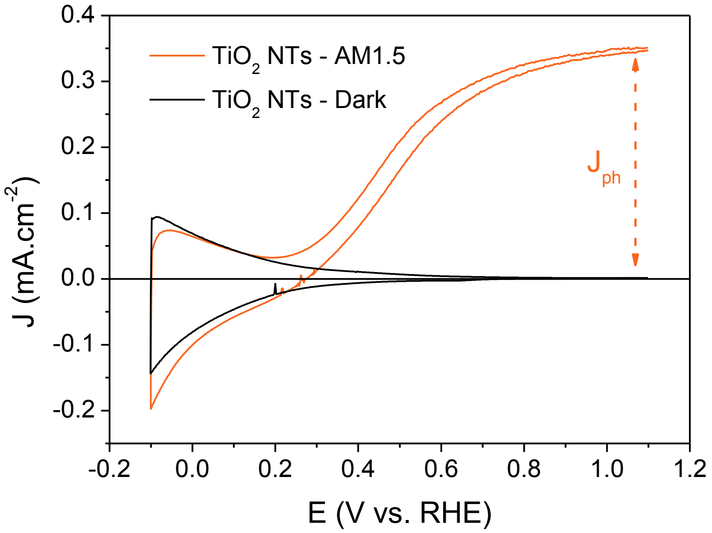

***Figure S6:** cyclic voltammogram of a 5 $C.cm^{-2}$ electrode under AM1.5 illumination.*

The NTs length of these electrodes was determined with SEM and the average length of the different electrodes is reported in figure S6.b). The TiO_2-NTs length is proportional to the charge applied during the synthesis. In the same figure S6.b), the yield as a function of the charge was also reported. The highest yield was measured for the sample with an applied charge density of 5 $C.cm^{-2}$, corresponding to nanotubes with a size of 4000 nm. The EQE of this last electrode is reported in figure S7 with an indication of the wavelength used for SPECM measurements.

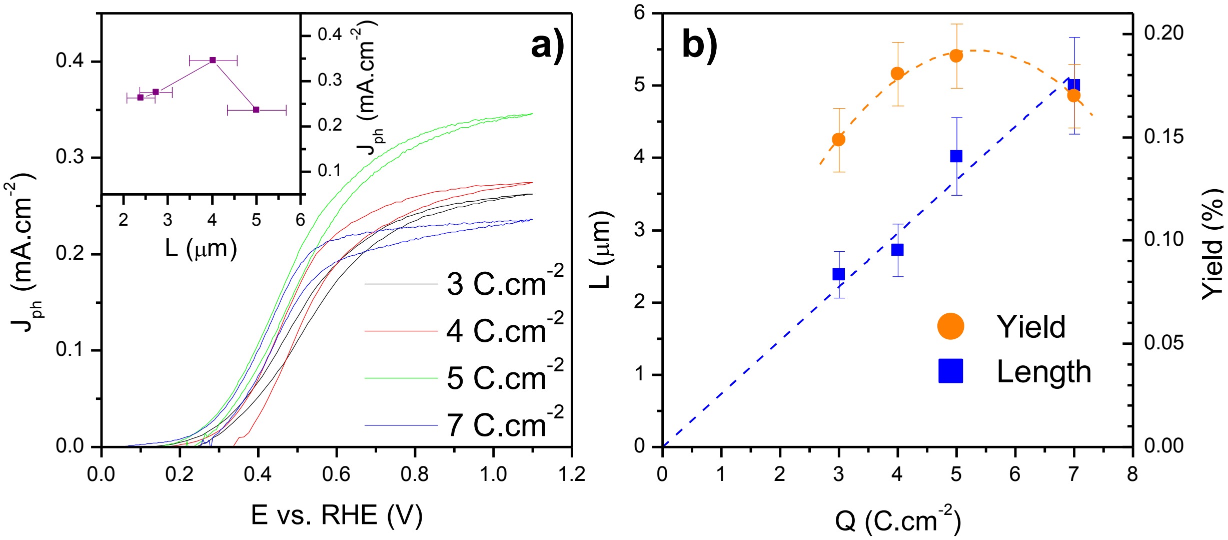

Figure S7: *a) J_{ph} obtained by cyclic voltametry for different NTs lengths and inset is the evolution of the photocurrent with the length. b) Calculated yield in function of the charge density applied during the synthesis.*

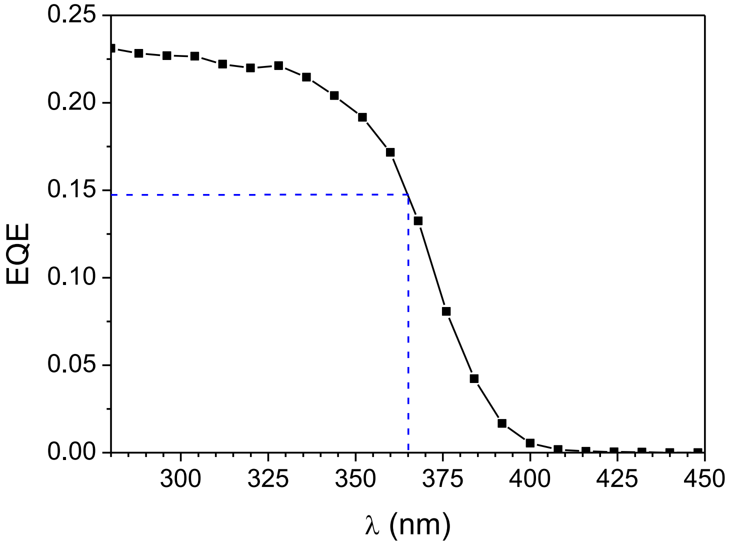

Figure S8: *EQE of TiO_2-NTs of a 5 C.cm^{-2} electrode and indication of the wavelength used for SPECM measurements.*

IV. Other characterizations:

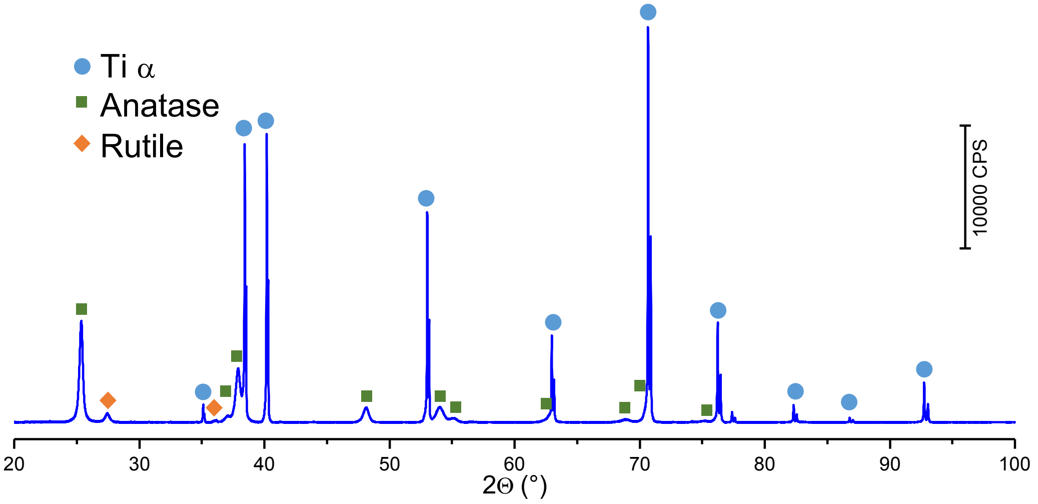

Figure S9: *XRD pattern of a VLTE electrode*

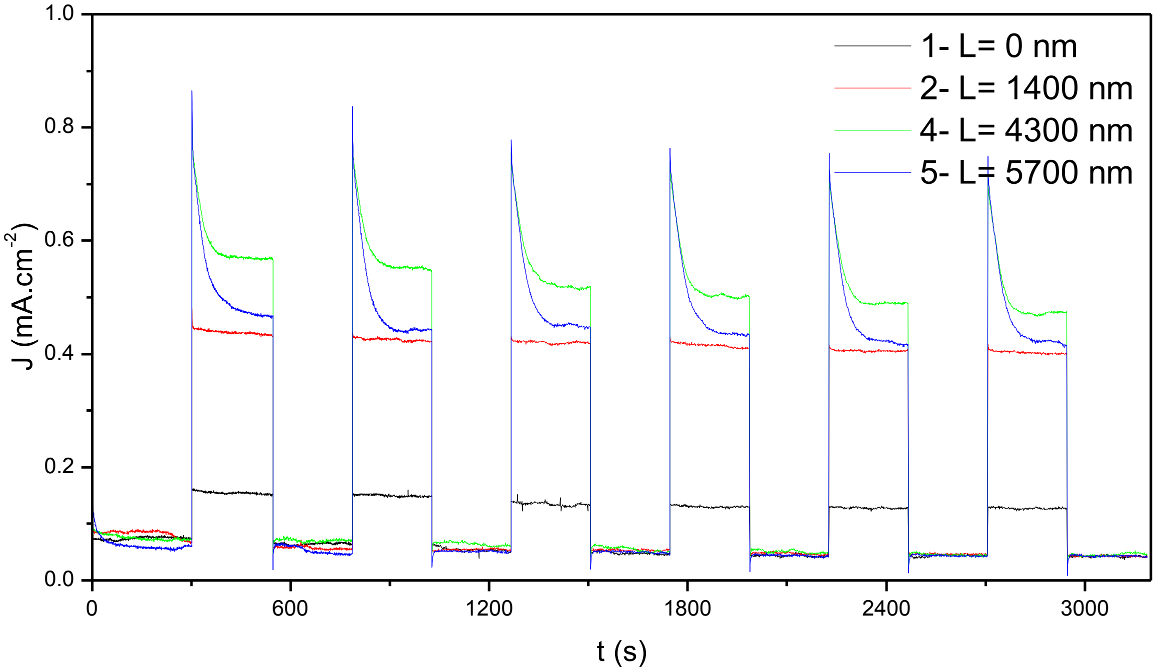

Figure S10: *potentiostatic measurements (E$_{applied}$ = 1V vs RHE) of different positions of the VLTE sample under chopped light (365 nm; 8.5 mW.cm^{-2})*

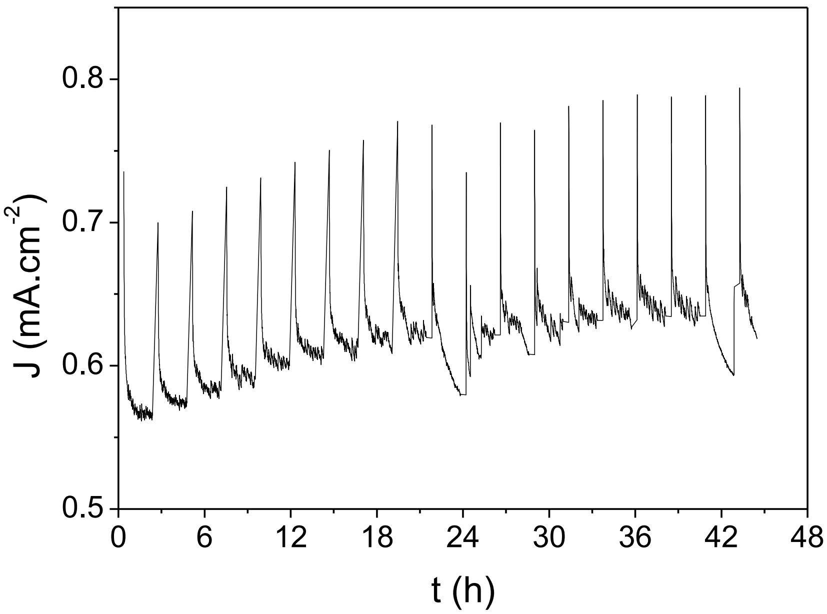

Figure S11: *Stability studies of a VTLE sample for 48 h. The sample was irradiated with a 365nm LED in a three electrodes configuration applying a potential of 1.0 V vs RHE. The spikes observed regularly are due to cyclic voltametry experiment done every two hours (high polarization between CV and potentiostatic periods).*

V. Data for the VTLE electrode with defects:

Figure S6 represents the NTs length and diameter together with the synthesis data and the calculated charge density of the second electrode presented in the manuscript.

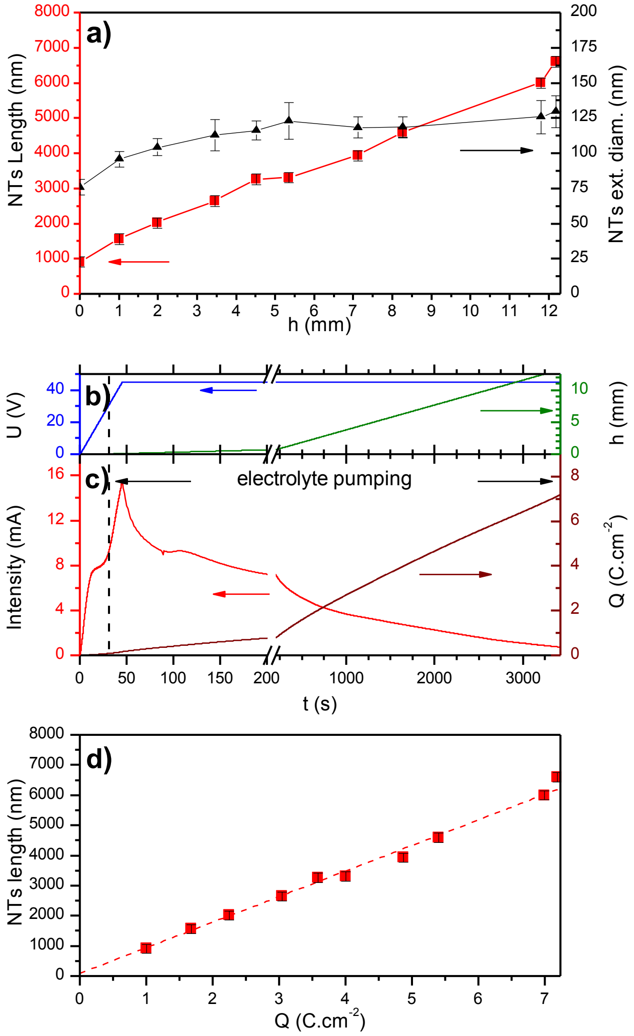

Figure S12: *a) Length and diameter of the nanotubes as a function of the position from the top of the electrode determined by SEM. b) Anodization parameters: applied voltage and height of electrolyte pumped out as a function of time. c) Anodization current and calculated charge density evolution during the VTLE synthesis. d) Measured* TiO_2*-NTs length as a function of the calculated charge density (Q) (correlation parameter estimated from linear regression: 850* $nm.C^{-1}.cm^{2}$*).*