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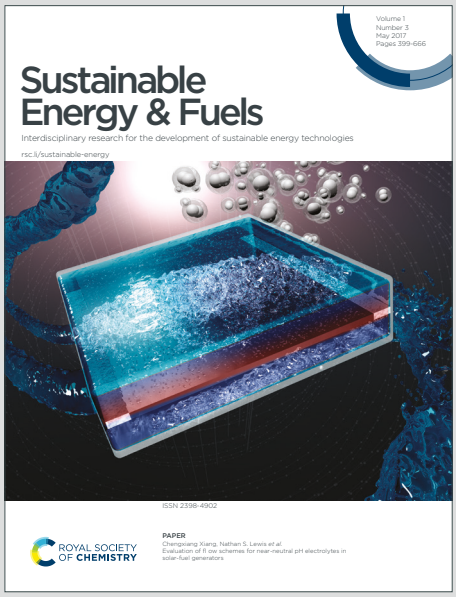

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Electrosynthesis of gradient TiO_2 nanotubes and rapid screening using Scanning PhotoElectroChemical Microscopy

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Herein, we report a new approach that allows a fast investigation of the influence of the thickness of a TiO_2 photoelectrochemical film. For this we developed a simple anodization method that allows to grow, in one step, on a single titanium electrode, aligned TiO_2 nanotubes with length changing gradualy between 0 to 10 µm. We were able to tune the length of the tubes by controling the immersion time within the electrolyte during the synthesis. The change of the nanotube length over the entire surface of the electrode requires local probes to measure their properties. Therefore, in order to determine the optimal length of the nanotubes for photoelectrochemical application, the response of these electrodes was locally analysed using Scanning PhotoElectroChemical Microscopy.

Introduction

Since several years there is a strong interest in light energy conversion motivated by the huge potential of renewable and clean energy provided by the sun combined to the urge related to climate change and to the diminution of fossil fuel resources easily accessible at low cost.[1] New concepts are investigated with the objectives to decrease the price and to improve the conversion efficiency such as dye sensitized solar cells (DSSC) or more recently cells based on perovskite absorber are promising PV systems.[2] Alternatively Photo-electrochemical cells (PEC) would pave the way to the direct production of solar fuel from sunligth.[3,4] Several of these new concepts relies on thick porous semiconducting films that are responsible of the charge carrier transport (for DSSC) and also for light absorption (PEC).[5,6] It is necessary to find the optimal thickness of these films in order to manage the light and charge carrier transportation in the cell.[7–9] This is particularly true for the case of tandem PEC cell in which two semi conductors absorbing in two different spectral domains would be associated.[10] The large band gap semiconductor would be in that case in front irradiation configuration and a compromise should be found on the film thickness. Indeed, if a thick layer of photoactive material maximizes the light absorption (mainly at the top of the film), it can result in a reduced photo-generated charge carrier collection at the back contact due to their probability of recombination on long distance.

In this context, the development of rapid screening methods of the film performances as a function of their thickness should be developed. Achieving such measurements requires two conditions: The first requirement is to obtain electrodes with a variable and well controlled thickness of photoactive material. The change of the thickness must not have any impact on the morphology or other properties of the material such as its conductivity or its composition. The second requirement is to have a system that can achieve local PEC analysis with the highest resolution possible which is mainly related to the irradiation area.

So far the large majority of rapid screening experiments were used to determine the optimal composition of ternary oxides.[11,12] For instance, an ambitious distributed combinatorial outreach program was conducted a few years ago using inkjet printing of semi-conductor with variable composition on conductive glass substrates.[13] The most relevant example we found concerning rapid PEC screening to study the influence of geometrical parameters on a single electrode, was done by Loget et al.[14] They used a bipolar anodization method to grow titanium dioxide nanotubes (TiO_2-NTs) with variable length on a single electrode. The bipolar anodization method was also employed to synthesize gradient of TiO_2-NTs for photo-catalytic and biomedical applications.[15,16] Nevertheless, considering the formation mechanism of anodic TiO_2-NTs,[17] the potential variation along the Ti foil in bipolar anodization induces a change of the NTs length but it also changes the diameter and the wall thickness of the tubes. Consequently, the apparent density of TiO_2 in the film will change and the mean free path of light will not be homogeneous for the whole electrode. Furthermore, during the bipolar synthesis, it is not possible to determine the charge transferred at each position of the electrode. The knowledge of this value is important since it can be directly related to the

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Electronic Supplementary Information (ESI) available: Detailed experimental parameters; Optical image and full set of SEM images for the VLTE sample; CV and EQE of reference TiO_2-NTs Electrode; XRD and stabillity tests of VLTE sample; anodization curve of the second VLTE sample. See DOI: 10.1039/x0xx00000x

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quantity of TiO_2 electrochemically formed during the anodization of the titanium foil. Furthermore, in all the studies mentioned above, the light source used had a spot diameter larger than 1 mm, which limits the accuracy on the local photocurrent determination.

Scanning PhotoElectroChemical Microscopy (SPECM) is a scanning probe technique that uses an optical fiber (or an optoelectrode) as a probe to analyze a surface locally.[18–20] Unlike conventional photoelectrochemical measurements, which give a global response of the surface, in SPECM a local response is obtained. In this configuration the spatial resolution is determined by the illuminated area. The use of an optical fiber allows the photoelectrochemical reaction to be triggered only where the surface is illuminated.[21–23] The small aperture of the optical fiber and the short distance between the fiber and the sample result in a small spot size of around 200 µm. Therefore, SPECM is a technique of choice to study an inhomogeneous surface or to screen different materials present on the same substrate. As an example, it was used to determine the optimal Zn doping of WO_3 on material spots deposited on a single electrode[24] and also to show that addition of Ag improves the behaviour of Fe_2O_3 by screening micrometer spots with different composition.[25] In our case, we were able, with the SPECM, to make a rapid screening, with a high resolution, of the nanotubes properties.

In the present work, we developed a new method to synthesize anodic TiO_2-NTs with a changing length on a single electrode (here after named VLTE for Variable Length TiO_2-NTs Electrode). This simple method allows making an electrode fully covered with these NTs which have an increasing length in one direction of the film. These model electrodes with variable nanotube length were then tested with SPECM in order to determine to optimal TiO_2-NTs film thickness for their use as photoanode for water splitting.

Variable length TiO_2-NTs electrode synthesis

To achieve the growth of TiO_2-NTs with a gradual length on a single electrode, we developed a simple method based on the control of the exposure time of the titanium to the electrolyte. Such approach was attempted earlier but in a configuration in which both the electrolyte exposure time and the applied potential were changed.[26] For this reason and also due to the use of aqueous based electrolyte, mainly the diameter of the NTs was changed and the length only increased from 300 to 500 nm.

In our case for growing NTs with different lengths, a titanium foil and the platinum electrode are placed vertically in a Teflon cell as schematically represented in **figure 1**. At the beginning of the synthesis, both electrodes are immerged in an ethylene glycol based electrolyte which is then slowly removed from the cell by a peristaltic pump. As the level of electrolyte goes down progressively, an increasing part of the titanium is not anymore in contact with the electrolyte and the nanotube growth is inhibited in that area. After the synthesis, the electrode is then carefully rinsed with deionized water and dry under nitrogen flux and annealed at 500°C under air for 4h.

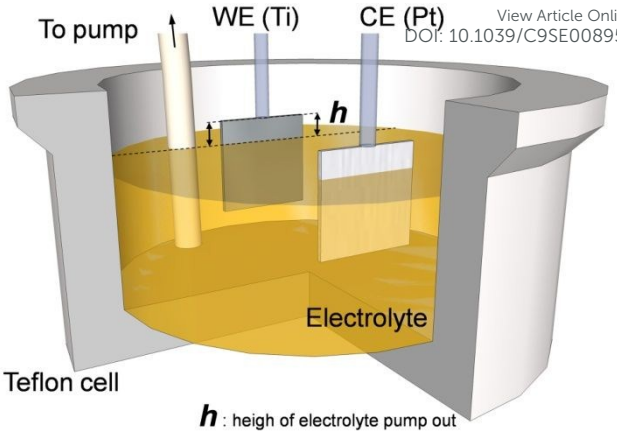

Figure 1 : Schematic principle of VLTE synthesis by electrolyte pumping.

(detailed synthesis conditions are given in Electronic Supplementary Information ESI)

After the experiment, the electrode exhibits horizontal iridescences which are a first indication of the change of the thickness of the TiO_2-NTs film (**ESI figure S1**). These lines arise from light interference in the porous film and as the thickness changes, different wavelength are successively reflected.[27]

The whole electrode was then introduced in a SEM and observed all along the z axis. In the **figure 2** are presented some SEM images of the TiO_2-NTs films at different height of the electrode (the whole set of image can be seen in **ESI figure S2**). They clearly show the growth of the nanotubes from the initial state with small nanotubes of a few hundred nm at the top of the electrode to NTs with a length of several micrometers at the bottom. It should be noticed that for the shortest nanotubes, an initiation layer resulting from a pre-anodization step is still present. This first anodization and the removal of the primary nanotube layer is necessary to ensure a better adhesion of the nanotubes to the film and without this initial step, delaminating of the longer NTs is observed on the VLTE.[28] The length of the NTs at different positions on the electrode was measured and plotted in **figure 3.a**. It can be seen that this length increase from 780 to 5950 nm ± 200 nm and then is slightly reduced at the bottom of the nanotubes. The initial length is not zero since the electrolyte pumping starts 100 s after the beginning of the anodization. This duration is enougth to form small NTs at the top of the electrode. The decrease of the length observed at the bottom of the electrode can be explained by the formation mechanism of the nanotubes which can be schematically described according to the following equations:

$$Ti + 2H_2O \rightarrow TiO_2 + 4e^- + 4H^+ \quad (1)$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O \quad (2)$$

TiO_2 is formed electrochemically at the Ti surface while the nanotubular structure is achieved by its partial dissolution by the fluoride present in the electrolyte. The top of the nanotubes is then formed at the beginning of the anodization.

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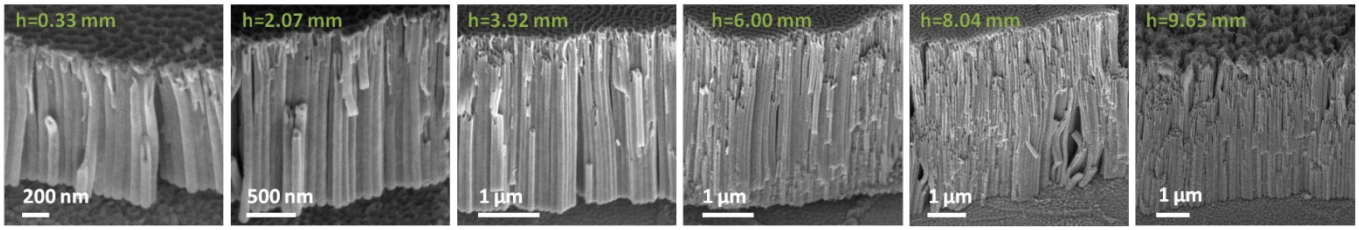

Figure 2 : SEM images of TiO_2-NTs observed at different height of the nanotubes (observed with a tilt angle of 45°).

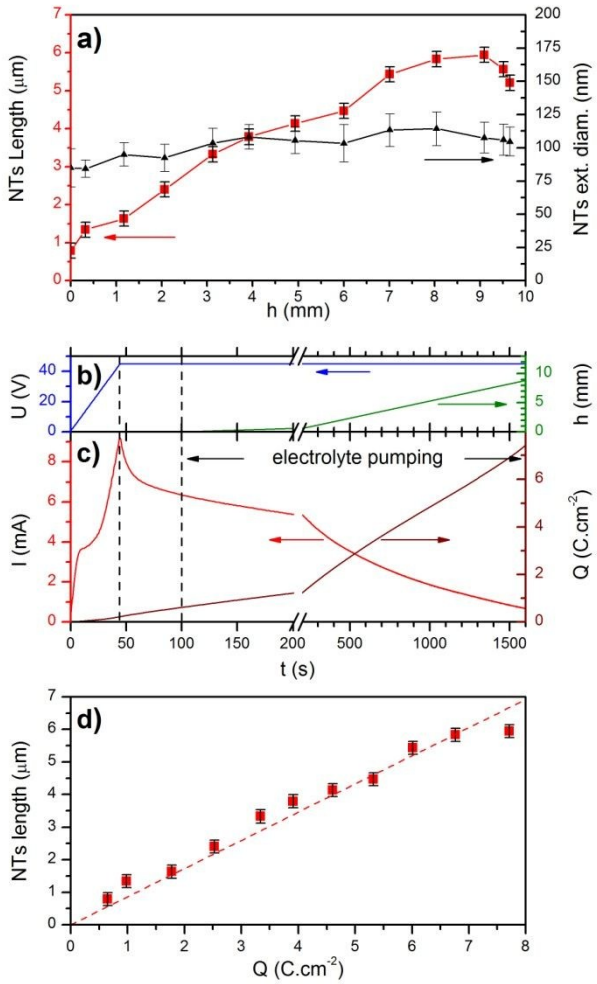

Figure 3: a) Length and diameter of the nanotubes as a function of the position from the top of the electrode determined by SEM. b) Anodization parameters: applied voltage and height of electrolyte pumped out as a function of time. c) Anodization current and calculated charge density evolution during the VLTE synthesis. d) Measured TiO_2-NTs length as a function of the calculated charge density (Q) (correlation parameter estimated from linear regression: 865 $nm.C^{-1}.cm^2$).

A too long exposure to the electrolyte results in the formation of a so-called "nanograss" layer at the top of the film.[17] This phenomenon results directly from a thinning of the nanotubes wall according to equation 2 and eventually the total dissolution and collapse of the nanotube top, consequently the length does not increase continuously. This thinning of the NTs wall at the top can be observed in ESI **figure S3**: the SEM images of the top of the NTs film at different heigh (or anodization time) clearly show the transition from the initiation layer to the nanograss. In figure 3.a is also represented the values of NTs external diameter measured at their half height (diameters at the top and bottom of the nanotubes are presented in ESI **figure S4**). As observed in these synthesis conditions, the diameter has an average value of 102±10 nm and does not change significantly depending on the position of the NTs on the electrode.

The anodization data as a function of time are represented in figure 3.b and c. At the beginning, the applied voltage *(U)* increases from 0 to 45 V this is accompanied by an increase of the current *(I)* that reaches a maximum and slowly decrease when the potential stabilized to 45 V. It should be noticed that the current tends to 0 in our case since less surface is exposed, while for classical anodization the current reaches a plateau when an equilibrium between oxide formation and dissolution is reached (eq. 1&2). According to equation 1 the quantity of TiO_2 formed during the anodization should be proportional to the charge transferred. In order to correlate this value with the length of the TiO_2 nanotubes, we used the VLTE anodization data (**figure 3.b**) to determine the charge density transferred at each position of the electrode: First, the height of electrolyte pumped out as a function of time, *h(t)*, can be calculated from the flow imposed by the pump (f_p) according to: (pump starts at t=100 s; for t<100s, h(t)=0)

$$h(t) = \frac{f_p(t-100)}{K} \qquad (3)$$

The constant (K) depends on the geometry of the container (its horizontal section) and correspond to the volume needed to change the height of 1 mm. In our case, the cell is a cylinder with a diametrer of 7 cm and K=3.848 $mL.mm^{-1}$. The value of h(t), represented in figure 3.b (green curve) can be used to determine the surface of the electrode in contact with the electrolyte at any time. Knowing the anodization current from the synthesis data *I(t)* the charge used for the nanotube synthesis as a function of time and consequently each position of the electrode, can be calculated by the following integral:

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$$Q(t) = \int_0^t \frac{I(t)}{W(L-h(t))} dt \quad (4)$$

with W and L the width and the length of the electrode. Then, the evolution between the nanotube length and the charge density can be represented (**figure 3.c**). Excluding the area were the nanograss is formed (*i.e.* h>9.1 mm or Q>7.7 C.cm^{-2}), this evolution is linear with a growing ratio of 865 nm.C^{-1}.cm^2.

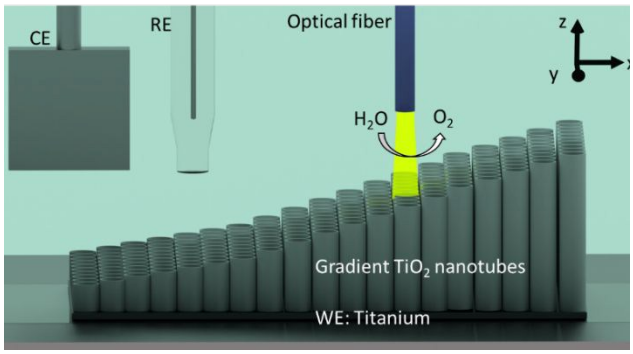

Figure 4: Scheme of the setup with the optical fiber scanning the gradient of TiO_2-NTs during the SPECM experiment.

This confirms, on a single electrode, that accordingly with equation 1, the NTs length is proportional to the quantity of TiO_2 formed electrochemically. The length of the nanotubes in the VLTE can thus be estimated by knowing the total charge transferred at each position of the electrode for a given set of synthesis conditions.

SPECM mapping

The VLTE 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 a Ag/AgCl (NaCl 3 M) as the reference electrode. The VLTE was the working electrode and its potential was set at 0.6 V vs Ag/AgCl. The sample was irradiated trough 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 every 40 µm each 0.1 s, z, the distance between the tip and the surface was constant (20 µm) during the measurement. When the UV source was turned on, the optical fiber illuminated locally the TiO_2-NTs, and the current was simultaneously recorded as a function of the optical fiber position. This current corresponds to the local photoelectrochemical oxidation of water, which happens only below the light spot. With this system, a 2D image of TiO_2 nanotube gradient was obtained on an area of 10*2 mm^2, located in the middle of the electrode, first in the dark then under illumination with UV light (**figure 5.a**).

In the dark, the current has a residual value below 6.5 µA. Under UV light irradiation, an increase of the current clearly appears on the sample even for short nanotubes. This current

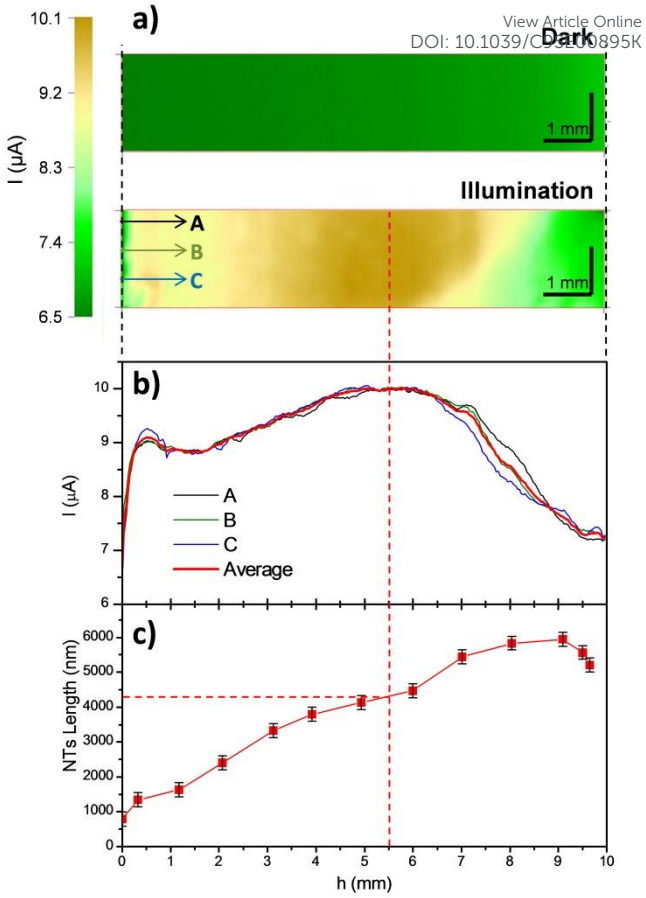

Figure 5: a) SPECM results in the dark and under illumination at λ=365 nm, b) Photocurrent profile at 3 positions and c) corresponding NTs length for the same VLTE.

increases until a maximum located approximately in the center of the electrode. Then, for the longer nanotubes, the photocurrent decreases. In figure 5.b are represented the photocurrent evolutions on three positions of the electrode and their average. The photocurrent appears for short nanotubes and reaches a local maximum at 0.5 mm from the top of the electrode. This local maximum, might be attributed to the partial contribution of the dense underlying TiO_2 layer located at the interface between the NTs and Ti substrate.[6] With longer nanotubes, the contribution of this dense layer is reduced since less light can reach it and mainly the NTs contribute to the photocurrent. After this local maximum, the photocurrent increases with the length of the NTs until a maximum of 10.1 µA at 5.5 mm from the top of the electrode; a position for which TiO_2-NTs have a length of 4.3±0.2 µm. The length corresponding to this maximal photocurrent is coherent with measurements performed for nanotubes of different lengths, synthesized by a classical method. As detailled in supplementary information (ESI **figure S6)**, TiO_2-NTs films with different lengths, were tested in a normal 3 electrodes PEC setup. The highest photocurrent and yield were measured for NTs with a length of approximately 4 µm. This value is also in agreement with the optimal thickness of NTs film reported, by other teams, to be between 4 and 6 µm in the case of photo-(electro)catalytic applications.[29,30] This maximum of efficiency

for this length is explained by a balance between two properties governing the photocurrent generation: (i) a good light absorption, resulting in high number of e^-/h^+ pairs generated which increases with the thickness and (ii) the efficienct transport of the electron to the back contact (the Ti foil). The latter is limited by the diffusion of electrons in TiO_2 and will then be reduced for thick nanotubes films.[6,9]

To determine the reliability of our approach combining variable length nanotubes synthesis and SPECM measurements, we compared our results with a reference TiO_2-NTs electrode. For this, nanotubes were grown in the same electrolyte and the charge transferred was limited to 5 $C.cm^{-2}$, resulting in a titanium foil covered with NTs having a length of 4050 ± 110 nm. The external quantum efficiency (EQE) of this electrode was then measured (data are in **figure S7**). EQE represents the ratio between the quantity of electron collected and the number of incident photon at a given wavelength according to:

$$EQE(\lambda) = \frac{h \cdot c}{e}\left(\frac{j_{ph}(\lambda)}{P(\lambda)\cdot\lambda}\right) \quad (5)$$

With $j_{ph}(\lambda)$ and $P(\lambda)$ are the measured photocurrent and the incident light power density at a given wavelength λ, respectively. For the reference electrode an EQE value of 0.15 was obtained at 365 nm which is the central wavelength of the UV light source used in SPECM setting. The same calculation can be done for the SPECM system knowing the irradiation power at the optical fiber exit (115±50 µW). For NTs having a length of 4000 nm the measured photocurrent triggered by this irradiation is 3.5 µA. By applying equation 5, an EQE of 0.15±0.06 is obtained. This value is in good agreement with the EQE obtained at 365 nm for the reference sample, confirming the good response of the VLTE electrode even with the localized spot of the SPECM system (estimated spot diameter 215±50 µm). The high uncertainty is explained by the difficulty to measure the power at the fiber output.

Defect identification with SPECM

In **figure 6** is presented the SPECM mapping of a part of a second VLTE electrode. For this electrode, the evolution of nanotubes length as a function of the anodization charge was calculated according the same protocol as earlier, and the growing factor of 850 $nm.C^{-1}.cm^2$ is consistent with the first sample. The calculation and data for this sample are presented in **figure S12**. On the photocurrent mapping, lines with lower photocurrent can be observed on the left of the image which corresponds to the bottom of the electrode. Their positions correspond to scratches that were done on one side of the electrode surface. As observed by SEM in **figure 6.b**, these scratches are 10 µm in width. Even if the optical fiber aperture is larger, the good spatial and electrochemical resolution of the SPECM, allows localizing these stripes. Similarly, a small round area can be observed in the center of the mapping image. Its position perfectly matches with a small punch that was done with an needle on the VLTE sample that can be observed optically in **image 6.c.**

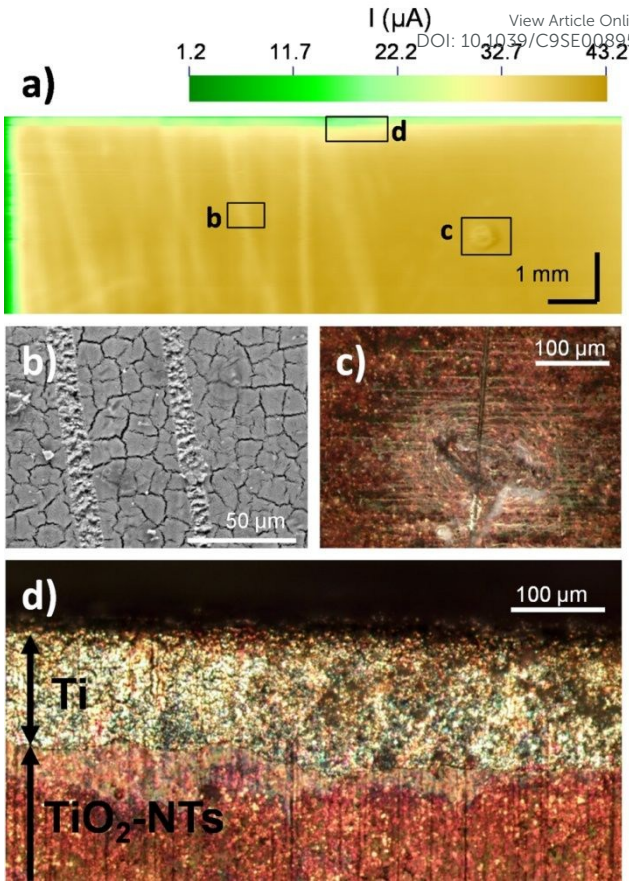

Figure 6: a) SPECM mapping of a second VLTE sample. b) SEM images of scratches made at the bottom of the nanotubes. c) and d), dark field optical images of a punching on the TiO_2-NTs electrode and of the side of the electrode.

The mapping of this VLTE surface was done on the side of the titanium foil and small strip with low photocurrent can be observed at the top and the left of the figure 6.a. This observation can be related to side effect phenomenon occurring during the growth of the nanotubes film. This can be optically related to the observation of **figure 6.d**: on this dark field image of the surface, at the top edge of the electrode, the TiO_2-NTs film appears in red and a strip of approximately 100 µm non covered with nanotubes appears on the side of the electrode in grey. This can be explained by a peeling of the nanotubes film on the side of the electrode during the synthesis or rincing/annealing step. This side effect was also observed for other samples (example of dark field images in **Figure S5**).

Besides confirming the reproducibility of the VLTE electrode synthesis, the observation of this second sample allows to highlight the good resolution and the potential application of the SPECM method to detect point defects in electrodes for PEC applications.

Conclusions

In this work we report a simple and reproducible synthesis method of aligned TiO_2-NTs electrode on which the length of the nanotubes can be tuned along one direction. By changing

the contact time between the electrolyte and the titanium substrate, NTs having a length ranging from a few hundred nm up to few µm can be grown on a single electrode. Furthermore, by this approach the diameter of the nanotubes does not change significantly and this type of electrode allows local studies of the influence of the NTs length independently of others parameters.

In order to measure the performance of these original samples with a variable thickness of photoactive material, we used by SPECM in order to study the influence of the nanotubes length on the generated photocurrent for water splitting reaction. The mapping image revealed significant photocurrent change in the direction of the length gradient while a good homogeneity of the photocurrent appears in the lateral direction. The photocurrent profile indicates a maximum for nanotubes having a length of 4300 nm; a value which is consistent with previously reported studies. This approach combining gradient synthesis and SPECM measurement can be used to measure quickly the optimal value of a parameter while limiting the synthesis time by doing all the test locally on a single electrode.

Furthermore the SPECM measurements present an excellent spatial and electrochemical resolution that could allows to detect defects in photo-electrochemical films in the perspective of electrodes diagnostic. We believe this resolution can further be improved by playing on the electrochemical parameters and the aperture of the optical fiber.

Conflicts of interest

There are no conflicts to declare.

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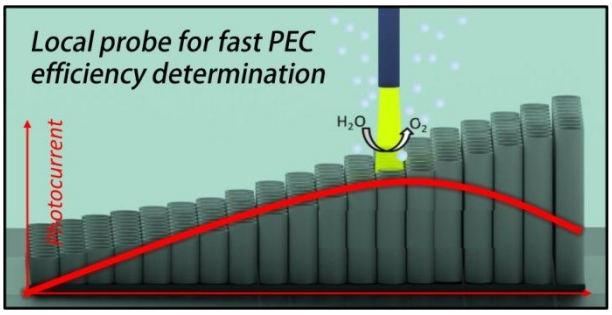

Electrodes of TiO_2-nanotubes with a gradient of length were synthesized by a simple anodization method and analyzed locally by scanning PhotoElectroChemical Microscopy.