

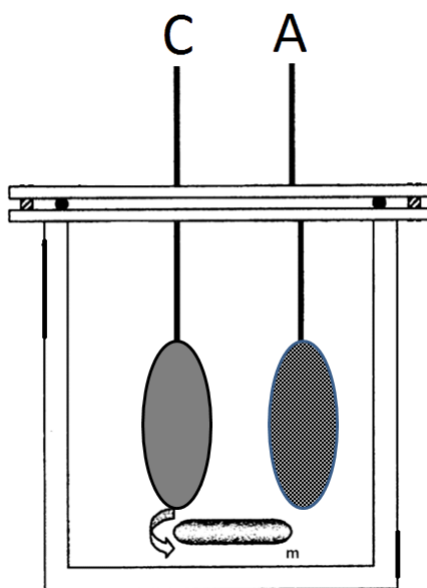
## Supporting Information

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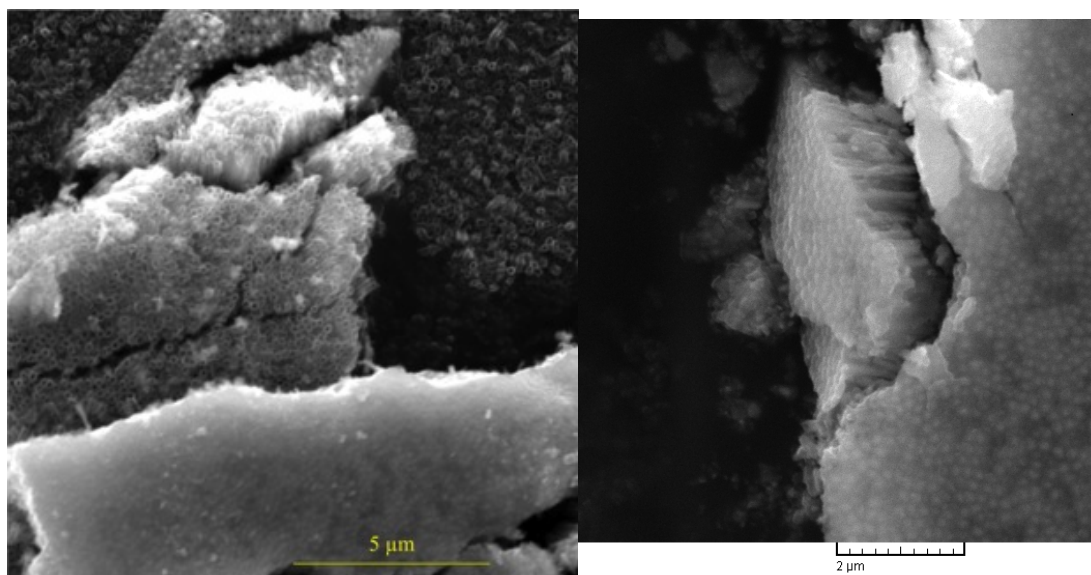
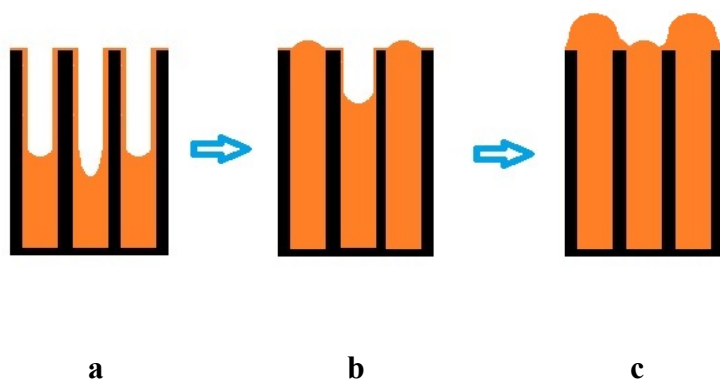
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**Electrochemical cell set-up using Ti disk for anodization process for preparing TiO<sub>2</sub> nanotubes:**



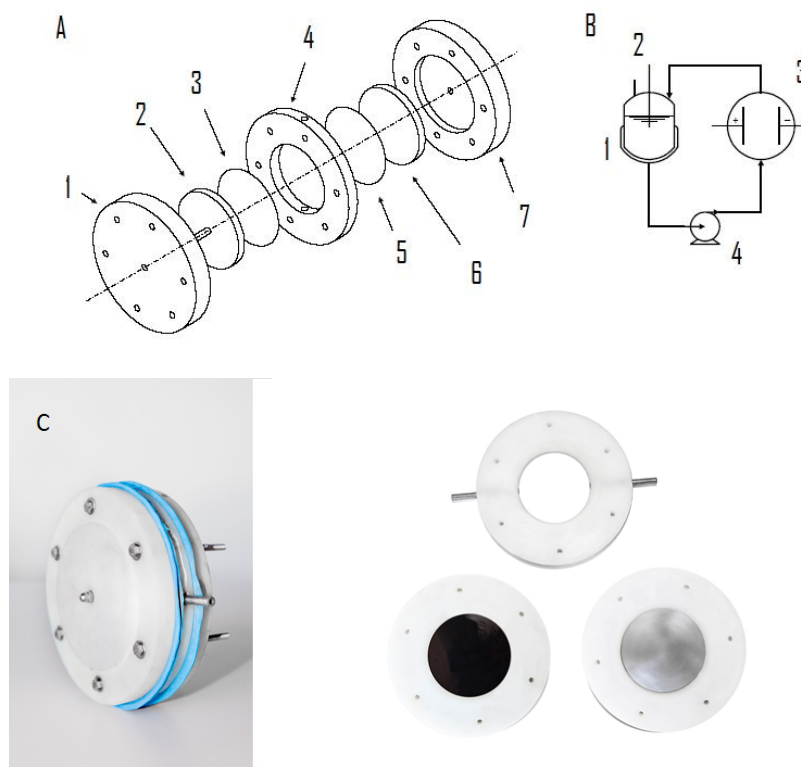
**Figure S1.** Scheme representation of TiO<sub>2</sub> nanotubes growth at disk by applying 30 V during 2 h of anodization. A) Ti serving as anode (65 cm<sup>2</sup> of geometrical area) ; C) Steel serving as the cathode.

**Electrodeposition of PbO<sub>2</sub> onto a Ti/TiO<sub>2</sub>-nanotubes disk array:**



**Figure S2.** Scheme representation of PbO<sub>2</sub> growth at different deposit times. SEM images: (left) synthesized nanotubes without PbO<sub>2</sub> deposit, and (right) TiO<sub>2</sub> nanotubes completely filled after PbO<sub>2</sub> growth, as showed in the SEM image of lateral section.

**Electrochemical flow cell with Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> electrode for treating synthetic dye solution:**

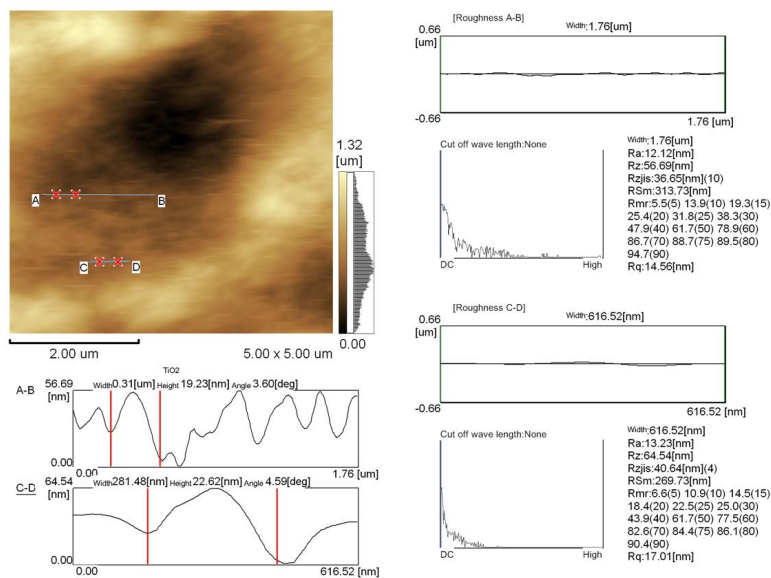


**Figure S3.** A: 1) Anodic part; 2) electric support to anode; 3) anode (Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub>); 4) reaction compartment, 5) cathode (steel disk); 6) Metallic support to electrical contact with cathode and 7) cathodic part. B) Electrochemical system: 1) Reservoir, 2) thermometer, 3) electrochemical cell e 4) peristaltic pump. C: Image of electrochemical cell and with the each one of the compartments.

**References**

(1) P.-A. Michaud, *PhD These* No. **2595**, EPFL, Switzerland, 2002.

## Atomic force microscopy (AFM) surface analysis

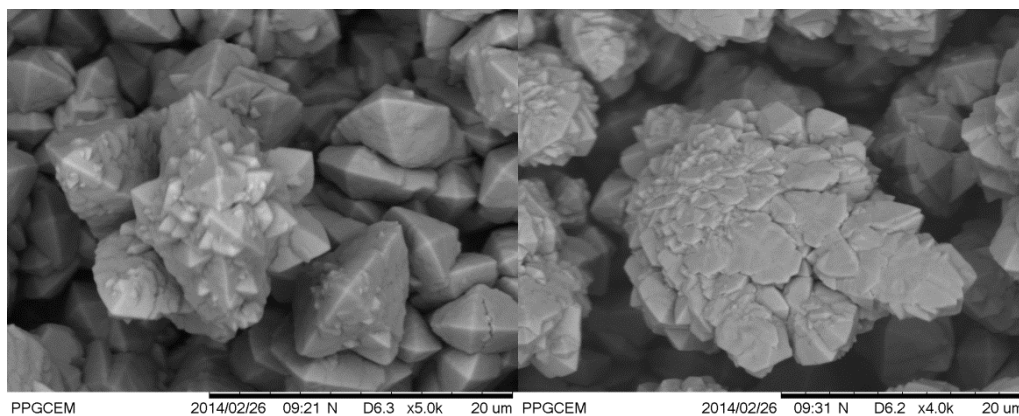


**Figure S4.** AFM image referent to the study of TiO<sub>2</sub>-nanotubes synthesized. A-B and C-D segments have been used to study the shape of TiO<sub>2</sub> nanotube (see Fig. S2).

**Gas Chromatographic – Mass Spectroscopy conditions:**

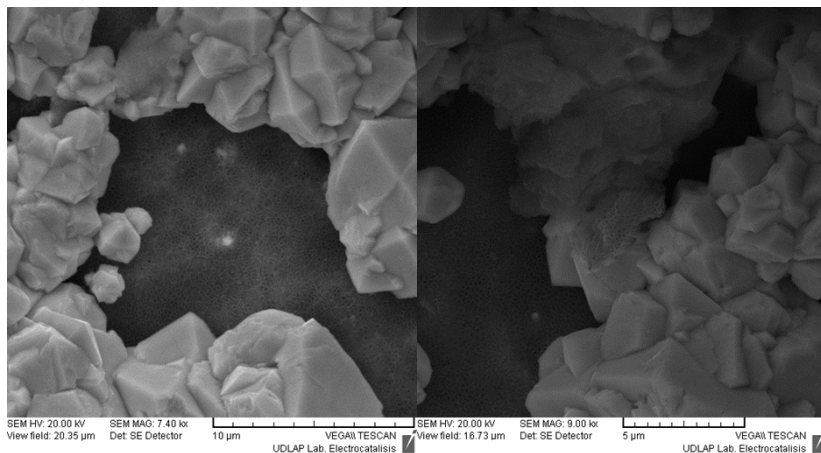
Samples of anolyte were extracted into non-aqueous medium (2 mL of acetonitrile HPLC grade with 20  $\mu$ L of electrolysis sample) and were subjected to GC-MS analysis using GC-FOCUS and MS-ISQ Thermo Scientific to identify the intermediates following the conditions: GC: Varian column VF5 ms with a composition of 5% de fenil-arylene and 95% de dimetilpolisiloxane. Temperature program: 40°C – 5 min; 12°C/min – 100°C; 10°C/min – 200 °C and 10°C/min - 270 °C – 5 min. Injector: 220°C. Mode: Splitless. Gas flow: 0.8 mL/min. MS: Transfer line: 270°C; ions source temperature: 220°C, Mass range: 40-500 m/z. Injection: 1 $\mu$ L.

## Tetragonal $\text{PbO}_2$ crystals



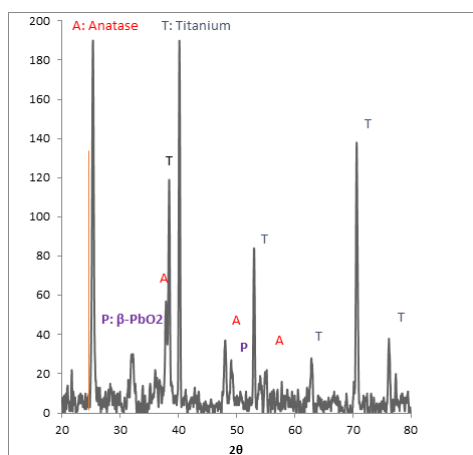
**Figure S5.** Tetragonal crystals organized in tree form when the electrodeposition time is significantly increased.

## Grown of PbO<sub>2</sub> crystals onto TiO<sub>2</sub>-nanotubes



**Figure S6.** The grown of PbO<sub>2</sub> crystals onto TiO<sub>2</sub> nanotubes after 30 min of electrodeposition time. Relevant amount of PbO<sub>2</sub> crystals was formed.

**Crystalline phases determined by X-ray diffractometer (XRD Bruker model D8Discover) using Cu K $\alpha$  ( $\lambda= 1.54 \text{ \AA}$ ) radiation.**



**Figure S7.** XRD spectrum from PbO<sub>2</sub> deposit over TiO<sub>2</sub> nanotubes showing that β-PbO<sub>2</sub> is its predominant crystalline structure.

**Large TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode**

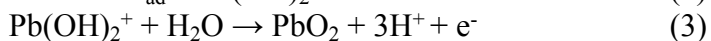


**Figure S8.** Large Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode in disk format before its use to treat a synthetic dye effluent by electrochemical oxidation.



### Deposition mechanisms:

The chemical equations involved for PbO<sub>2</sub> formation during electrochemical deposition can be described as follows:



### References

- (1) J. Lee, H. Varela, S. Uhm and Y. Tak, *Electrochem. Commun.*, 2000, **2**, 646-652.
- (2) A. B. Velichenko, D. U. Girenko and F. I. Danilov, *Electrochim. Acta*, 1995, **40**, 2803-2807.
- (3) A. B. Velichenko, D. U. Girenko and F. I. Danilov, *J. Electroanal. Chem.*, 1996, **405**, 127-132.
- (4) D. Devilliers, T. Baudin, M.T. Dinh Thi and E. Mahé, *Electrochimica Acta*, 2004, **49**, 2369-2377.
- (5) X. Li, D. Pletcher and F. C. Walsh. *Chem. Soc. Rev.*, 2011, **40**, 3879–3894.
- (6) D. Pletcher and F. C. Walsh, *Industrial Electrochemistry*, Chapman and Hall, London, 2nd ed., 1990.

## Decolorization, mineralization and energetic parameters

The decay in color of dyes wastewaters during electrochemical treatment is usually monitored from the decolorization efficiency or percentage of color removal by:

$$\text{Color removal (\%)} = ([\text{ABS}^{\text{M}} - \text{ABS}_t^{\text{M}}]/\text{ABS}_0^{\text{M}}) \times 100$$

where  $\text{ABS}_0^{\text{M}}$  and  $\text{ABS}_t^{\text{M}}$  are the average absorbances before electrolysis and after an electrolysis time  $t$ , respectively, at the maximum visible wavelength ( $\lambda_{\text{max}}$ ) of the wastewater determined from UV-Vis spectrophotometry Varian, model Cary 50 Com.

We also monitored the COD decay, as a function of time through a multiparameter HANNA photometer COD-HI 83099, after digestion procedure. From this data, the percentages of COD were calculated:

$$\% \text{COD decay} = \left( \frac{[\text{COD}_0 - \text{COD}_t]}{\text{COD}_0} \right) \times 100 \quad (4)$$

The energy consumption per volume of treated effluent was estimated and expressed in  $\text{kWh.m}^{-3}$ . The cell voltage during the electrolysis was taken for calculation of the energy consumption, as follows:

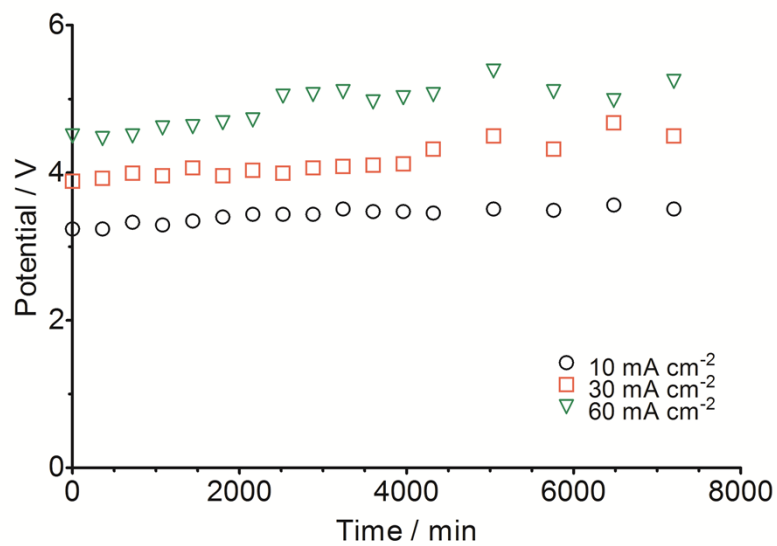
$$\text{Energy consumption} = \left( \frac{V \times A \times t}{V_s} \right) \quad (1)$$

where  $t$  is the time of electrolysis (h);  $V$  (volts) and  $A$  (amperes) are the cell voltage and the electrolysis current, respectively; and  $V_s$  is the sample volume ( $\text{m}^3$ ).

## References

- (1) C. A. Martínez-Huitle, E. Brillas, *Appl. Catal., B Environ.* 2009, **87**, 105.

### Electrochemical stability of the Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> electrode



**Figure S9.** Variation of  $E_{\text{appl}}$ , as a function of time, during fixed current density measurements for prolonged electrolysis times at Ti/TiO<sub>2</sub>-nanotubes/PbO<sub>2</sub> anode.