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## Preparation and optimization of TiO<sub>2</sub> photoanodes fabricated by pulsed laser deposition for photoelectrochemical water splitting

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<b>Abstract:</b>	Quasi-1D TiO <sub>2</sub> nanostructures prepared by Pulsed Laser Deposition (PLD) are tested as photoanodes for photoelectrochemical water splitting application and compared with TiO <sub>2</sub> nanotube arrays prepared by anodic oxidation. PLD TiO <sub>2</sub> films with controlled structure and morphology ranging from compact to vertically oriented or hierarchical porous nanostructures are deposited by ablating a TiO <sub>2</sub> target with ns UV laser pulses in the presence of O <sub>2</sub> background atmosphere at different pressures. Thermal treatments at different temperatures are used to transform the so-obtained amorphous systems into nanocrystalline structures (mainly anatase). The effect of film density and thickness are also considered by depositing different amounts of material per unit surface. The morphology and the phase composition of the samples are characterized by SEM and Raman Spectroscopy, while the photoelectrochemical water splitting performances are investigated by monitoring the photocurrent generated under illumination in a three-electrode cell. Voltammetric scans and EIS analysis were also used to correlate the morphology of PLD samples with their electrochemical properties and their working mechanism in the absence and presence of a light radiation. A clear correlation between structural/morphological properties and photoelectrochemical behavior is found and ideal values of the synthesis parameters are identified, which allow the identification of the optimal quasi-1D nanoporous morphology for water splitting applications. The use of sacrificial organic reagents as hole scavengers was also considered to improve the photoelectrochemical performance of the samples.
<b>Response to Reviewers:</b>	see attachment

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## Preparation and optimization of TiO<sub>2</sub> photoanodes fabricated by pulsed laser deposition for photoelectrochemical water splitting

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## Abstract

1  
2 Quasi-1D TiO<sub>2</sub> nanostructures prepared by Pulsed Laser Deposition (PLD) are tested as photoanodes for  
3 photoelectrochemical water splitting application and compared with TiO<sub>2</sub> nanotube arrays prepared by anodic  
4 oxidation. PLD TiO<sub>2</sub> films with controlled structure and morphology ranging from compact to vertically oriented or  
5 hierarchical porous nanostructures are deposited by ablating a TiO<sub>2</sub> target with ns UV laser pulses in the presence of O<sub>2</sub>  
6 background atmosphere at different pressures. Thermal treatments at different temperatures are used to transform the  
7 so-obtained amorphous systems into nanocrystalline structures (mainly anatase). The effect of film density and  
8 thickness are also considered by depositing different amounts of material per unit surface. The morphology and the  
9 phase composition of the samples are characterized by SEM and Raman Spectroscopy, while the photoelectrochemical  
10 water splitting performances are investigated by monitoring the photocurrent generated under illumination in a three-  
11 electrode cell. A clear correlation between structural/morphological properties and photoelectrochemical behavior is  
12 found and ideal values of the synthesis parameters are identified, which allow the identification of the optimal quasi-1D  
13 nanoporous morphology for water splitting applications. The use of sacrificial organic reagents as hole scavengers was  
14 also considered in order to improve the photoelectrochemical performance of the samples.  
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## Keywords

53 Photoelectrochemical water splitting, TiO<sub>2</sub>, nanostructured materials, quasi-1D/hierarchical nanostructures, Pulsed  
54 Laser Deposition, sacrificial agent  
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## Introduction

In recent years, the increasing environmental concerns and the rising energy demand have led to focus the attention on new and sustainable sources of energy. In particular, many efforts are underway to develop ecologically clean technologies based on the applications of hydrogen as a fuel instead of fossil fuels [1,2]. In this context, the production of hydrogen by photocatalytic water splitting using solar energy represents a promising way to provide a clean and renewable energy resource [3-6].

In the 1970s Fujishima and Honda [7] reported for the first time water splitting into  $H_2$  and  $O_2$  with a  $TiO_2$  photoanode via the so-called photoelectrochemical (PEC) approach. The typical PEC cell consists of a semiconductor photoanode (e.g.  $TiO_2$ ) and a metal counter electrode (usually Pt) which are connected through an external load. Photo-irradiation of the anode results in the formation of charge carriers (electron-hole pairs): the holes oxidize water to form  $O_2$  on the anode while the electrons are channelled through the external circuit towards the cathode, where they reduce water to form  $H_2$ . Often, when the energetics of photoanode or cathode are not suitable for the process, an external voltage or chemical bias (i.e. by  $\Delta pH$ ) needs to be applied to effect water splitting [3].

Despite other metal oxide semiconductors, also with rather complex structures, have been investigated in PEC applications,  $TiO_2$  still remains the most investigated photocatalyst because of its activity, low-cost, non-toxicity and chemical stability (i.e. corrosion-resistance) [8,9]. Unfortunately, the industrial exploitation of photocatalytic hydrogen production via water splitting over  $TiO_2$  is still limited, the major problems being a poor activation by visible light and the low quantum efficiency of the process, also related to the high degree of recombination between the photogenerated charges carriers (electron-hole pairs) [10]. In this regard, various strategies have been proposed to improve the PEC performance of  $TiO_2$ , such as  $TiO_2$  doping/sensitization to enhance visible light absorption [4,5,11-13], or controlling photocatalysts structure and morphology to enhance the active surface, to increase light harvesting and to minimize electron trapping and recombination probabilities [13,14].

In the latter case, several nanostructured  $TiO_2$  networks (e.g. tubes [15-17], rods [18-20], wires [21,22], sponges [23,24]) emerged as promising materials that can be used as photoanodes in water photoelectrolysis cells. In particular, as summarized in very recent reviews [25-30], extensive research has been performed on  $TiO_2$  nanotube arrays (T-NTs) because their unique high surface-to-volume ratios (even though not as high as those obtained with nanoparticle assemblies), ordered geometry and tunable morphologies are claimed for fast charge separation and transport, and electrolyte infiltration as well.

Recently, novel 3-D architectures consisting of quasi-1D hierarchical nanostructures have received attention for direct solar energy conversion, because of their advantages in combining (i) large surface area, (ii) light scattering due to the presence of features of size comparable to visible wavelengths, (iii) mesopores for infiltration of molecules (e.g.

1 electrolytes in the case of photoelectrochemical solar cells, pollutants or reagents in the case of photocatalysis), and also  
2 (iv) anisotropic morphology (similarly to nanotubes or nanowires) to ensure better electron transport towards the  
3 electrical contact [31,32]. Such structures, characterized by multiscale features or self-affine morphologies over  
4 different length scales (from the nano- to the micro-scale) through low energy assembling of fine nanoparticles, can be  
5 produced by carefully tuning the plasma expansion dynamics in a Pulsed Laser Deposition (PLD) process [33-36]. In  
6 particular, nanocrystalline tree-like TiO<sub>2</sub> hierarchical structures prepared by reactive PLD have been proposed for  
7 application in dye-sensitized solar cells (DSSCs), showing long electron lifetime with respect to back recombination  
8 and high performances in terms of ion liquid electrolytes diffusion [31]. Improved light harvesting has been observed  
9 even when hierarchical photoanodes were employed in solid state (polymeric) DSSCs [32]. Moreover, the potential  
10 photocatalytic efficacy of such quasi-1D, hierarchical TiO<sub>2</sub> architectures has been proved in the mineralization (i.e.  
11 oxidation) of stearic acid, as a model molecule [34].

12 In this work, by exploiting the versatility of the PLD deposition process, we focus on the potential of vertically oriented  
13 assemblies of TiO<sub>2</sub> nanoparticles as photoanodes for the photoelectrochemical water splitting process. In particular, the  
14 existing correlations between structural/morphological properties and photoelectrochemical behaviour are analysed with  
15 the aim of identifying the optimal structures for water splitting applications.

16 A preliminary assessment of the suitability of structures prepared by PLD for photoelectrochemical water splitting was  
17 synthetically presented in a previous communication [37]: herein, we aim at a more detailed and comprehensive  
18 investigation of the effect of the variation of the preparation conditions (i.e. pressure, deposited mass and annealing  
19 temperature), in order to deep inside the effect of crystalline structure and morphology (i.e. porosity and thickness),  
20 ranging from compact to vertically oriented or hierarchical nanostructures, and the photoelectrochemical behaviour,  
21 which is evaluated in terms of generated photocurrent. Moreover, the behaviour of a TiO<sub>2</sub> nanotubular (i.e. a model  
22 vertical-oriented and non-hierarchical nanostructure) photonaode, prepared by anodic oxidation, is also considered for  
23 comparison purposes. Finally, the performances of the PLD grown photoanodes are here investigated in the presence of  
24 glycerol, ethylene glycol and ethanol which are used as model organic sacrificial reagents to improve the PEC  
25 performances. In fact, from a practical point of view, photo-reforming of organic solutions instead of photo-cleavage of  
26 pure water looks more advantageous because most water pollutants are organics, and in this way hydrogen production  
27 can be usefully combined with the purification of water [38]. Moreover, it has been demonstrated that under favourable  
28 conditions and in the presence of O<sub>2</sub>, photoelectrochemical (PEC) cells can act as Photofuelcells (PFC), consuming an  
29 organic substance (i.e. the fuel), and utilizing light energy to produce electricity [39].

## Experimental

### Synthesis of TiO<sub>2</sub> photoanodes

TiO<sub>2</sub> nanostructured films have been deposited at room temperature by ablating a TiO<sub>2</sub> target with UV ( $\lambda=266$  nm) laser pulses from a frequency quadrupled Nd:YAG Q-switched laser with a pulse duration of about 5-7 ns. The laser fluence on the target was set at about 2.5 J cm<sup>-2</sup> with a spot size of about 3 mm<sup>2</sup>. The ablation was performed in the presence of a fixed background gas pressure of pure oxygen (99.999%) which was varied in the 3-15 Pa range to control the material structure/morphology. Silicon, glass and Ti were used as substrates mounted on an off-axis rotating sample holder at a fixed target-to-substrate distance of 50 mm. TiO<sub>2</sub> films deposited on silicon and glass substrates were used for SEM and Raman characterization while those deposited on Ti for photoelectrochemical experiments (see below). Further details on the PLD experimental setup and procedures are reported in previous works [32-34]. In particular, those results demonstrated that the structure and morphology of TiO<sub>2</sub> films deposited by PLD can be tuned by controlling the pressure of the background gas, where other parameters, such as the target-to-substrate distance, the laser fluence and the gas flux and have been previously set [33].

Ti plate substrates for photoelectrochemical measurements were masked to deposit on a 2x1 cm<sup>2</sup> area and to leave a clean surface for electrical contacts. All the substrates were kept at room temperature and no substrate heating was observed during deposition. The deposited mass per unit surface was measured by a quartz crystal microbalance at the same position as the substrates. Since the deposition rate changes depending on the background gas pressure, keeping constant the oxygen partial pressure (5 Pa) films were deposited at a constant mass per unit surface of 0.5*M* (*M* about 0.3-0.4 mg cm<sup>-2</sup>), of *M* and of 2*M*, in order to study the influence of thickness. Post deposition thermal annealing processes were performed for 2 hours in air in a muffle furnace at 500 °C, 650 °C and 800 °C to induce crystalline order. In fact, as well known in literature [5,25,28], a high degree of crystallinity has positive effects on water splitting activity, mainly due to a decrease of defect concentration which reduces recombination between photogenerated carriers.

For comparison purpose, a TiO<sub>2</sub> nanotubes photoanode (TNT) was prepared through an electrochemical anodization method already tested in previous works [16, 40]. Briefly, starting from Titanium foil (0.25 mm thick, 99.7% metal basis, Aldrich) which was preliminarily degreased, the anodization was performed in water/glycerol solution containing NH<sub>4</sub>F (Glycerol/H<sub>2</sub>O 80:20 vol.% + 0.1 M NH<sub>4</sub>F). A potential ramp was applied from open-circuit voltage (OCV) to a fixed potential (20 V) with a scan rate of 100 mV s<sup>-1</sup>; then, the applied potential was maintained at this fixed value for 3 h. After oxidation, the sample was rinsed in deionized water, dried in a nitrogen stream and subsequently thermally treated in air at 400 °C for 1 h.

## Morphological and structural characterization

1  
2 PLD grown films morphology was observed with a ZEISS Supra 40 FEG-SEM without any sample preparation. SEM  
3  
4 analyses (top view and cross sectional) were performed on TiO<sub>2</sub> films obtained on silicon substrates. Film density was  
5  
6 evaluated by combining information on the deposited mass per unit surface with thickness measurements by cross-  
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8 sectional SEM images ( $\rho_{\text{film}}=M h^{-1}$  where  $M$  is the mass/cm<sup>2</sup> and  $h$  is the film thickness). The porosity of the systems  
9  
10 has been then estimated as percentage of voids and evaluated from the ratio between film density and bulk anatase  
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12 density ( $1-\rho_{\text{film}}/\rho_{\text{bulk}}$ ), with  $\rho_{\text{bulk}} = 3.9 \text{ g cm}^{-3}$ .

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14 The crystalline structure of the PLD films obtained from TiO<sub>2</sub> on glass/silicon was characterized by Raman  
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16 spectroscopy using a Renishaw InVia micro Raman spectrometer with 514.5 nm laser excitation wavelength. The laser  
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18 power on the sample was low enough (1 mW) to avoid laser induced modifications during measurements.

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20 In order to evaluate the specific surface area of a representative PLD sample annealed at 500 °C, a deposition at 5 Pa O<sub>2</sub>  
21  
22 on a large area Al foil (corresponding to a deposited mass of several mg) was also performed. The surface area was  
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24 determined by N<sub>2</sub> adsorption–desorption at -196 °C with the BET method using a Micromeritics TriStar 3000  
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26 instrument.

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28 TNT photoanode was also characterized by SEM and Raman spectroscopy.

## Photoelectrochemical experiments

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34 The PEC water splitting behaviour of the PLD films was investigated in aqueous KOH solution (0.1 M). Experiments  
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36 were performed in a three-electrode cell in which a Ti/TiO<sub>2</sub> photo-anode (working area of 1 cm<sup>2</sup>) was used as the  
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38 working electrode, a platinum grid as the counter electrode, and a saturated calomel electrode (SCE) as the reference:  
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40 all the values of potential in the text are referred to SCE. The light source was a tungsten filament and a high-pressure  
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42 UV-vis lamp (Osram Ultra-Vitalux, 300 W) with a main emission line in the UV region near 360 nm [41-43]. An  
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44 average UVA/UVB (280-400 nm) light intensity, striking on the electrodes surface, of about 1350 μW cm<sup>-2</sup> was  
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46 measured by a light meter HD2302.0 (Delta OHM). For comparison purpose, the same experiment was performed over  
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48 the TiO<sub>2</sub> nanotube layer photoanode.

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50 The performance of the TiO<sub>2</sub> photo-anodes was evaluated by measuring the photocurrents produced under an external  
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52 bias [15-17, 44-46], provided by a potentiostat (Amel 7050). Polarization curves (potential ramps from -0.8 V to about  
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54 0.5 V, with a scan rate of 5 mV s<sup>-1</sup>) were used to compare the performance of different samples.

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56 PEC experiments were also performed with an aqueous KOH solution (0.1 M) in the presence of ethanol (Carlo Erba,  
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58 99.9%), ethylene glycol (Sigma-Aldrich, 99.8%) or glycerol (Sigma-Aldrich, >99%) by varying their volume fraction in  
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60 the 2-40% range.

## Results and discussion

### Photoanode structure and morphology

The morphology of *as deposited* (as grown) TiO<sub>2</sub> films obtained by PLD at room temperature at different oxygen background pressures (keeping constant the total deposited mass per unit surface ( $0.5M$ )) is shown in the SEM images of Figure 1 A-D (i.e. 3, 5, 10 and 15 Pa, respectively). Moving from 3 Pa to 15 Pa of oxygen, the effect of increasing the spatial confinement of the plasma plume by the surrounding gas is evident in an increase of porosity, as discussed in previous works [34, 47]. In fact, the gas pressure favours nucleation of the ablated species in the gas phase, leading to the formation of clusters which are subsequently slowed down upon diffusion in the background gas. This allows the tuning of the growth mechanisms from atom-by-atom deposition in vacuum towards low kinetic energy, forward directed cluster assembling at higher gas pressure, with a corresponding gradual variation of film morphology from compact and dense to a columnar structure, and eventually to a nanoporous quasi-1D, vertically oriented assembly. Indeed, as shown in Figure 1 (as deposited films), the above-mentioned parameters were optimized to grow a compact and dense film at 3 Pa O<sub>2</sub>, which evolves when increasing pressures are considered. Starting from 5 Pa O<sub>2</sub>, a vertically oriented, columnar-like nanostructure, is obtained; at pressures higher than 10 Pa, it clearly evolves into hierarchical structure resembling a forest of nano-trees [33]. Fine nanoparticles (about 10 nm in size) are observed, which are organized at a multi-scale level, from the single nanoparticle (~10 nm scale) to the branches (~100 nm scale) up to the entire structure (micron-scale). The insert of Figure 1B shows a magnification of the structures obtained at 5 Pa, highlighting the fine structure at the nanoscale, and the hierarchical organization of fine nanoparticles into quasi vertical mesostructures.

By varying the oxygen pressure in the 5-15 Pa range the shape and packing of the quasi-1D structures are thus tuned, and, as a result of the different growth mechanisms, film density and porosity are thus strongly related to the background gas pressure. Figure 2 (dashed black line) shows the variation of film density as a function of the oxygen partial pressure: as expected, moving from 3 to 15 Pa O<sub>2</sub> pressure, the density decreases from 3.2 g cm<sup>-3</sup> to about 0.5 g cm<sup>-3</sup>. The corresponding estimated porosity is also shown in Figure 2 (solid red line): in line with the density decrease, the film porosity increases from 18% at 3 Pa O<sub>2</sub> to about 85% at 15 Pa O<sub>2</sub>.

SEM images in Figure 1 also provide the film thickness for the  $0.5M$  samples, which increases from about 500 nm to more than 3  $\mu$ m when moving from 3 Pa to 15 Pa deposition pressure. The effect of different thickness was then addressed for films grown at 5 Pa O<sub>2</sub> by varying the mass per unit surface in the  $0.5M$ - $2M$  range. SEM images (not shown) point out that moving from mass  $0.5M$  to mass  $2M$  film thickness increases from about 900 nm to about 3600



1 nm, respectively; however, the overall morphology is not significantly affected by the variation of the mass of deposited  
2 material.

3  
4 To investigate the effect of the post-deposition thermal treatments on samples morphology, SEM analyses were  
5 accomplished on the samples annealed at 500 °C, 650 °C and 800 °C. Figure 3 shows SEM images of TiO<sub>2</sub> films  
6 deposited at 5 Pa and 10 Pa O<sub>2</sub> after annealing at different temperatures, and compared to the as-deposited materials.  
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9 For films grown at 5 Pa, the sintering effect at 500 °C and 650 °C results in vertically oriented nanostructures, while  
10 when the annealing temperature is elevated up to 800 °C a strong coalescence within the structures is observed, leading  
11 to a marked decrease in nanoscale porosity. In the case of the films deposited at 10 Pa, inspection of Figure 3 points out  
12 that the post-deposition thermal treatment in air at 500 °C or 650 °C does not change the overall morphology of the  
13 more open, tree-like structures grown at this pressure: thermal treatments mainly affect the shape of single nanoparticles  
14 and the size, that results slightly increased by higher annealing temperatures. Also, a change in their mutual degree of  
15 connectivity is visible, with an increased coalescence among particles (sintering effect). Conversely, for the sample  
16 annealed at 800 °C a marked coalescence effect is observed, although to a lesser extent than what detected for the  
17 sample grown at 5 Pa.  
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19  
20 The crystalline structure of the films was characterized by Raman spectroscopy, which is sensitive to the local  
21 crystalline order/disorder and provides a fingerprint of the TiO<sub>2</sub> crystalline phase (anatase/rutile) [48]. As an example,  
22 the Raman spectra for the film grown at 5 Pa O<sub>2</sub>, as deposited and after annealing at 500 °C, are reported in Figure 4  
23 (spectrum a and b, respectively). The spectra of the as deposited films are characterized by two large bands, which are  
24 fingerprints of a highly disordered and almost amorphous structure due to the room temperature growth process.  
25 Conversely, as expected, high temperature annealing in air induces transition to a crystalline structure. As a result of the  
26 thermal treatment, the dominant TiO<sub>2</sub> crystalline phase is anatase, as evidenced by the presence of narrow peaks at 144,  
27 197, 399, 519 and 639 cm<sup>-1</sup> [48].  
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29  
30 No substantial difference in the Raman spectra is observed for samples grown at 3 Pa and 5 Pa, both for as deposited  
31 films and after annealing at different temperatures. Only for films deposited at higher pressures (10 Pa and 15 Pa) peaks  
32 at 443 cm<sup>-1</sup> and 610 cm<sup>-1</sup>, corresponding to the rutile phase, can be observed after annealing at 500 °C or higher  
33 temperatures (not shown); for these films the estimated rutile content is within 20% for annealing at 500 °C, in  
34 agreement with previous results [34], and it increases up to 50 % for the 15 Pa sample at higher temperatures. Such  
35 observed structural features, and, in particular, the oxide phase evolution upon annealing, is in agreement with previous  
36 XRD and Raman characterizations of TiO<sub>2</sub> films grown under similar experimental conditions [34], for which an  
37 average domain size in the range 10-20 nm was estimated from the width of XRD reflections.  
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Figures 5A and 5B show SEM images of the annealed TNT photoanode (top view and cross-view, respectively). Nanotubes were found to have an outer diameter of approximately 80-90 nm and a length of about 700 nm. Figure 4 shows the Raman analysis (spectrum c) indicating that also in this case the dominant TiO<sub>2</sub> crystalline phase is anatase.

### Photoelectrochemical response

To assess the functionality of the TiO<sub>2</sub> nanostructures prepared by PLD in view of water splitting applications we investigated the behavior of so prepared films as photoanodes in a photoelectrochemical cell, analyzing the effects of different background pressures, deposited mass, and annealing temperatures.

In order to compare the performances of different film morphologies, the photoelectrochemical behaviour of TiO<sub>2</sub> films grown at different pressures was first investigated, keeping the total deposited mass per unit surface of the photoactive material constant (0.5M). All the amorphous as deposited samples showed negligible photoresponse (not reported) due to the presence of a high number of defects which can act as traps and recombination centers for the photogenerated charge carriers. Instead, a significant enhancement in photoresponse was observed for annealed samples. The trend of polarization curves obtained under light irradiation may be used to compare the different photoactivity of the samples. A typical example of polarization curves is depicted in Figure 6, for the sample deposited at 5 Pa and annealed at 500 °C, in the dark and under illumination. As expected, under dark conditions negligible photocurrent is observed (less than 3 μA cm<sup>-2</sup>), over the whole investigated potential range, indicating that no reaction occurred at the photoanodes in the absence of light illumination. On the contrary, upon illumination photocurrent evolution is observed starting at approximately -0.8 V (photopotential onset), as a result of the charge carriers (i.e. electron-holes pairs) generation from the incident light and the subsequent water oxidation occurring at the photoanodes by holes. An almost linear dependence of the photocurrent density on the potential is observed in the first part of the curve, because of the efficient charge carrier separation, under the effect of the applied bias [49-51]. Then, after a certain value  $V^*$ , a decrease of slope is generally measured, and finally a saturation condition is reached, where the effect of the applied potential becomes not more significant. Analogous trends of polarization curves, were obtained at the other samples: however, depending on the sample, different values of photopotential onset, saturation current density, and  $V^*$ , were measured. Thus, in order to make a quantitative comparison between the performances of the different samples, the photopotential onset values and the photocurrent density measured at a fixed potential are firstly considered. The third parameter,  $V^*$ , is then taken into account when the photoconversion efficiency is evaluated, as reported in the following.

A clear effect of the oxygen deposition pressure (and in turn of the morphology) on the photoresponses is evidenced in Figure 7, where the photopotential onset, and the steady-state photocurrent density recorded at 0.5 V (Figure 7A and

7B, respectively), are reported. Data refer to samples with constant deposited mass per unit surface (0.5M), but also data referring to sample with M and 2M are included in the same graph for comparison.

Of note, the strongest negative effect on the performance of the photoanodes seems to be correlated to the porosity increase corresponding to the highest deposition pressure values. As a matter of fact, for samples deposited at the highest oxygen pressures (i.e. 10 and 15 Pa) the photopotential onset is shifted considerably to less negative values (i.e. near -0.7 V), and the photocurrent density is significantly lower than that for the samples at lower pressure, approaching values close to 15  $\mu\text{A cm}^{-2}$ . This suggests a less efficient generation and transfer of photogenerated charge carriers and higher recombination losses, as well [52-54].

If the most performing samples are compared, a photopotential onset of about -0.75 V is measured for the sample deposited at 3 Pa (i.e. compact and dense film), which is less negative than that of samples deposited at 5 Pa (i.e. -0.8 V). Lower photocurrent density is correspondingly measured for sample at 3 Pa (i.e. 55  $\mu\text{A cm}^{-2}$  vs. 65  $\mu\text{A cm}^{-2}$ ). However, it must be observed that values in figure 7b refer to data measured at a fixed potential of 0.5 V. This value could correspond to different overpotential, depending on the specific sample, and on its photopotential onset. So, for example the little differences in photocurrent measured for samples at 3 and 5 Pa could be considered consistent with the corresponding differences in the relevant photopotential potential.

It is thus clear that these two parameters could not be sufficient to evaluate the performances of the samples. In order to make a more exhaustive comparison also the photoconversion efficiency ( $\eta\%$ ) has been evaluated. In electrically driven photo-processes, as in this case, equation (1) can be properly used [55,56] as it takes into account not only the light power, but also the external potential applied which needs to be considered to obtain the overall photoconversion efficiency:

$$\eta (\%) = \frac{J(E^{\circ} - |E_{\text{app}}|)}{I} * 100 \quad (1)$$

where,  $J$  is the photocurrent density ( $\mu\text{A cm}^{-2}$ ),  $E^{\circ}=1.23\text{V}$  is the standard reversible potential for water splitting,  $|E_{\text{app}}|$  is the applied potential evaluated as the difference between the bias potential and the OCV under the irradiated power light, and  $I$  is the UV incident light power density of about 1350  $\mu\text{W cm}^{-2}$ . Of note, dedicated experiments [57] performed at selected wavelengths, indicated the negligible contribution of the visible-light on the total activity of the investigated samples which is in line with previous work showing that the optical gap for PLD hierarchical  $\text{TiO}_2$  deposited under  $\text{O}_2$  atmosphere and annealed in air at 500  $^{\circ}\text{C}$  is about 3.2-3.3 eV [34], i.e. about 370-390 nm, without any detectable trend with respect to deposition pressure.

1 Figure 8A shows the variation of  $\eta\%$  as a function of the applied potential. As typical [55, 56], voltage-dependent  
2 trends can be observed, i.e. the efficiency increases at low applied bias, reaching a maximum, and then begins to  
3 decrease at higher applied bias. It must be observed that the maximum in this curve is obtained at a potential value  
4 about corresponding to the  $V^*$  in the polarization curve (see Figure 6): it can be individuated as the optimal working  
5 potential, at which the process could be carried out.  
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9 On these bases, the sample deposited at 5 Pa results the best performing, not only because it achieves the highest  
10 maximum efficiency of ca. 4%, but also because this efficiency is obtained at very low bias (near -0.6 V). Conversely,  
11 the sample deposited at 3 Pa and those deposited at 10-15 Pa show lower values of maximum efficiencies, of ca. 2.0%  
12 and 0.5%, respectively, which are obtained at higher potential.  
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17 On the basis of the above results, the effect of film thickness, on the photoresponses was further investigated for  
18 samples deposited at 5 Pa (i.e. for the morphology that had shown the best performances) by varying the mass of  
19 deposited material in the  $0.5M$ - $2M$  range. All the investigated samples were annealed at the same temperature (i.e. 500  
20 °C).  
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25 As it clearly appears from Figures 7A and 7B the photopotential onset is approximately the same (i.e. near -0.8 V) for  
26 all the samples deposited at 5 Pa; however, a clear effect of film thickness on the photoresponse is apparent, and  
27 moving from sample- $0.5M$  to sample- $M$  (i.e. from ca. 900 nm to ca. 1400 nm of thickness) the photocurrent is  
28 remarkably improved. In particular, sample- $M$  yields a photocurrent density of roughly  $130 \mu\text{A cm}^{-2}$  at 0.5 V, which  
29 represents ca. a 2-fold increase of the photocurrent response if compared to sample- $0.5M$ . Besides, the further increase  
30 of the thickness up to 3600 nm (sample- $2M$ ) results in a photoresponse decrease, so that a photocurrent density  
31 comparable to that of sample- $0.5M$  is attained. This outcome suggests the existence of an optimal thickness value for  
32 the quasi 1D structures, which can guarantee improved photoactivity. This is clearly shown by the corresponding  
33 photoconversion efficiencies, plotted in Figure 8B. As a matter of fact, the maximum photoconversion efficiency of the  
34 sample- $M$  is increased to ca. 6.3% (vs. 4 and 3.7%, for sample- $0.5M$  and sample- $M$ , respectively). Such a behaviour  
35 seems peculiar of quasi 1D structures. Indeed, the effect of the variation of thickness was further investigated for  
36 samples deposited at 3 Pa that are conventional thin films (i.e. compact and dense). Of note, in this case we observe that  
37 photocurrents results (see Figure 7A and 7B) and the corresponding photoconversion efficiencies data (Figure 8C),  
38 show a negligible effect on the photoactivity in the whole potential range when moving from sample- $0.5M$  to sample- $M$   
39 (i.e. from about 500 nm to about 1500 nm of thickness).  
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56 For comparison purpose, in Figure 8B, the results obtained for the TNT photoanode are also reported. Of note, in this  
57 case, the photoconversion efficiencies are very similar to those calculated for sample- $0.5M$  which is in line with their  
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comparable thickness. However, in the case of the TNT photoanode the maximum efficiency is obtained with an applied potential which is higher than that for the PLD sample.

Furthermore, in order to investigate the effect of the post-thermal treatment (and thus of crystallinity) on the photoelectrochemical performances, additional tests were performed over TiO<sub>2</sub> photoanodes prepared at different background pressures and annealed at 650 °C. For comparison the same mass (i.e. 0.5M) was deposited in this case. The photoelectrochemical results are shown, in terms of photocurrent density generated at 0.5 V and photocurrent efficiency, in Figures 9 (see with bars) and 8D, respectively.

In line with the results obtained in the case of samples annealed at 500 °C, also for samples annealed at 650 °C the best performances are associated with the sample deposited at 5 Pa oxygen. In fact, as shown in Figure 9, the sample deposited at 5 Pa oxygen shows the highest photocurrent densities reaching a value of 200 μA cm<sup>-2</sup> at 0.5 V which represents ca. a 4-fold increase of the photocurrent response if compared to all the other samples. Accordingly, the sample deposited at 5 Pa oxygen exhibits conversion efficiencies as high as 8% (see Figure 8D), which are highly enhanced as compared to the other investigated samples. Indeed, great care must be paid in evaluating the existing literature photoconversion efficiency results [3] because the use of very different experimental conditions (e.g. light source and energy, photo-anode preparing conditions, electrolyte nature and concentration) prevents us from a direct and exhaustive comparison. However, such a value of photoconversion efficiency is quite comparable to those typically obtained over other TiO<sub>2</sub> based photoanodes under UV irradiation [15, 58, 59].

The clear effect of the post-thermal treatment on the photocatalytic performances can be observed, by comparing Figures 7B and 9, i.e. considering samples deposited at the same pressure but annealed at 500 and 650 °C, respectively. Except in the case of the sample deposited at 3 Pa oxygen, upon increasing the annealing temperature from 500 to 650 °C, the photocatalytic activity considerably increases. As a matter of fact, the photoresponse of samples deposited in the 5-15 Pa oxygen range is almost trebled, whereas it was very similar for samples deposited at 3 Pa.

Of note, the photo-electrochemical response of samples annealed at 800 °C was also investigated and representative results are reported in Figure 9 for samples deposited at 5 and 15 Pa (i.e. see black bars). Extremely low activity was found in this case. As a matter of fact very low values of photocurrent density (i.e. close to 10 μA cm<sup>-2</sup> at 0.5 V) were measured.

Finally, photoelectrochemical tests were also carried out in the presence of ethanol, ethylene glycol or glycerol. For this purpose, the behaviour of the sample prepared at 5 Pa of oxygen (i.e. for the morphology that had shown the best performances) and annealed at 500 °C (mass = M) was investigated. Figure 10 shows the results in terms of the parameter  $\gamma$  evaluated as ratio between the photocurrent values obtained at 0.5 V with and without the organics as a

1 function of their volume fraction. Accordingly, when  $\gamma > 1$ , it accounts for the performance gain due to the presence of  
2 the organic compounds.

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4 As it clearly appears from Figure 10, all the investigated organic compounds improves the PEC performances which is  
5 mainly attributed to the great increase of charge separation efficiency since they act as sacrificial electron donor by  
6 consuming photogenerated holes and/or oxygen, thus lowering the electron-hole recombination and/or  $\text{H}_2\text{-O}_2$  back  
7 reaction, i.e. the most important reactions for decreasing the light-to hydrogen conversion efficiency [60]. According to  
8 several literature reports [61-64] the photo performances gain using ethanol as scavenger is the lowest if compared to  
9 ethylene glycol and glycerol because of the different chemico-physical properties of the alcohols (e.g. number of  $\alpha\text{-H}$   
10 and OH groups, the proportion between carbon and hydroxyl groups number, alcohol polarity and their standard  
11 oxidation potentials). However, specific optimum concentration values were found for each organic compound. In the  
12 case of ethanol the increase of photo response is evident at the lowest investigated concentration (i.e. 5 vol.%) and then,  
13 according to the literature [65, 66] it stabilizes at higher concentrations. The same saturation effect is observed in the  
14 case of ethylene glycol. Besides, in the case of glycerol, the highest performances are obtained with very low  
15 concentrations of the sacrificial agent (i.e. 2 and 3 vol.%) while further concentration increase has adverse effect  
16 resulting in a photoresponse even lower (i.e.  $\gamma < 1$ ) than the pure KOH solution. This may be explained considering that  
17 the solution becomes very viscous which is expected to negatively affect light penetration and/or electrolyte  
18 transport/diffusion.  
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34 The bulk of the above results reveals a strong dependence of the photoelectrochemical performances on samples  
35 structure, morphology and multiscale organization, as well. A tentative explanation for the observed trends in  
36 photocurrent performances as a function of deposition pressure and annealing treatment can be proposed, in relation to  
37 the accessible active surface (depending on total surface area and thus on nanoscale porosity), carrier recombination  
38 (affected by degree of crystallinity and grain boundaries) and electrical transport (which is expected to depend on the  
39 film connectivity, vertical or quasi-1D morphology and crystallinity). As for morphology, we found that 5 Pa deposition  
40 pressure corresponds to an optimum condition for the film performance. More in particular, for samples annealed at  
41 500°C, the photocurrent response was found to increase by moving from 3 to 5 Pa  $\text{O}_2$  pressure, whereas there was a  
42 drastic decrease in performance associated with the samples deposited at higher  $\text{O}_2$  pressures, i.e. 10 and 15 Pa  $\text{O}_2$ . This  
43 trend can be ascribed to the peculiar morphology of PLD grown samples in the 3-15 Pa range. As previously discussed,  
44 the deposition background gas pressure strongly affects the  $\text{TiO}_2$  film growth mechanisms and its final porosity. In fact,  
45 while at the lowest pressure (i.e. 3 Pa) a 500 nm thick, dense and compact film develops, the increasing deposition  
46 pressure in the 5-15 Pa range allows a vertically oriented, quasi-1D organization (from a columnar-like to a hierarchical  
47 tree-like nanostructure) with structures reaching more than 1  $\mu\text{m}$  in length. As a consequence, since the same mass was  
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1 deposited for each sample, the increasing deposition pressure leads to a parallel decrease in film density, i.e. to an  
2 increase in film porosity and thus in the available active surface area. On this regard, it was found that the BET specific  
3 surface area of films deposited at 5 Pa O<sub>2</sub> after thermal treatment at 500 °C was around 25 m<sup>2</sup> g<sup>-1</sup>, with a pore size  
4 distribution in the range from a few nm to ~100 nm. This surface area value is representative also of films annealed at  
5 650 °C, since SEM shows that no significant change in morphology occurs at this temperature, while annealing at 800  
6 °C results in a strong coalescence and, presumably, in a strong decrease of the available surface.  
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8 In a previous work [32], it was shown that, as the deposition pressure increases, specific surface area increases while  
9 density decreases, so that the *roughness factor*, i.e. the ratio between the available material surface and the geometrical  
10 footprint of the film, has an optimum value for intermediate pressure conditions. In our case, by knowing film density,  
11 thickness and specific surface, it is possible to evaluate the roughness factor: in the case of films deposited at 5 Pa we  
12 calculated a *roughness factor* per unit thickness around 50 μm<sup>-1</sup> (i.e. 50 cm<sup>2</sup> of active surface for a film 1 μm thick and  
13 with a footprint of 1 cm<sup>2</sup>).  
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15 On this basis, it is not surprising that samples deposited at 3 Pa O<sub>2</sub> show a lower photoactivity. In fact, in order to  
16 achieve high photoelectrochemical performances, a large surface area is desired along with suitable electronic features  
17 (e.g. adequate band edge positions and rapid charge separation properties): however, in the case of sample deposited at  
18 3 Pa O<sub>2</sub> a compact TiO<sub>2</sub> film is obtained with small porosity (18%) and thus low surface area. Conversely, the enhanced  
19 performances observed for the sample deposited at 5 Pa O<sub>2</sub> could be reasonably ascribed to the larger surface area  
20 which entails the availability of an increased number active sites for the reaction. Moreover, it may be argued that a  
21 more open structure with vertical void channels, typical of quasi-1D nanomorphologies obtained with the increased  
22 deposition pressure, can offer the advantage of better electrolyte transport/diffusion allowing the whole surface to be  
23 active in the photoelectrochemical process.  
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25 On the other hand, the significant photoresponse decrease observed for samples deposited at the highest deposition  
26 pressures (i.e. 10 and 15 Pa O<sub>2</sub>) could be tentatively ascribed to the higher recombination losses as a consequence of the  
27 excessive thickness and more open morphology of tree-like structures, i.e. lack of connectivity (see the discussion  
28 below).  
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30 Once the structure/morphology of the material has been optimized, it was found that the increase of the film thickness  
31 does not correspond to a monotonic increase in the photocurrent, even though, of course, the total surface area  
32 increases. Possible explanations for this behaviour include non-optimized carrier transport for very high thicknesses. In  
33 addition, several reports focused on nanotubular TiO<sub>2</sub> photoanodes [67-70] or other TiO<sub>2</sub> nanostructures [20,71],  
34 reported the existence of a critical thickness value which has been explained as a result of an optimum balance between  
35 light absorption and charge carriers life-time. Accordingly, for films with low thickness as in the case of mass-0.5M  
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1 sample, the amount of the material is likely too low and the light absorption too weak as well, thus leading to low  
2 efficiencies. Otherwise, for films with too high thickness, as in the case of mass-2M sample, the long transport distance  
3 for charge carriers may lead to undesirable recombination phenomena. In addition, electrolyte mass-transport  
4 limitations could be invoked to explain the inefficiencies observed for the longer hierarchical treelike structures, e.g.  
5 leading to a minor electrolyte infiltration and limiting the true active surface only to the top part of the film.  
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9 Concerning the effect of thermal treatments, the increased photoelectrochemical performances observed for samples  
10 annealed at 650 °C can be related to the efficient sintering between nanoparticles, that can reduce amorphous regions or  
11 grain boundaries and consequently can ensure a slightly higher degree of cristallinity. This likely improves conductivity  
12 and charge transport and also favours a probable defect healing (e.g. at grain boundaries) which may reduce carrier  
13 recombination. On the contrary, for films annealed at 800 °C the reduction in active surface, resulting from the strong  
14 degree of coalescence, probably plays a major role, resulting in a negligible photocurrent.  
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18 As a final point, the photoresponse was further strengthened with the presence of organic sacrificial reagents who  
19 served as hole scavengers. In particular, the performance gain observed in the presence of very low amounts of glycerol  
20 is particularly attractive. In fact, glycerol is the major byproduct of biodiesel production and its photoelectrochemical  
21 re-utilization is of great industrial interest in order to improve the global biodiesel economy [72, 73].  
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## 32 **Conclusions**

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34 Quasi-1D and tree-like hierarchical nanostructured TiO<sub>2</sub> films were prepared by Pulsed Laser Deposition (PLD) and  
35 evaluated as potential photoanodes for the photoelectrochemical (PEC) water splitting reaction.  
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38 In particular, the photoelectrochemical responses have been discussed as a function of the different material  
39 morphologies and structures, which were tailored by varying the preparation conditions.  
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43 At first, samples were prepared by changing the oxygen pressure (in the range 3-15 Pa): it was found that film growth  
44 can be tuned at the nanoscale from compact/dense films to columnar/vertically oriented or hierarchical porous  
45 nanostructures. In relation to optimized values of density/surface area, cristallinity and electron transport, the best  
46 photoelectrochemical performances were associated with the sample prepared using 5 Pa of oxygen, which showed a  
47 photo-activity even higher (i.e. depending on thickness) than TiO<sub>2</sub> nanotubular arrays prepared by anodic oxidation, but  
48 presented a lower value of  $V^*$  at which the maximum electrical yield may be reached.  
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53 The effect of the variation in the mass of deposited material, that leads to an increased thickness of the catalytic layers,  
54 suggested the existence of an optimal thickness value that likely improves the electron transfer.  
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58 The study of the effect of the annealing temperature showed that the photoelectrochemical response increases for  
59 samples annealed at 650 °C, indicating the importance of cristallinity and structure connectivity.  
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1 The set of results indicates that the TiO<sub>2</sub> nanostructures prepared by reactive pulsed laser deposition (PLD) can be  
2 considered of practical interest for photoelectrochemical water splitting applications. In particular, open morphologies  
3 characterized by relevant nanoscale porosity and by a vertically oriented morphology have shown promising results  
4 achieving photocurrent efficiencies up to 8%, under UV irradiation.  
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6 Conversely, tree-like nanostructures (i.e. more open morphologies prepared at 10 and 15 Pa O<sub>2</sub>) showed lower PEC  
7 water splitting activities, possibly due to the occurrence of higher recombination losses as a consequence of their  
8 excessive thickness.  
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10 Eventually, the use of organic sacrificial reagents (i.e. ethanol, ethylene glycol or glycerol) has been proved to be  
11 exploitable to improve PLD photoanodes performances.  
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13 Further optimization of the material structure-morphology, and possible routes for enhancing the response to visible  
14 light (e.g. doping, sensitization) offer future opportunities for improving PEC water splitting devices based on  
15 nanostructured TiO<sub>2</sub> films prepared by Pulsed Laser Deposition.  
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**Figures captions**

**Fig 1.** SEM images of as deposited PLD grown  $\text{TiO}_2$  photoanodes produced with  $\text{mass}=0.5M$  and at different background gas pressure: a=3 Pa, b=5 Pa, c=10 Pa, d=15 Pa  $\text{O}_2$ .

**Fig 2.** Film density variation (black squares and dotted line) and the related film porosity (red circles and solid line) of as deposited PLD grown  $\text{TiO}_2$  photoanodes produced at different background gas pressure ( $\text{mass}=0.5M$ ).

**Fig 3.** SEM images showing the effect of thermal treatment on PLD grown  $\text{TiO}_2$  films deposited at 5 Pa and 10 Pa  $\text{O}_2$  ( $\text{mass}=0.5M$ ).

**Fig4.** Raman spectra: PLD grown film deposited at 5 Pa ( $\text{mass}=0.5M$ ), as deposited (a) and after annealing in air at 500 °C (b); annealed TNT photoanode (c).

**Fig 5.** SEM images of the annealed TNT photoanode: top-view (a); cross-view (b).

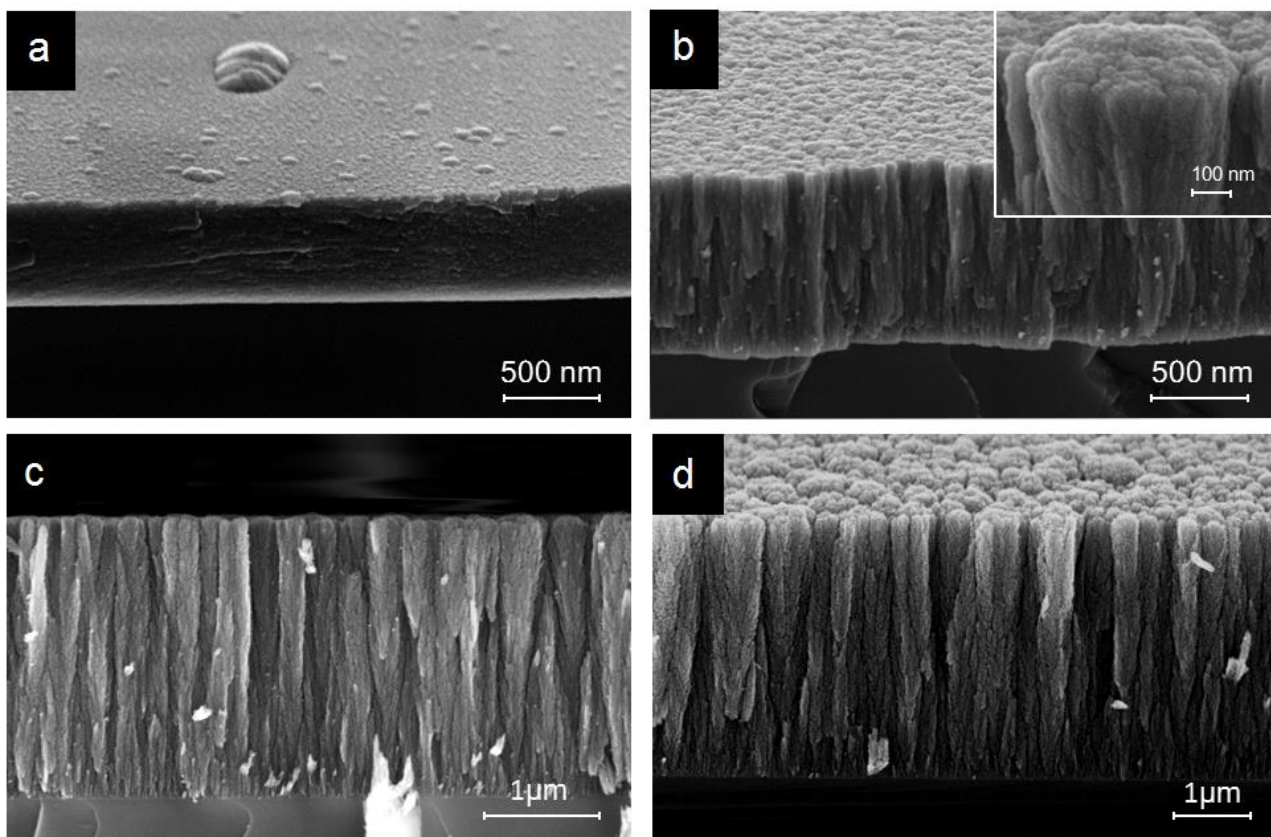
**Fig 6.** Current-potential response of the PLD grown  $\text{TiO}_2$  photoanode produced at 5 Pa pressure and annealed at 500 °C ( $\text{mass}=0.5M$ ) in the dark and under illumination.

**Fig 7.** Photoelectrochemical behaviour for PLD grown  $\text{TiO}_2$  photoanodes produced at different background pressure and annealed at 500 °C (White bars:  $\text{mass}=0.5M$ ; Brown bars:  $\text{mass}=M$ ; Gray bars:  $\text{mass}=2M$ ). a: photopotential on-set; b: photocurrent densities measured at 0.5 V.

**Fig 8.** Photoconversion efficiency as a function of the applied potential. a: Effect of the background pressure for the PLD grown  $\text{TiO}_2$  photoanodes annealed at 500 °C ( $\text{mass}=0.5M$ ); b: Effect of thickness for the PLD grown  $\text{TiO}_2$  photoanodes produced at 5Pa (annealing temperature = 500 °C) and photoconversion efficiency for the TNT photoanode); c: Effect of thickness for the PLD grown  $\text{TiO}_2$  photoanodes produced at 3 Pa (annealing temperature = 500 °C); d: Effect of the background pressure for the PLD grown  $\text{TiO}_2$  photoanodes annealed at 650 °C ( $\text{mass}=0.5M$ )

**Fig 9.** Photoelectrochemical behaviour for the PLD grown  $\text{TiO}_2$  photoanodes produced at different background pressure and annealed at 650 °C (With bars) and 800 °C (Black bars): photocurrent densities measured at 0.5 V.

**Fig 10.** Photoelectrochemical behaviour in the presence of organic sacrificial reagents in terms of performance gain  $\gamma$  evaluated as ratio between the photocurrent values obtained 0.5 V with and without the organics as a function of their volume fraction (PLD grown TiO<sub>2</sub> photoanodes deposited at 5 Pa (mass= $M$ ) and annealed at 500 °C)



**Fig 1.**



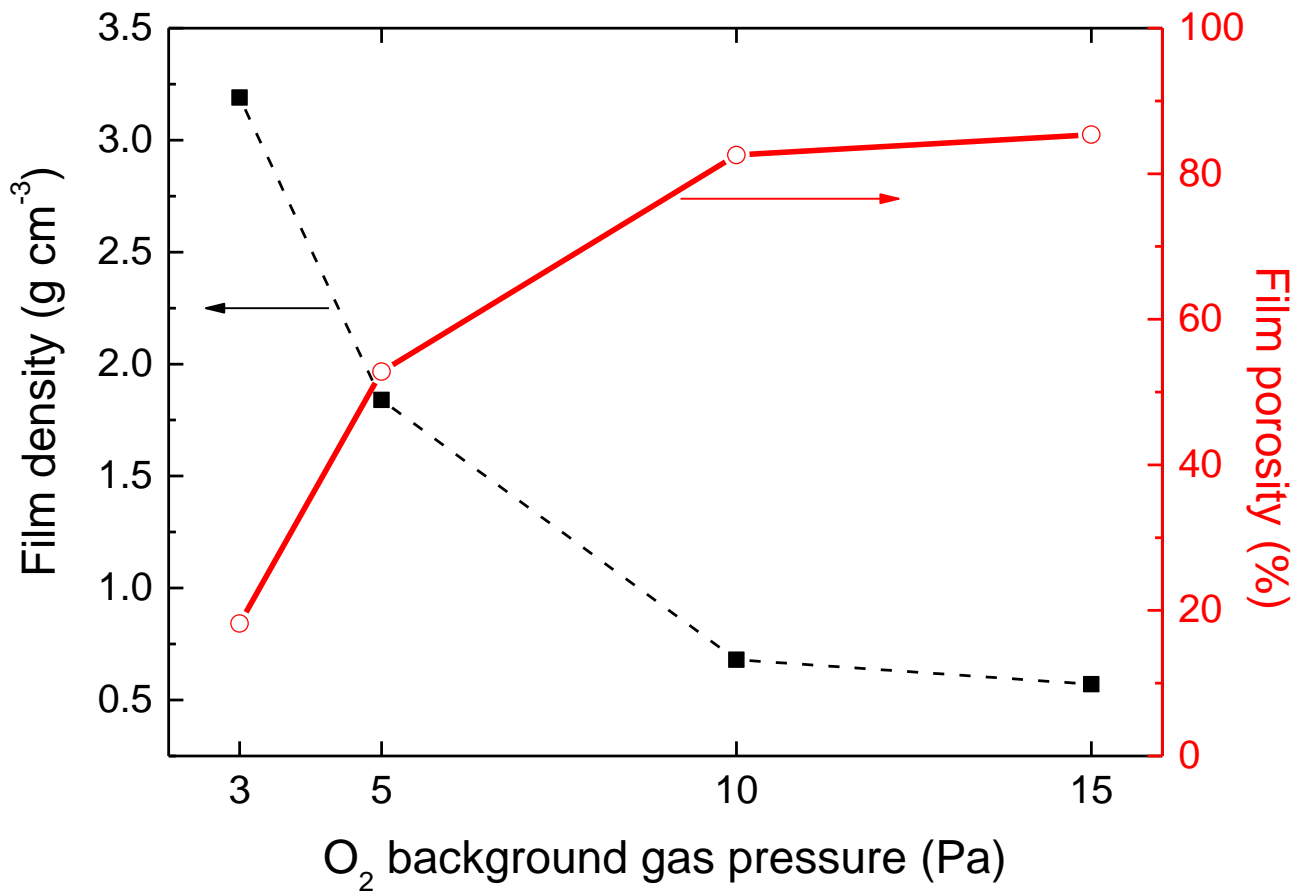
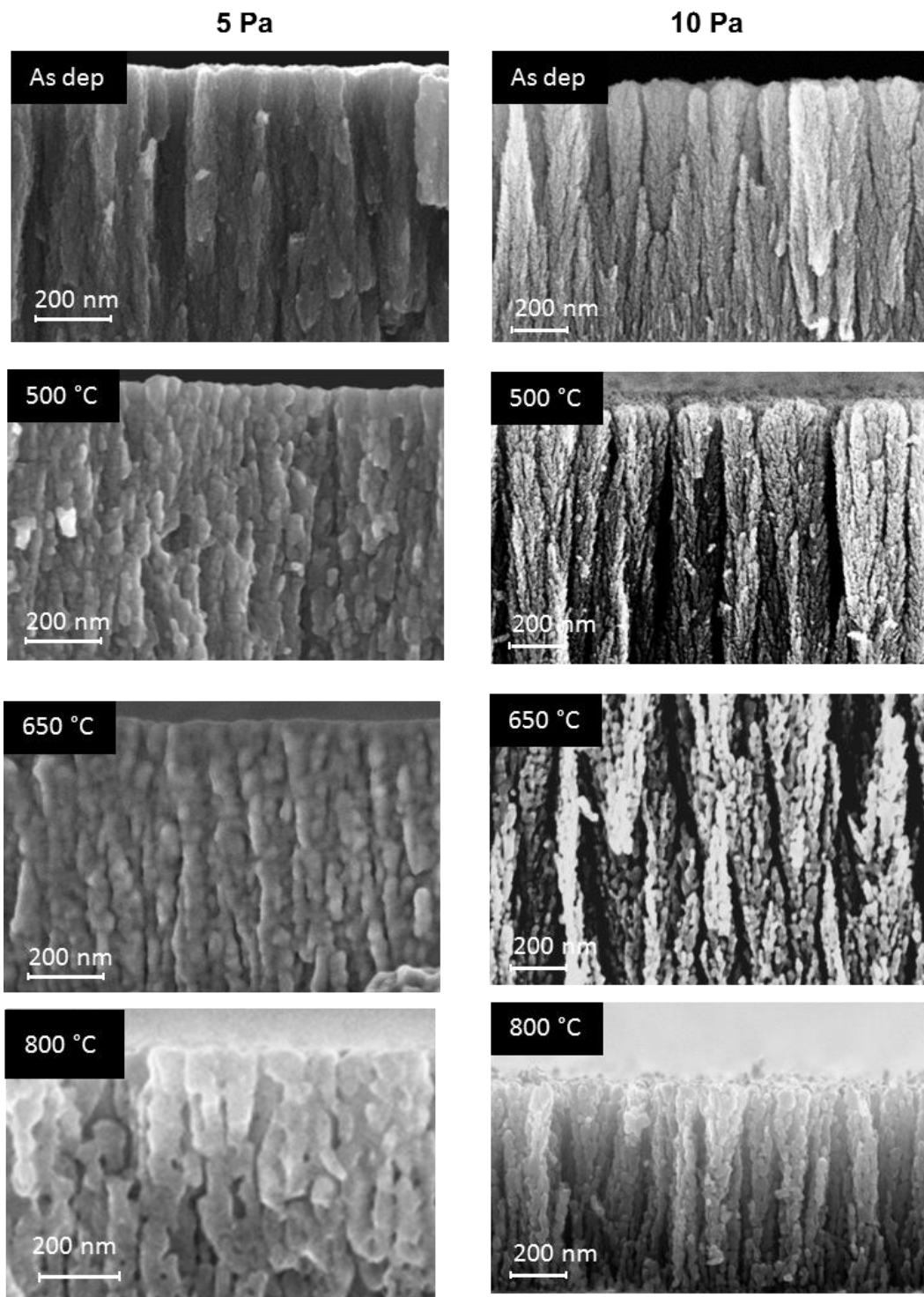


Fig 2.



**Fig 3.**

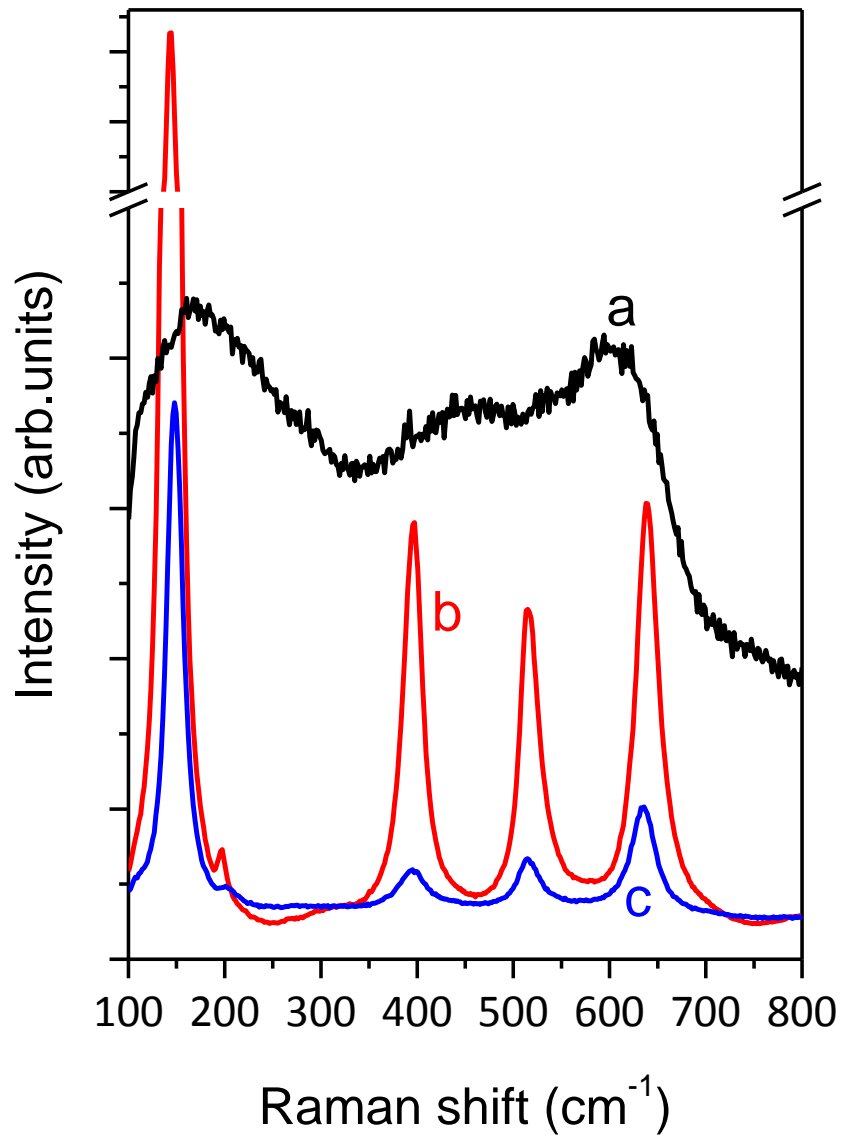


Fig 4.

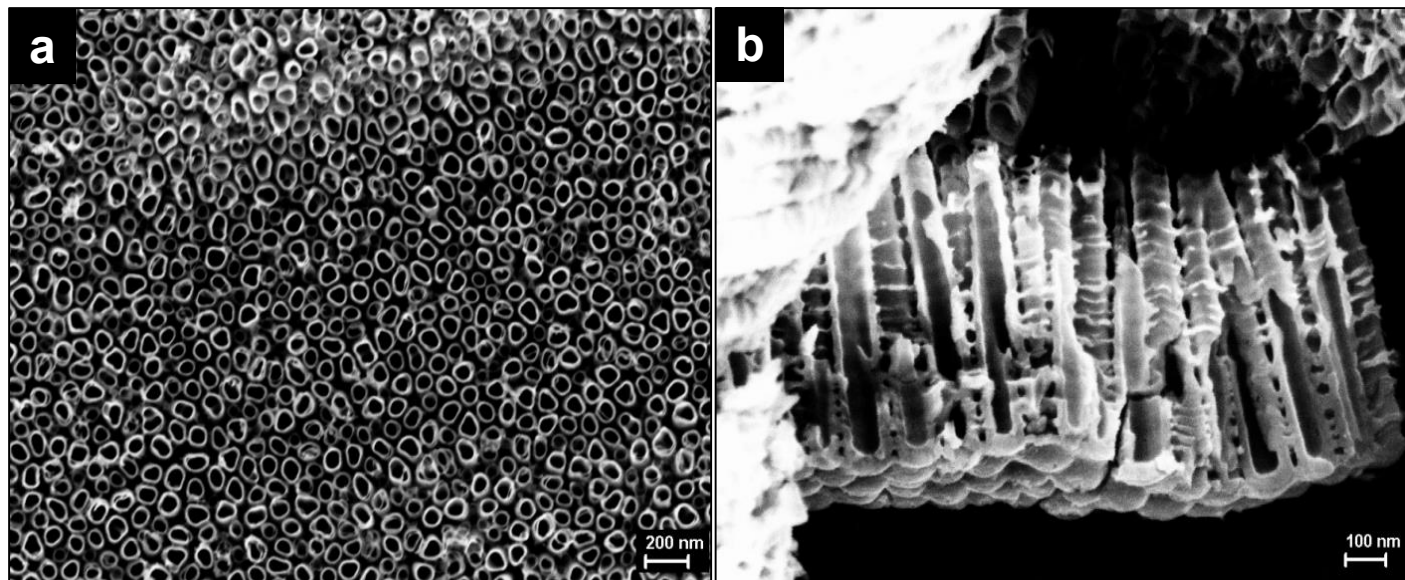


Fig 5.

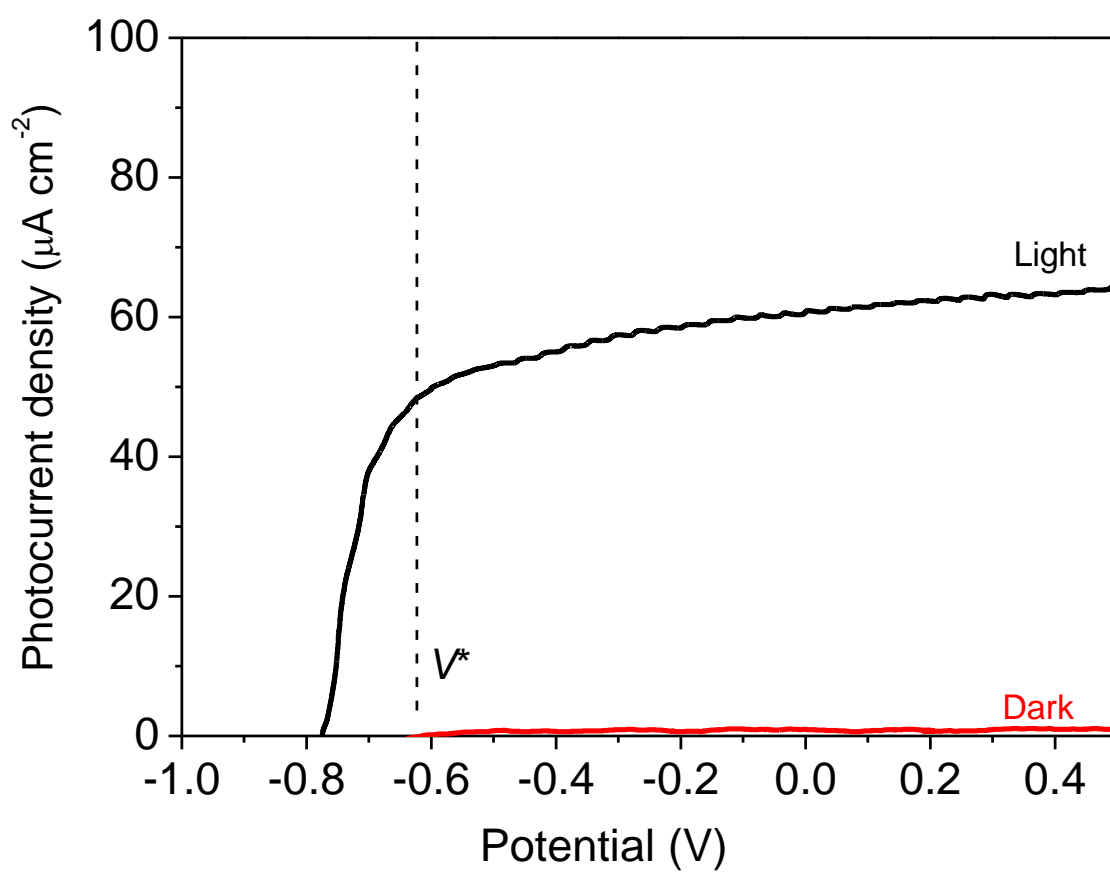
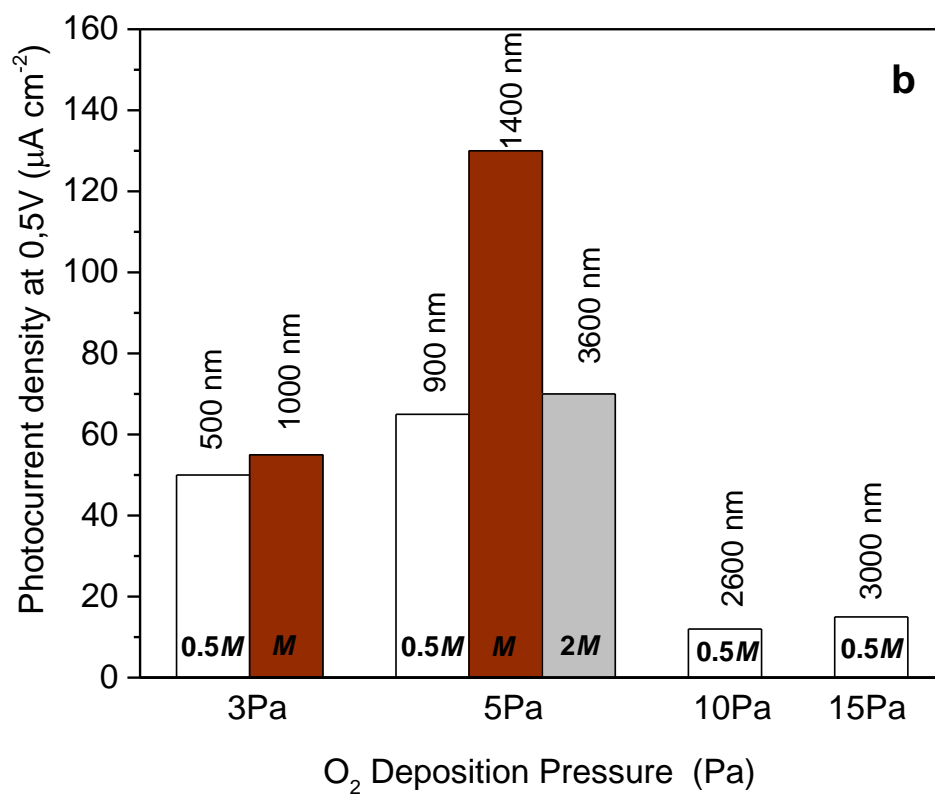
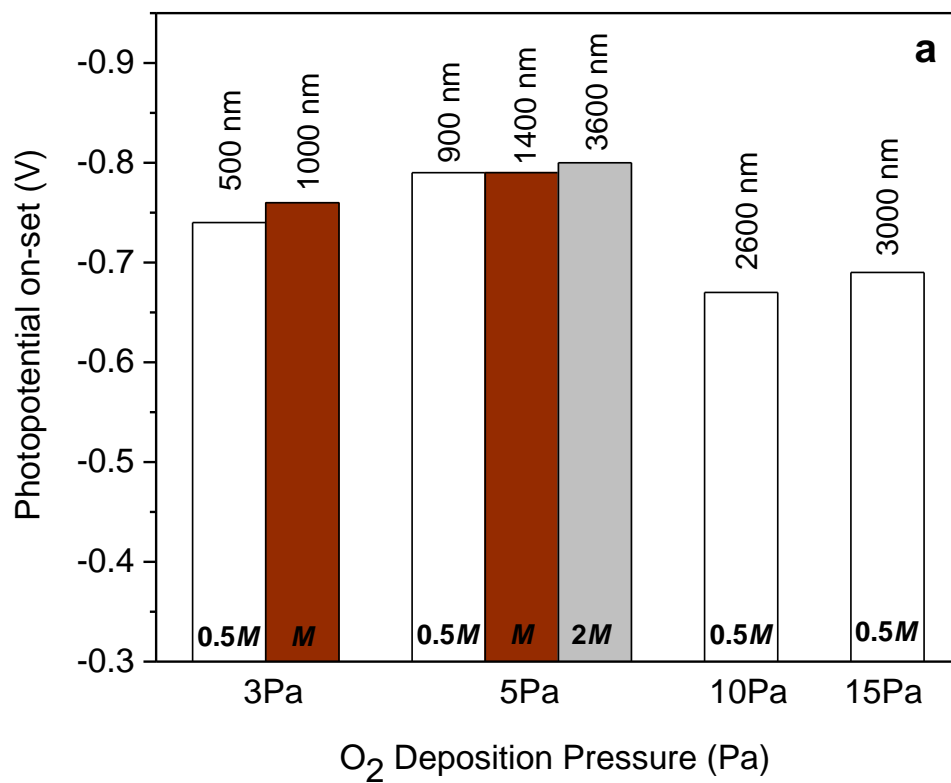
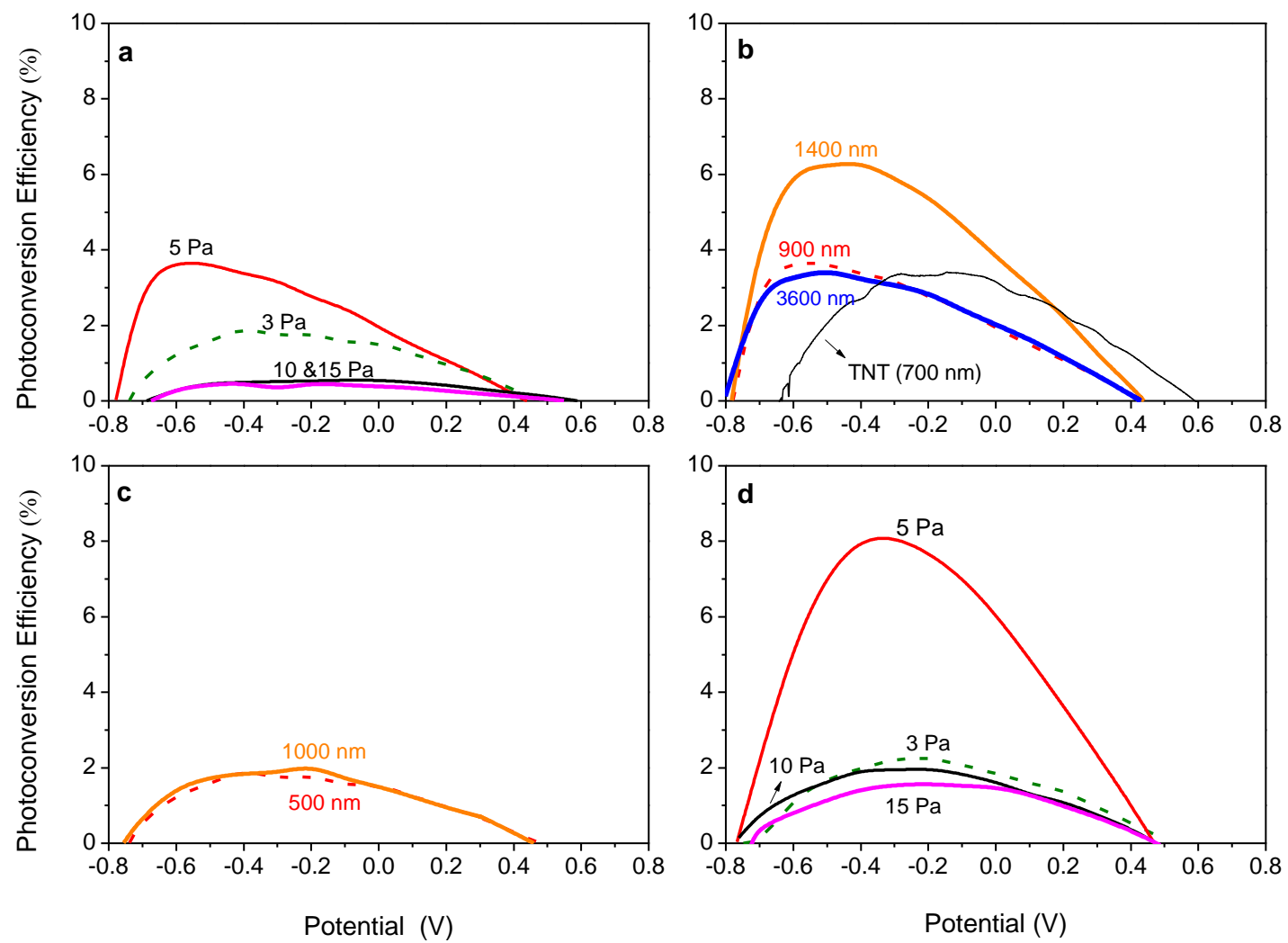


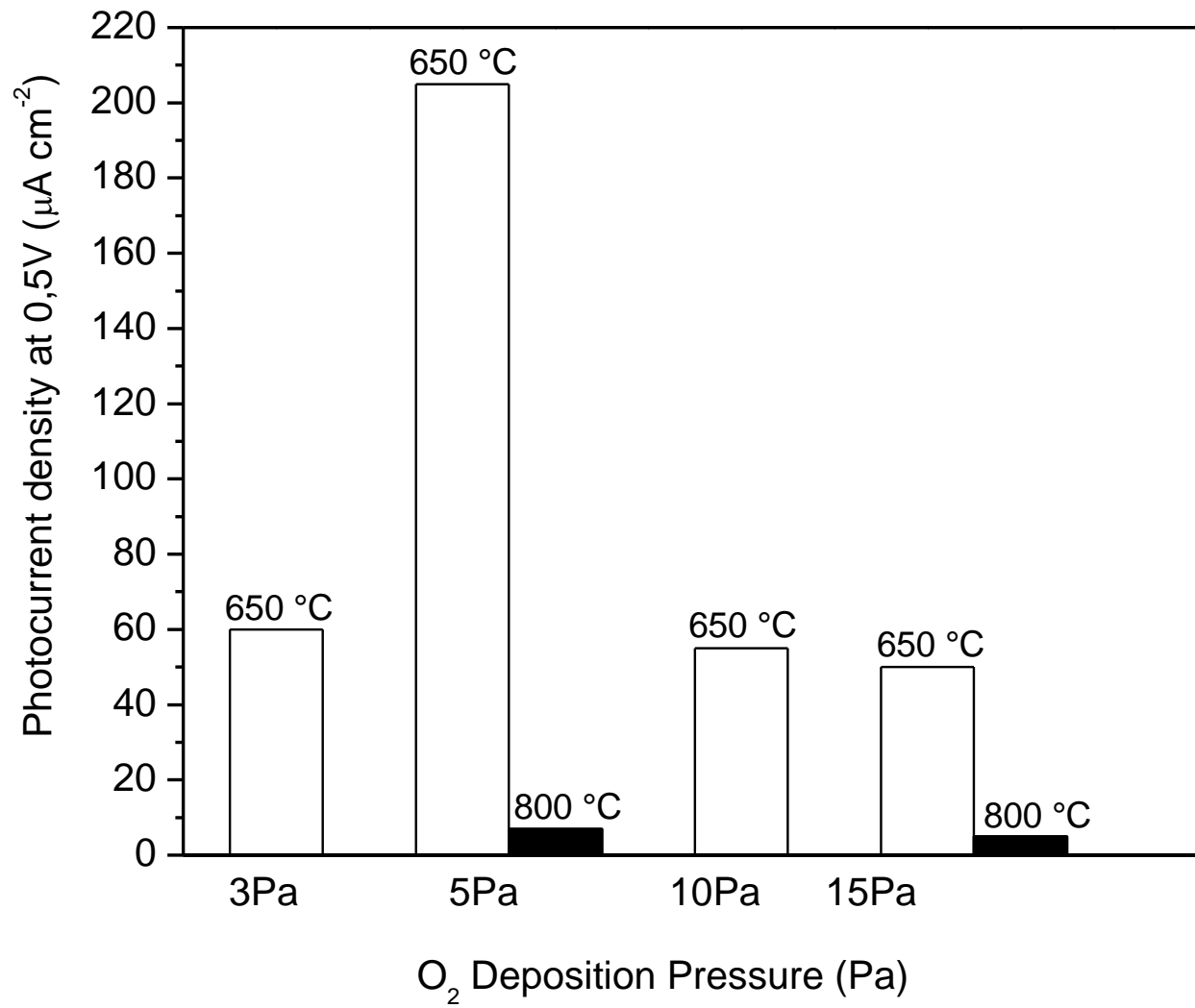
Fig 6.



**Fig 7.**

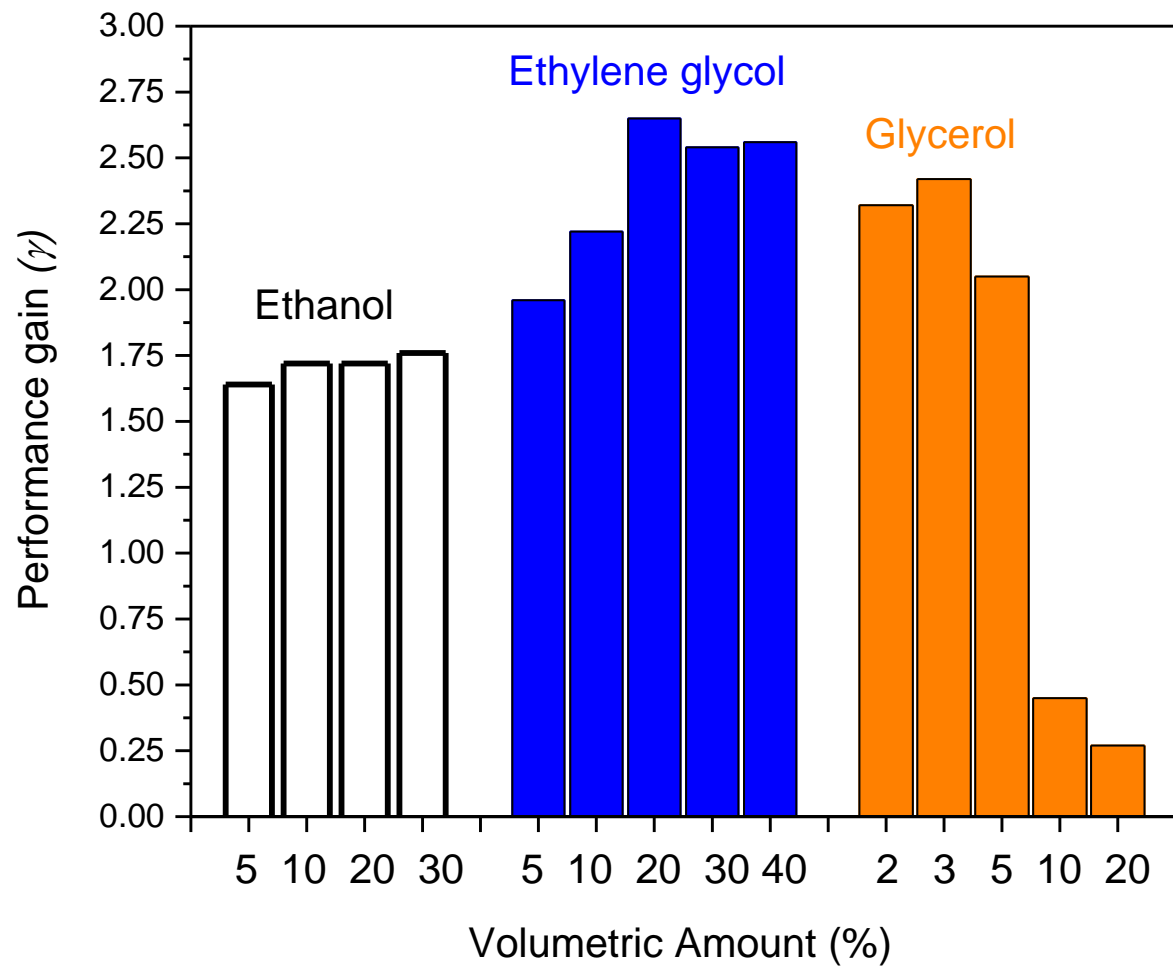


**Fig 8.**  
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**Fig 9.**  
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**Fig 10.**



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**Milan, May 3<sup>rd</sup>, 2017**

## **Reviewer responses**

Dear Editor, we would like to thank you for the opportunity to submit a revised copy of our manuscript, and the reviewers for their useful comments. It is our belief that the quality of manuscript will substantially benefit from the review process.

The paper has been thoroughly revised according to the Reviewers' indications, as discussed in the following, where the Reviewers' comments are italicized, while our responses are shown in regular font. Major changes and additions to the original text are highlighted in yellow in the revised manuscript

### **Reviewer #1**

*This manuscript deals with the synthesis of titanium dioxide by using pulsed laser deposition technique. Different amounts of material were analyzed, including film density and thickness. The obtained semiconductors were used for water splitting reaction in alkaline conditions. The materials were also characterized by RAMAN spectroscopy and SEM microscopy. Although the results are interesting, some comments are made here before a possible publication in the Journal of Solid State Electrochemistry...*

*a) It is true that, as stated from the authors, the morphology has an important role in the redox process. Nevertheless, from my point of view, no more fundamental or detailed analysis is presented in the manuscript. In this context, experimental analysis from electrochemical impedance spectroscopy (EIS) could be of major impact in order to understand the surface state of the materials in study during polarization and as a function of pressure deposition or oxygen atmosphere. Also, EIS could give important information concerning the surface-state linked with structural modifications during synthesis, and during dark and illumination conditions, and with the impact in the band gap alteration.*

**ANSW:** we agree with the reviewer's suggestions. Accordingly, we have performed additional EIS and CV experiments, both under dark conditions and under illumination, in order to gain information on the effect of the preparation conditions variation (i.e. oxygen deposition pressure) and hence of the PLD samples morphology on their electrochemical and photoelectrochemical behavior. The results are reported in the new Figures 6, 7, 10 and Tables 1, 2 in the revised version of the manuscript. Experimental and Results/Discussion Sections have been modified accordingly (Major changes: p. 6, lines 28-31; p. 7, lines 1-7; p. 9, lines 24-31; p 10. lines 1-30; p. 11 lines 9-16; p. 13 lines 1-13 of the revised version).

b) On the other hand, the authors also put in clear that the area of the material is important for water splitting reaction. However, no calculations of the electrochemical active surface area (ECSA, obtained (for example) from the current versus potential characteristic in a quasi-reversible system as a function of scan rate) is presented here. This information could also be of major impact as ECSA is highly linked with morphology and structural properties, even as a function of heat-treatment temperature... or pH...

**ANSW:** indeed, the effect of morphology on the capacitive performance of PLD samples was investigated through CV measurements as a function of scan rate and the results have been included in a previous work. Anyway, in line with the referee's observation, we have now improved the discussion by citing and considering also the previously published results (p. 11, lines 1-7 of the revised version).

c) The authors establish that "...the efficiency increases at low potential bias, reaching a maximum, and then begins to decrease at higher applied bias." Why this decrement in the current is observed...??? This situation should be explained in detailed form. In this context, the authors indicated that "... the optimal working potential, at which the process could be carried out" ... what is the induced-electrochemical "process" ...? Please, should be more specific...

**ANSW:** The manuscript has been modified to better describe the efficiency results (p. 13 lines 28-30; p. 14 lines 1-4 of the revised version).

Please is not the "electrolyte" but ions that move to or from the electrode-electrolyte interface...

**ANSW:** The text has been corrected accordingly.

## **Reviewer #2**

*This paper is devoted to find the correlation between structural/morphological properties of TiO<sub>2</sub> photoanodes fabricated by PLD and photoelectrochemical behavior for water splitting applications. By investigating the effect of the variation of preparation conditions, such as O<sub>2</sub> pressure (3-15 Pa), deposited TiO<sub>2</sub> density (0.5-2 M) and thickness (500-3600 nm), thermal treatment temperature (500, 650, 800 °C), optimized synthesis parameters were identified. However, before its publishing in Journal of Solid State Electrochemistry, some important problems for the provided results need still to be resolved or clarified.*

*1. Crystalline structure characterizations. In a common sense, remarkable evolution of rutile TiO<sub>2</sub> can be expected at high temperatures close to 800 °C. But for the 3 and 5 Pa PLD films, only anatase was detected in Raman spectra. So, it is very necessary to show the XRD results for support the related discussion in the text. On page 8, line 45-59, it seems that XRD measurements were done, but the XRD results were not shown. Moreover, in Fig. 4, not only the Raman spectra for 500°C annealing TiO<sub>2</sub>, but also that for 650 and 800 °C should be shown.*

*The correlation between annealing temperatures and crystalline structures, and therefore, that between crystalline structures and photoelectrochemical performances, need to be further clarified.*

**ANSW:** The reviewer's comments have been taken into account in the revised version of the manuscript where the Raman analysis of the crystalline structure of all the PLD samples has been discussed more in details (p. 9, lines 1-15). Accordingly, Figure 4 has been modified by showing Raman spectra for the film grown at 5 Pa O<sub>2</sub>, representative of a more compact morphology, and for the film grown at 10 Pa O<sub>2</sub>, with a more open morphology, both for as deposited films and after annealing at 500, 650 and 800°C (i.e. all the investigated temperatures). Of note, the samples grown

at 3 and 15 Pa showed a behavior very similar to those grown at 5 and 10 Pa, respectively. For this reason the results are not shown in the figure but they are discussed in the text.

Furthermore, as already reported in the text, the results of the Raman analysis are in agreement with previous XRD characterizations performed over TiO<sub>2</sub> films prepared under similar experimental conditions. A comment on this point has been better included in the revised version of the manuscript (p. 9, lines 16-17).

Finally, in line with the reviewer's suggestions, the effect of the crystalline structures on photoelectrochemical performances have been discussed in the revised version of the manuscript (p.17, lines 28-31).

*2. Comparison with nanotubular TiO<sub>2</sub>. For this comparison, the annealing temperature should have been equal for PLD and nanotubular TiO<sub>2</sub>. But at present, PLD TiO<sub>2</sub> films were annealed at 500, 650, 800 °C, and nanotubular TiO<sub>2</sub> was annealed at 400°C, which makes it lack of comparability. Again, it should be considered the effect of crystalline structures on photoelectrochemical performances.*

**ANSW:** We agree with the reviewer's comment. Indeed, PLD and nanotubular TiO<sub>2</sub> samples were annealed at different temperatures. However, previous results [see Ref. 34] clearly showed that the crystalline structure of PLD films annealed at 500°C is completely comparable with that of the samples annealed at 400°C (i.e. the same annealing temperature of the nanotubular TiO<sub>2</sub> sample). Accordingly, we strongly believe that the comparison between PLD and TNT photoanodes is fully reasonable. To better address this point, this has been specified in the revised version of the manuscript (p. 9, lines 17-19).

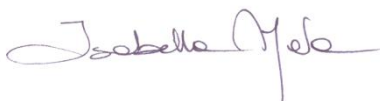
*3. Photoelectrochemical characterizations. It is highly recommended to show the originally measured data in a paper. However, in this paper, most photoelectrochemical results (Figure 6-10) are shown indirectly, as is seen, only one photocurrent-potential curve was shown in Figure 6. So, some essential photocurrent-potential curves need to be presented.*

**ANSW:** According to reviewer's suggestion most of the photocurrent results have been reported in Figure 8 in the revised version of the manuscript. Discussion has been modified accordingly.

We wish to thank the Reviewers for their careful examination of our manuscript, and look forward to further communications.

With kind regards

Isabella Nova



[Click here to view linked References](#)

1 **Preparation and optimization of TiO<sub>2</sub> photoanodes fabricated by pulsed laser deposition for**  
2 **photoelectrochemical water splitting**

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## 1 Abstract

1  
2 2 Quasi-1D TiO<sub>2</sub> nanostructures prepared by Pulsed Laser Deposition (PLD) are tested as photoanodes for  
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4 3 photoelectrochemical water splitting application and compared with TiO<sub>2</sub> nanotube arrays prepared by anodic  
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6 4 oxidation. PLD TiO<sub>2</sub> films with controlled structure and morphology ranging from compact to vertically oriented or  
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8 5 hierarchical porous nanostructures are deposited by ablating a TiO<sub>2</sub> target with ns UV laser pulses in the presence of O<sub>2</sub>  
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10 6 background atmosphere at different pressures. Thermal treatments at different temperatures are used to transform the  
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12 7 so-obtained amorphous systems into nanocrystalline structures (mainly anatase). The effect of film density and  
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14 8 thickness are also considered by depositing different amounts of material per unit surface. The morphology and the  
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16 9 phase composition of the samples are characterized by SEM and Raman Spectroscopy, while the photoelectrochemical  
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18 10 water splitting performances are investigated by monitoring the photocurrent generated under illumination in a three-  
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20 11 electrode cell. Voltammetric scans and EIS analysis were also used to correlate the morphology of PLD samples with  
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22 12 their electrochemical properties and their working mechanism in the absence and presence of a light radiation. A clear  
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24 13 correlation between structural/morphological properties and photoelectrochemical behavior is found and ideal values of  
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26 14 the synthesis parameters are identified, which allow the identification of the optimal quasi-1D nanoporous morphology  
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28 15 for water splitting applications. The use of sacrificial organic reagents as hole scavengers was also considered to  
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30 16 improve the photoelectrochemical performance of the samples.

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## 50 Keywords

51 26 Photoelectrochemical water splitting, TiO<sub>2</sub>, nanostructured materials, quasi-1D/hierarchical nanostructures, Pulsed  
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53 27 Laser Deposition, sacrificial agent  
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# 1 Introduction

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3 2 In recent years, the increasing environmental concerns and the rising energy demand have led to focus the attention on  
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5 3 new and sustainable sources of energy. Many efforts are underway to develop ecologically clean technologies based on  
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7 4 the applications of hydrogen as a fuel instead of fossil fuels [1,2]. In this context, the production of hydrogen by  
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9 5 photocatalytic water splitting using solar energy represents a promising way to provide a clean and renewable energy  
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11 6 resource [3-6].

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13 7 In the 1970s Fujishima and Honda [7] reported for the first-time water splitting into H<sub>2</sub> and O<sub>2</sub> with a TiO<sub>2</sub> photoanode  
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15 8 via the so-called photoelectrochemical (PEC) approach. The typical PEC cell consists of a semiconductor photoanode  
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17 9 (e.g. TiO<sub>2</sub>) and a metal counter electrode (usually Pt) which are connected through an external load. Photo-irradiation of  
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19 10 the anode results in the formation of charge carriers (electron-hole pairs): the holes oxidize water to form O<sub>2</sub> on the  
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21 11 anode while the electrons are channelled through the external circuit towards the cathode, where they reduce water to  
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23 12 form H<sub>2</sub>. Often, when the energetics of photoanode or cathode are not suitable for the process, an external voltage or  
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25 13 chemical bias (i.e. by  $\Delta pH$ ) needs to be applied to effect water splitting [3].

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27 14 Despite other metal oxide semiconductors, also with rather complex structures, have been investigated in PEC  
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29 15 applications, TiO<sub>2</sub> still remains the most investigated photocatalyst because of its activity, low-cost, non-toxicity and  
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31 16 chemical stability (i.e. corrosion-resistance) [8,9]. Unfortunately, the industrial exploitation of photocatalytic hydrogen  
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33 17 production via water splitting over TiO<sub>2</sub> is still limited, the major problems being a poor activation by visible light and  
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35 18 the low quantum efficiency of the process, also related to the high degree of recombination between the photogenerated  
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37 19 charges carriers (electron-hole pairs) [10]. In this regard, various strategies have been proposed to improve the PEC  
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39 20 performance of TiO<sub>2</sub>, such as TiO<sub>2</sub> doping/sensitization to enhance visible light absorption [4,5,11-13], or controlling  
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41 21 photocatalysts structure and morphology to enhance the active surface, to increase light harvesting and to minimize  
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43 22 electron trapping and recombination probabilities [13,14].

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45 23 In the latter case, several nanostructured TiO<sub>2</sub> networks (e.g. tubes [15-17], rods [18-20], wires [21,22], sponges  
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47 24 [23,24]) emerged as promising materials that can be used as photoanodes in water photoelectrolysis cells. In particular,  
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49 25 as summarized in very recent reviews [25-30], extensive research has been performed on TiO<sub>2</sub> nanotube arrays (T-NTs)  
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51 26 because their unique high surface-to-volume ratios (even though not as high as those obtained with nanoparticle  
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53 27 assemblies), ordered geometry and tunable morphologies are claimed for fast charge separation and transport, and  
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55 28 **electrolyte ions diffusion** as well.

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57 29 Recently, novel 3-D architectures consisting of quasi-1D hierarchical nanostructures have received attention for direct  
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59 30 solar energy conversion, because of their advantages in combining (i) large surface area, (ii) light scattering due to the  
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1 presence of features of size comparable to visible wavelengths, (iii) mesopores for **diffusion** of molecules (e.g.  
2 **electrolytes ions** in the case of photoelectrochemical solar cells, pollutants or reagents in the case of photocatalysis), and  
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4 also (iv) anisotropic morphology (similarly to nanotubes or nanowires) to ensure better electron transport towards the  
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6 electrical contact [31,32]. Such structures, characterized by multiscale features or self-affine morphologies over  
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8 different length scales (from the nano- to the micro-scale) through low energy assembling of fine nanoparticles, can be  
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10 produced by carefully tuning the plasma expansion dynamics in a Pulsed Laser Deposition (PLD) process [33-36]. In  
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12 particular, nanocrystalline tree-like TiO<sub>2</sub> hierarchical structures prepared by reactive PLD have been proposed for  
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14 application in dye-sensitized solar cells (DSSCs), showing long electron lifetime with respect to back recombination  
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16 and high performances in terms of ion liquid electrolytes diffusion [31]. Improved light harvesting has been observed  
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18 even when hierarchical photoanodes were employed in solid state (polymeric) DSSCs [32]. Moreover, the potential  
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20 photocatalytic efficacy of such quasi-1D, hierarchical TiO<sub>2</sub> architectures has been proved in the mineralization (i.e.  
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22 oxidation) of stearic acid, as a model molecule [34].

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24 In this work, by exploiting the versatility of the PLD deposition process, we focus on the potential of vertically oriented  
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26 assemblies of TiO<sub>2</sub> nanoparticles as photoanodes for the photoelectrochemical water splitting process. In particular, the  
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28 existing correlations between structural/morphological properties and photoelectrochemical behaviour are analysed with  
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30 the aim of identifying the optimal structures for water splitting applications.

31  
32 A preliminary assessment of the suitability of structures prepared by PLD for photoelectrochemical water splitting was  
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34 synthetically presented in a previous communication [37]: herein, we aim at a more detailed and comprehensive  
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36 investigation of the effect of the variation of the preparation conditions (i.e. pressure, deposited mass and annealing  
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38 temperature), in order to deep inside the effect of crystalline structure and morphology (i.e. porosity and thickness),  
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40 ranging from compact to vertically oriented or hierarchical nanostructures, and the photoelectrochemical behaviour,  
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42 which is evaluated **through photocurrent tests, voltammetric scans, and electrochemical impedance spectroscopy (EIS)**  
43  
44 **analysis**. Moreover, the behaviour of a TiO<sub>2</sub> nanotubular (i.e. a model vertical-oriented and non-hierarchical  
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46 nanostructure) photoanode, prepared by anodic oxidation, is also considered for comparison purposes. Finally, the  
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48 performances of the PLD grown photoanodes are here investigated in the presence of glycerol, ethylene glycol and  
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50 ethanol which are used as model organic sacrificial reagents to improve the PEC performances. In fact, from a practical  
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52 point of view, photo-reforming of organic solutions instead of photo-cleavage of pure water looks more advantageous  
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54 because most water pollutants are organics, and in this way hydrogen production can be usefully combined with the  
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56 purification of water [38]. Moreover, it has been demonstrated that under favourable conditions and in the presence of  
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58 O<sub>2</sub>, photoelectrochemical (PEC) cells can act as Photofuelcells (PFC), consuming an organic substance (i.e. the fuel),  
59  
60 and utilizing light energy to produce electricity [39].  
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# 1 Experimental

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## Synthesis of TiO<sub>2</sub> photoanodes

TiO<sub>2</sub> nanostructured films have been deposited at room temperature by ablating a TiO<sub>2</sub> target with UV ( $\lambda=266$  nm) laser pulses from a frequency quadrupled Nd:YAG Q-switched laser with a pulse duration of about 5-7 ns. The laser fluence on the target was set at about 2.5 J cm<sup>-2</sup> with a spot size of about 3 mm<sup>2</sup>. The ablation was performed in the presence of a fixed background gas pressure of pure oxygen (99.999%) which was varied in the 3-15 Pa range to control the material structure/morphology. Silicon, glass and Ti were used as substrates mounted on an off-axis rotating sample holder at a fixed target-to-substrate distance of 50 mm. TiO<sub>2</sub> films deposited on silicon and glass substrates were used for SEM and Raman characterization while those deposited on Ti for photoelectrochemical experiments (see below). Further details on the PLD experimental setup and procedures are reported in previous works [32-34]. In particular, those results demonstrated that the structure and morphology of TiO<sub>2</sub> films deposited by PLD can be tuned by controlling the pressure of the background gas, while other parameters, such as the target-to-substrate distance, the laser fluence and the gas flux have been previously set [33].

Ti plate substrates for photoelectrochemical measurements were masked to deposit on a 2x1 cm<sup>2</sup> area and to leave a clean surface for electrical contacts. All the substrates were kept at room temperature and no substrate heating was observed during deposition. The deposited mass per unit surface was measured by a quartz crystal microbalance at the same position as the substrates. In order to study the influence of thickness, films with a different mass per unit surface were deposited, i.e. 0.5*M*, *M* and 2*M* (where *M* is about 0.3-0.4 mg cm<sup>-2</sup>), keeping constant the oxygen partial pressure during deposition (5 Pa). Post deposition thermal annealing processes were performed for 2 hours in air in a muffle furnace at 500 °C, 650 °C and 800 °C to induce crystalline order. In fact, as well known in literature [5,25,28], a high degree of crystallinity has positive effects on water splitting activity, mainly due to a decrease of defect concentration which reduces recombination between photogenerated carriers.

For comparison purpose, a TiO<sub>2</sub> nanotubes photoanode (TNT) was prepared through an electrochemical anodization method already tested in previous works [16, 40]. Briefly, starting from Titanium foil (0.25 mm thick, 99.7% metal basis, Aldrich) which was preliminarily degreased, the anodization was performed in water/glycerol solution containing NH<sub>4</sub>F (Glycerol/H<sub>2</sub>O 80:20 vol.% + 0.1 M NH<sub>4</sub>F). A potential ramp was applied from open-circuit voltage (OCV) to a fixed potential (20 V) with a scan rate of 100 mV s<sup>-1</sup>; then, the applied potential was maintained at this fixed value for 3 h. After oxidation, the sample was rinsed in deionized water, dried in a nitrogen stream and subsequently thermally treated in air at 400 °C for 1 h.

## 1 Morphological and structural characterization

2 PLD grown films morphology was observed with a ZEISS Supra 40 FEG-SEM without any sample preparation. SEM  
3 analyses (top view and cross sectional) were performed on TiO<sub>2</sub> films obtained on silicon substrates. Film density was  
4 evaluated by combining information on the deposited mass per unit surface with thickness measurements by cross-  
5 sectional SEM images ( $\rho_{\text{film}} = M h^{-1}$  where  $M$  is the mass/cm<sup>2</sup> and  $h$  is the film thickness). The porosity of the systems  
6 has been then estimated as percentage of voids and evaluated from the ratio between film density and bulk anatase  
7 density ( $1 - \rho_{\text{film}}/\rho_{\text{bulk}}$ ), with  $\rho_{\text{bulk}} = 3.9 \text{ g cm}^{-3}$ .

8 The crystalline structure of the PLD films obtained from TiO<sub>2</sub> on glass/silicon was characterized by Raman  
9 spectroscopy using a Renishaw InVia micro Raman spectrometer with 514.5 nm laser excitation wavelength. The laser  
10 power on the sample was low enough (1 mW) to avoid laser induced modifications during measurements.

11 In order to evaluate the specific surface area of a representative PLD sample annealed at 500 °C, a deposition at 5 Pa O<sub>2</sub>  
12 on a large area Al foil (corresponding to a deposited mass of several mg) was also performed. The surface area was  
13 determined by N<sub>2</sub> adsorption–desorption at -196 °C with the BET method using a Micromeritics TriStar 3000  
14 instrument.

15 TNT photoanode was also characterized by SEM and Raman spectroscopy.

## 16 Electrochemical and photoelectrochemical characterization

17 All the electrochemical and photoelectrochemical experiments were performed in a three-electrode cell in which a  
18 Ti/TiO<sub>2</sub> photo-anode (working area of 1 cm<sup>2</sup>) was used as the working electrode, a platinum grid as the counter  
19 electrode, and a saturated calomel electrode (SCE) as the reference: all the values of potential in the text are referred to  
20 SCE.

21 Depending on the runs, irradiation of the samples was guaranteed by a 300-W Xe lamp (Lot Oriel) equipped with  
22 suitable filters to select the right wavelength, or by a tungsten filament and a high-pressure UV-vis lamp (Osram Ultra-  
23 Vitalux, 300 W) with a main emission line in the UV region near 360 nm [41-43]. The average UVA/UVB (280-400  
24 nm) power light density, striking on the electrodes surface, was measured by a light meter HD2302.0 (Delta OHM);  
25 average values in the range from 1000 and 1350  $\mu\text{W cm}^{-2}$  were measured, depending on the relative position of the  
26 sample, with respect to the light source.

27 Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were performed for PLD  
28 samples deposited at 3, 5 and 10 Pa annealed at 500°C with constant deposited mass per unit surface (0.5M), in order to  
29 investigate the effect of their different morphology on the mechanism of charge transfer at the semi-  
30 conductor/electrolyte interphase. EIS measurements were performed in KOH 0.1M solutions in a frequency range from  
31

1 100 kHz to 0.1 Hz with a frequency response analyzer (FRA, Model 7200 AMEL) coupled with a potentiostat (AMEL  
2 7050). The runs were conducted both in the dark and under illumination at 365nm wavelength.. EIS data were  
3  
4 quantitatively interpreted by the equivalent circuit approach. Zassist and ZSimpWin software packages were used to  
5  
6 perform impedance experiments and data manipulation, respectively.

7  
8 CV measurements were performed without illumination in a nominal range of potential from 0.4V to -1,4 V, in (0.1M)  
9  
10 ferro/ferricyanide solution, i.e. a well-known reversible redox couple which is generally used to gain information on the  
11  
12 charge transfer process at solid/solution interfaces.

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14 The PEC water splitting behaviour of all the PLD films was investigated in aqueous KOH solution (0.1 M). For  
15  
16 comparison purpose, the same experiment was performed over the TiO<sub>2</sub> nanotube layer photoanode.

17  
18 The performance of the TiO<sub>2</sub> photo-anodes was evaluated by measuring the photocurrents produced under an external  
19  
20 bias [15-17, 44-46], provided by a potentiostat (Amel 7050). Polarization curves (potential ramps from -0.8 V to about  
21  
22 0.5 V, with a scan rate of 5 mV s<sup>-1</sup>) were used to compare the performance of different samples.

23  
24 PEC experiments were also performed with an aqueous KOH solution (0.1 M) in the presence of ethanol (Carlo Erba,  
25  
26 99.9%), ethylene glycol (Sigma-Aldrich, 99.8%) or glycerol (Sigma-Aldrich, >99%) by varying their volume fraction in  
27  
28 the 2-40% range.

## 32 Results and discussion

### 34 Photoanode structure and morphology

35  
36 The morphology of *as deposited* (as grown) TiO<sub>2</sub> films obtained by PLD at room temperature at different oxygen  
37  
38 background pressures (keeping constant the total deposited mass per unit surface (0.5M)) is shown in the SEM images  
39  
40 of Figure 1 a-d (i.e. 3, 5, 10 and 15 Pa, respectively). Moving from 3 Pa to 15 Pa of oxygen, the effect of increasing the  
41  
42 spatial confinement of the plasma plume by the surrounding gas is evident in an increase of porosity, as discussed in  
43  
44 previous works [34, 47]. In fact, the gas pressure favours nucleation of the ablated species in the gas phase, leading to  
45  
46 the formation of clusters which are subsequently slowed down upon diffusion in the background gas. This allows the  
47  
48 tuning of the growth mechanisms from atom-by-atom deposition in vacuum towards low kinetic energy, forward  
49  
50 directed cluster assembling at higher gas pressure, with a corresponding gradual variation of film morphology from  
51  
52 compact and dense to a columnar structure, and eventually to a nanoporous quasi-1D, vertically oriented assembly.  
53  
54 Indeed, as shown in Figure 1 (as deposited films), the above-mentioned parameters were optimized to grow a compact  
55  
56 and dense film at 3 Pa O<sub>2</sub>, which evolves when increasing pressures are considered. Starting from 5 Pa O<sub>2</sub>, a vertically  
57  
58 oriented, columnar-like nanostructure, is obtained; at pressures higher than 10 Pa, it clearly evolves into hierarchical  
59  
60 structure resembling a forest of nano-trees [33]. Fine nanoparticles (about 10 nm in size) are observed, which are

1 organized at a multi-scale level, from the single nanoparticle (~10 nm scale) to the branches (~100 nm scale) up to the  
2 entire structure (micron-scale). The insert of Figure 1B shows a magnification of the structures obtained at 5 Pa,  
3 highlighting the fine structure at the nanoscale, and the hierarchical organization of fine nanoparticles into quasi vertical  
4 mesostructures.  
5

6 By varying the oxygen pressure in the 5-15 Pa range the shape and packing of the quasi-1D structures are thus tuned,  
7 and, as a result of the different growth mechanisms, film density and porosity are thus strongly related to the  
8 background gas pressure. Figure 2 (dashed black line) shows the variation of film density as a function of the oxygen  
9 partial pressure: as expected, moving from 3 to 15 Pa O<sub>2</sub> pressure, the density decreases from 3.2 g cm<sup>-3</sup> to about 0.5 g  
10 cm<sup>-3</sup>. The corresponding estimated porosity is also shown in Figure 2 (solid red line): in line with the density decrease,  
11 the film porosity increases from 18% at 3 Pa O<sub>2</sub> to about 85% at 15 Pa O<sub>2</sub>.  
12

13 SEM images in Figure 1 also provide the film thickness for the 0.5M samples, which increases from about 500 nm to  
14 more than 3 μm when moving from 3 Pa to 15 Pa deposition pressure. The effect of different thickness was then  
15 addressed for films grown at 5 Pa O<sub>2</sub> by varying the mass per unit surface in the 0.5M-2M range. SEM images (not  
16 shown) point out that moving from mass 0.5M to mass 2M film thickness increases from about 900 nm to about 3600  
17 nm, respectively; however, the overall morphology is not significantly affected by the variation of the mass of deposited  
18 material.  
19

20 To investigate the effect of the post-deposition thermal treatments on samples morphology, SEM analyses were  
21 accomplished on the samples annealed at 500 °C, 650 °C and 800 °C. Figure 3 shows SEM images of TiO<sub>2</sub> films  
22 deposited at 5 Pa and 10 Pa O<sub>2</sub> after annealing at different temperatures, and compared to the as-deposited materials.  
23 For films grown at 5 Pa, the sintering effect at 500 °C and 650 °C results in vertically oriented nanostructures, while  
24 when the annealing temperature is elevated up to 800 °C a strong coalescence within the structures is observed, leading  
25 to a marked decrease in nanoscale porosity. In the case of the films deposited at 10 Pa, inspection of Figure 3 points out  
26 that the post-deposition thermal treatment in air at 500 °C or 650 °C does not change the overall morphology of the  
27 more open, tree-like structures grown at this pressure: thermal treatments mainly affect the shape of single nanoparticles  
28 and the size, that results slightly increased by higher annealing temperatures. Also, a change in their mutual degree of  
29 connectivity is visible, with an increased coalescence among particles (sintering effect). Conversely, for the sample  
30 annealed at 800 °C a marked coalescence effect is observed, although to a lesser extent than what detected for the  
31 sample grown at 5 Pa.

32 The crystalline structure of the films was characterized by Raman spectroscopy, which is sensitive to the local  
33 crystalline order/disorder and provides a fingerprint of the TiO<sub>2</sub> crystalline phase (anatase/rutile) [48]. In figure 4  
34 Raman spectra of the film grown at 5 Pa O<sub>2</sub>, representative of a more compact morphology, and Raman spectra of the  
35

1 film grown at 10 Pa O<sub>2</sub>, with a more open morphology, are reported, both for as deposited film and after annealing at  
2 500, 650 and 800°C. The spectra of the as deposited films are characterized by two large bands, which are fingerprints  
3 of a highly disordered and almost amorphous structure due to the room temperature growth process. Conversely, as  
4 expected, high temperature annealing in air induces transition to a crystalline structure. As a result of the thermal  
5 treatment, at all the explored temperatures the dominant TiO<sub>2</sub> crystalline phase of the film grown at 5 Pa O<sub>2</sub> (left panel  
6 of figure 4) is anatase, as evidenced by the presence of narrow peaks at 144, 197, 399, 519 and 639 cm<sup>-1</sup> (another  
7 expected anatase peak at 519 cm<sup>-1</sup> is hidden by the intense peak at 521 cm<sup>-1</sup> of the silicon substrate) [48]. The same  
8 behaviour is observed for the sample grown at 3 Pa (spectra not reported).

9 Moving to films deposited at higher pressures (10 Pa, spectra on the right panel of the figure 4, and 15 Pa, not reported)  
10 peaks at 443 cm<sup>-1</sup> and 610 cm<sup>-1</sup>, corresponding to the rutile phase, start to appear together with the anatase peaks after  
11 annealing at 500 °C. The relative intensity of these two peaks with respect to the anatase peaks increases with increasing  
12 annealing temperature. From this parameter it is possible to estimate the rutile content [48] that results within 20% for  
13 annealing at 500 °C, in agreement with previous results [34], and it increases up to 50 % for the 15 Pa sample at higher  
14 temperatures. Such observed structural features, and, in particular, the oxide phase evolution upon annealing, is in  
15 agreement with previous [34] Raman characterizations of TiO<sub>2</sub> films grown under similar experimental conditions. In  
16 the same work [34] XRD measurements confirmed this evolution of the crystalline structure for which an average  
17 domain size in the range 10-20 nm was estimated from the width of XRD reflections. Of note, in line with previous  
18 results [34] the crystalline structure of PLD films annealed at 500°C is fully comparable with those annealed at 400°C,  
19 i.e. the same annealing temperature of the nanotubular TiO<sub>2</sub> sample (see below).

20 Figures 5a and 5b show SEM images of the annealed TNT photoanode (top view and cross-view, respectively).  
21 Nanotubes were found to have an outer diameter of approximately 80-90 nm and a length of about 700 nm. Figure 4  
22 shows the Raman analysis (spectrum c) indicating that also in this case the dominant TiO<sub>2</sub> crystalline phase is anatase.

#### 23 **Electrochemical response**

24 EIS and CV measurements in the dark were performed to investigate the electrochemical behavior of the TiO<sub>2</sub>  
25 nanostructures prepared by PLD. Samples deposited in the 3-10 Pa O<sub>2</sub> pressure range (i.e. ranging from compact to  
26 vertically oriented or hierarchical nanostructures) with constant deposited mass per unit surface (0.5M) and annealed at  
27 500°C were investigated, in order to gain information on the electrochemical properties and transport phenomena, with  
28 particular reference to the different films morphology (i.e. porosity and thickness). Of note, both EIS and CV  
29 measurements were performed at negative applied potentials, since no charge transfer is expected in the dark, at  
30 oxidative potentials, according to the nature of the TiO<sub>2</sub>-based photoanodes (i.e. n-type semiconductors).

1 The results of EIS measurements performed in the dark at -0.7 V are reported in Figure 6, in terms of Nyquist plots.  
2 Data were quantitatively interpreted by means of the equivalent circuit approach. Among the several equivalent circuits  
3 that have been proposed in the literature in order to represent the processes involved at the interphase  
4 electrode/electrolyte of porous structures, a quite simple circuit was successfully applied in the present case, where an  
5 element that accounts for the resistance of the solution ( $R_s$ ), is connected in series with three capacitor/resistance  
6 elements [ $R_s(C_1R_1)(C_2R_2)C_3R_3$ ]. Solid lines in Figure 6 refer to the model fits, while Table 1 resumes the values of the  
7 circuitual parameters calculated by the fit of experimental data. Of note, the solution resistance ( $R_s$ ) is not reported since  
8 in all cases it was found very low, due to the high conductivity of the solution. Depending on the case, constant phase  
9 elements are used instead of pure capacitors, for a better agreement with experimental data: their admittance is  
10 expressed by  $Y = Q(j\omega)^n$ , being  $n = 1$  for perfect capacitors. The values of time constant ( $\tau = (RQ)^{1/n}$ ), are also reported  
11 in Table 1; actually, the analysis of the time constants  $\tau$ , can be useful for the interpretation of the circuit, and hence of  
12 the occurring processes. If data in Table 1 are compared, slight differences among the parameters related to the first  
13 element  $R_1C_1$ , which is associated to the high frequency range, are observed for the samples obtained at different  
14 pressures, being the one at 10 Pa, that with the higher conductivity. However, values of time constants calculated for the  
15 three samples are almost of the same order, indicating very similar rate of the processes involved at highest frequency.  
16 In particular, the low values obtained for the  $\tau_1$  constants (i.e. order of microseconds) can be attributable to phenomena  
17 of charges adjustment occurring in the solid bulk.  
18 Greater differences are observable between the responses of the three samples, at lower frequency. The related arc may  
19 be considered as the convolution of two semicircles, associated to two slower processes ( $\tau_2$  in the order of s and  $\tau_3$  in  
20 the order of ms, respectively), which may indicate diffusive and reactive processes. In particular, the values of the  
21 exponent  $n_2$  quite lower than 1, can be related to possible presence of diffusive effects in the porous structure of the  
22 electrode ( $n=0.5$  should correspond to a Warburg impedance). Besides, the cathodic reaction can be reasonably  
23 represented by the  $R_3C_3$  element.  
24 The above interpretation is in agreement with the morphology of the samples. In particular, the sample deposited at the  
25 lowest pressure value, 3 Pa, i.e. dense and non-porous  $\text{TiO}_2$  film, shows the highest diffusive limitation (i.e. high value  
26 of  $R_2$  and  $\tau_2$ ). Conversely, lower values for  $R_2$  and  $\tau_2$ , are measured at the sample deposited at 5 Pa, where higher  
27 porosity is obtained. However, this effect is maintained only when the regular structure is obtained (a columnar-like  
28 structure has been revealed at 5 Pa sample). Actually, low resistance to the charge transfer (i.e. low value of  $R_3$ ) is  
29 measured for samples at 10 Pa, but the high value of  $R_2$  suggests that high diffusive limitations are again present at this  
30 sample, probably because the hierarchical, tree-like, morphology which is obtained at this sample.

1 In fact, previous work [49] was carried out in our lab on similar PLD samples, in which CVs measurements, performed  
2 at different potential scan rates, allowed us deriving information on the capacitance and in turn, on the  
3 electrochemically active surface of the samples. Of note, samples deposited at high pressures (i.e. 10 Pa) showed the  
4 highest value of global capacitance, but a lower value for the ratio between external and global capacitance if compared  
5 to samples deposited at intermediate pressure (i.e. 5 Pa). Accordingly, this indicated that the increasing porosity  
6 observed for open tree-like morphologies mainly affects internal porosity leading to negligible interaction with the ions  
7 electrolyte.

8  
9 Dedicated CV experiments in a ferro/ferricyanide solution were performed for samples deposited at 3, 5 and 10 Pa to  
10 analyze more in details the effect of the deposition pressure, and hence of films structure/morphology, on the  
11 corresponding charge transfer properties. Figure 7 shows a comparison between the trends of the CVs where only the  
12 cathodic region is reported. In fact, in all cases no oxidative peaks were observed as typical for n-type photoanodes  
13 under dark conditions (see inset). The results clearly show that samples deposited at 5 and 10 Pa are by far more active  
14 than that deposited at 3 Pa. In particular, the higher current measured at the cathodic peak for sample deposited at 10 Pa  
15 confirms its superior conductive properties. Besides, the shift at more negative potential observed for its cathodic peak  
16 indicates a slightly lower activity if compared with sample deposited at 5 Pa.

### 17 18 **Photoelectrochemical response**

19 To assess the functionality of the TiO<sub>2</sub> nanostructures prepared by PLD in view of water splitting applications we  
20 investigated the behavior of so prepared films as photoanodes in a photoelectrochemical cell in 0.1M KOH solution,  
21 analyzing the effects of different background pressures, deposited mass, and annealing temperatures. The PEC  
22 performances are shown in Figures 8 for PLD samples grown at 5, 3, 10 and 15 Pa O<sub>2</sub> (Fig. 8a, 8b, 8c and 8d,  
23 respectively). The results obtained in the case of TNT photoanode are reported in Figure 6b for comparison purpose.

24 In order to compare the performances of different film morphologies, the photoelectrochemical behaviour of TiO<sub>2</sub> films  
25 grown at different pressures was first investigated, keeping the total deposited mass per unit surface of the photoactive  
26 material constant (0.5M) as well as the annealing temperature (i.e. 500°C). All the amorphous as deposited samples  
27 showed negligible photoresponse (not reported) due to the presence of a high number of defects which can act as traps  
28 and recombination centers for the photogenerated charge carriers. Instead, a significant enhancement in photoresponse  
29 was observed for annealed samples and the trends of the polarization curves obtained under light irradiation may be  
30 used to compare the different photoactivity of the samples. A typical example of polarization curves, both in the dark  
31 and under illumination, is depicted in Figure 8a for the sample deposited at 5 Pa and annealed at 500 °C (see curves a

1 and b, respectively). As expected, under dark conditions negligible photocurrent is observed (less than  $3 \mu\text{A cm}^{-2}$ ), over  
2 the whole investigated potential range, indicating that no reaction occurred at the photoanodes in the absence of light  
3 illumination. On the contrary, upon illumination photocurrent evolution is observed starting at approximately  $-0.8 \text{ V}$   
4 (photopotential onset), as a result of the charge carriers (i.e. electron-holes pairs) generation from the incident light and  
5 the subsequent water oxidation occurring at the photoanodes by holes. An almost linear dependence of the photocurrent  
6 density on the potential is observed in the first part of the curve, because of the efficient charge carrier separation, under  
7 the effect of the applied bias [50-52]. Then, after a certain value  $V^*$ , a decrease of slope is generally measured, and  
8 finally a saturation condition is reached, where the effect of the applied potential becomes not more significant.  
9 Analogous trends of polarization curves, were obtained at the other samples: however, depending on the sample,  
10 different values of photopotential onset, saturation current density, and  $V^*$ , were measured. Thus, in order to make a  
11 quantitative comparison between the performances of the different samples, the photopotential onset values and the  
12 photocurrent density measured at a fixed potential are firstly considered. The third parameter,  $V^*$ , is then taken into  
13 account when the photoconversion efficiency is evaluated, as reported in the following.

14 **The effect of the oxygen deposition pressure (and in turn of the morphology) on the photoresponses can be observed by**  
15 **comparing curve *a* in Figure 8a (i.e. film deposited at 5Pa) with curves *a* in Figures 8b, 8c and 8d (i.e. films deposited at**  
16 **3, 10 and 15 Pa, respectively). For sake of clarity, the effect of the oxygen deposition pressure is evidenced in Figure 9,**

17 where the photopotential onset, and the steady-state photocurrent density recorded at  $0.5 \text{ V}$  (Figure 9a and 9b,  
18 respectively), are reported for samples annealed at  $500^\circ\text{C}$ . Data refer to samples with constant deposited mass per unit  
19 surface ( $0.5M$ ), but also data referring to sample with  $M$  and  $2M$  are included in the same graph for comparison.

20 Of note, the strongest negative effect on the performance of the photoanodes seems to be correlated to the porosity  
21 increase corresponding to the highest deposition pressure values. As a matter of fact, for samples deposited at the  
22 highest oxygen pressures (i.e. 10 and 15 Pa) the photopotential onset is shifted considerably to less negative values (i.e.  
23 near  $-0.7 \text{ V}$ ), and the photocurrent density is significantly lower than that for the samples at lower pressure, approaching  
24 values close to  $15 \mu\text{A cm}^{-2}$ . This suggests a less efficient generation and transfer of photogenerated charge carriers and  
25 higher recombination losses, as well [53-55]. If the most performing samples are compared, a photopotential onset of  
26 about  $-0.75 \text{ V}$  is measured for the sample deposited at 3 Pa (i.e. compact and dense film), which is less negative than  
27 that of samples deposited at 5 Pa (i.e.  $-0.8 \text{ V}$ ). Lower photocurrent density is correspondingly measured for sample at 3  
28 Pa (i.e.  $55 \mu\text{A cm}^{-2}$  vs.  $65 \mu\text{A cm}^{-2}$ ).

29  
30 **Figure 10 a and 10b depict the results of EIS measurements carried out under 365 nm wavelength irradiation, at 0.5V of**  
31 **bias potential. The resulting spectra are reported in Figure 10a and 10b in terms of Bode and Nyquist plots, respectively,**



for samples deposited at 3, 5 and 10 Pa. The quantitative analysis of data has been done using the equivalent circuit approach with the same electrical circuit used for the EIS measurement performed in the dark (see above). Table 2 resumes the values of the fitting circuit parameters. Also in this case, the circuit elements associated to the high and medium frequencies could be attributable to the response of the bulk structure, and to possible diffusion effects, respectively. Besides, the third circuit element, associated to the lowest frequency range, may be related to the transfer of photogenerated holes toward the electrolyte. As it can be observed, the data related to the sample deposited at 10 Pa justify the low photoresponse obtained at this sample. As a matter of fact, the value of  $\tau_3$ , higher than that related to the samples obtained at the lowest pressures, confirms the slow charge transfer at this sample. Moreover, the high value of  $\tau_2$  indicates that also diffusive processes could negatively affect the whole photocatalytic process at this sample. If the samples deposited at lower pressures are considered (i.e. 3 and 5 Pa), the higher photoresponse observed for the sample deposited at 5 Pa can be explained in view of a combined effect of both diffusive and charge transfer processes. Accordingly, by comparing  $\tau_2$  and  $\tau_3$ , the vertical oriented structure is expected to favor the accessibility by ions electrolyte which compensates for the slow charge transfer.

In order to make a more exhaustive comparison, also the photoconversion efficiency ( $\eta\%$ ) has been evaluated. In electrically driven photo-processes, as in this case, equation (1) can be properly used [56,57] as it takes into account not only the light power, but also the applied external potential:

$$\eta (\%) = \frac{J(E^\circ - |E_{app}|)}{I} * 100 \quad (1)$$

where,  $J$  is the photocurrent density ( $\mu\text{A cm}^{-2}$ ),  $E^\circ=1.23\text{V}$  is the standard reversible potential for water splitting,  $|E_{app}|$  is the applied potential evaluated as the difference between the bias potential and the OCV under the irradiated power light, and  $I$  is the UV incident light power density. Of note, dedicated experiments [49] performed at selected wavelengths, indicated the negligible contribution of the visible-light on the total activity of the investigated samples which is in line with previous work showing that the optical gap for PLD hierarchical  $\text{TiO}_2$  deposited under  $\text{O}_2$  atmosphere and annealed in air at  $500^\circ\text{C}$  is about 3.2-3.3 eV [34], i.e. about 370-390 nm, without any detectable trend with respect to deposition pressure.

Figure 11a shows the variation of  $\eta\%$  as a function of the applied potential. As typical [56,57], voltage-dependent trends can be observed: initially the efficiency increases with the increasing applied potential reaching a maximum, where the electron-hole separation is superior under the effect of the applied bias, and then begins to decrease at higher applied

1 bias, where the external electrical work, done to separate the charges, negatively affects the overall photoconversion  
2 efficiency. It must be observed that the maximum in this curve is obtained at a potential value about corresponding to  
3  
4 the  $V^*$  in the polarization curve (see Figure 8a) which can be individuated as the optimal working potential, at which the  
5  
6 photoelectrochemical water splitting process could be carried out.

7  
8 On these bases, the sample deposited at 5 Pa results the best performing, not only because it achieves the highest  
9  
10 maximum efficiency of ca. 4%, but also because this efficiency is obtained at very low bias (near -0.6 V). Conversely,  
11  
12 the sample deposited at 3 Pa and those deposited at 10-15 Pa show lower values of maximum efficiencies, of ca. 2.0%  
13  
14 and 0.5%, respectively, which are obtained at higher potential.

15  
16 On the basis of the above results, the effect of film thickness, on the photoresponses was further investigated for  
17  
18 samples deposited at 5 Pa (i.e. for the morphology that had shown the best performances) by varying the mass of  
19  
20 deposited material in the 0.5M-2M range. All the investigated samples were annealed at the same temperature (i.e. 500  
21  
22 °C).

23  
24 As it clearly appears from Figures 9a the photopotential onset is approximately the same (i.e. near -0.8 V) for all the  
25  
26 samples deposited at 5 Pa; however, a clear effect of film thickness on the photoresponse is apparent from Figure 9b,  
27  
28 and moving from sample-0.5M to sample-M (i.e. from ca. 900 nm to ca. 1400 nm of thickness) the photocurrent is  
29  
30 remarkably improved. In particular, sample-M yields a photocurrent density of roughly  $130 \mu\text{A cm}^{-2}$  at 0.5 V, which  
31  
32 represents ca. a 2-fold increase of the photocurrent response if compared to sample-0.5M. Besides, the further increase  
33  
34 of the thickness up to 3600 nm (sample-2M) results in a photoresponse decrease, so that a photocurrent density  
35  
36 comparable to that of sample-0.5M is attained. This outcome suggests the existence of an optimal thickness value for  
37  
38 the quasi 1D structures, which can guarantee improved photoactivity. This is clearly shown by the corresponding  
39  
40 photoconversion efficiencies, plotted in Figure 11b. As a matter of fact, the maximum photoconversion efficiency of the  
41  
42 sample-M is increased to ca. 6.3% (vs. 4 and 3.7%, for sample-0.5M and sample-M, respectively). Such a behaviour  
43  
44 seems peculiar of quasi 1D structures. Indeed, the effect of the variation of thickness was further investigated for  
45  
46 samples deposited at 3 Pa that are conventional thin films (i.e. compact and dense). Of note, in this case we observe that  
47  
48 photocurrents results (see Figures 8b, 9a and 9b) and the corresponding photoconversion efficiencies data (Figure 11c),  
49  
50 show a negligible effect on the photoactivity in the whole potential range when moving from sample-0.5M to sample-M  
51  
52 (i.e. from about 500 nm to about 1500 nm of thickness).

53  
54 For comparison purpose, in Figure 11b, the results obtained for the TNT photoanode are also reported. Of note, in this  
55  
56 case, the photoconversion efficiencies are very similar to those calculated for sample-0.5M which is in line with their  
57  
58 comparable thickness. However, in the case of the TNT photoanode the maximum efficiency is obtained with an  
59  
60 applied potential which is higher than that for the PLD sample.

1 Furthermore, in order to investigate the effect of the post-thermal treatment (and thus of crystallinity) on the  
2 photoelectrochemical performances, additional tests were performed over TiO<sub>2</sub> photoanodes prepared at different  
3 background pressures and annealed at 650 °C. For comparison the same mass (i.e. 0.5M) was deposited in this case. The  
4 photoelectrochemical results are shown, in terms of photocurrent density generated at 0.5 V and photocurrent  
5 efficiency, in Figures 12 (see white bars) and 11d, respectively.

6 In line with the results obtained in the case of samples annealed at 500 °C, also for samples annealed at 650 °C the best  
7 performances are associated with the sample deposited at 5 Pa oxygen. In fact, as shown in Figure 12, the sample  
8 deposited at 5 Pa oxygen shows the highest photocurrent densities reaching a value of 200 μA cm<sup>-2</sup> at 0.5 V which  
9 represents ca. a 4-fold increase of the photocurrent response if compared to all the other samples. Accordingly, the  
10 sample deposited at 5 Pa oxygen exhibits conversion efficiencies as high as 8% (see Figure 11d), which are highly  
11 enhanced as compared to the other investigated samples. Indeed, great care must be paid in evaluating the existing  
12 literature photoconversion efficiency results [3] because the use of very different experimental conditions (e.g. light  
13 source and energy, photo-anode preparing conditions, electrolyte nature and concentration) prevents us from a direct  
14 and exhaustive comparison. However, such a value of photoconversion efficiency is quite comparable to those typically  
15 obtained over other TiO<sub>2</sub> based photoanodes under UV irradiation [15, 58, 59].

16 The clear effect of the post-thermal treatment on the photocatalytic performances can be observed, by comparing  
17 Figures 9b and 12, i.e. considering samples deposited at the same pressure but annealed at 500 and 650 °C, respectively.  
18 Except in the case of the sample deposited at 3 Pa oxygen, upon increasing the annealing temperature from 500 to 650  
19 °C, the photocatalytic activity considerably increases. As a matter of fact, the photoresponse of samples deposited in the  
20 5-15 Pa oxygen range is almost trebled, whereas it was very similar for samples deposited at 3 Pa.

21 Of note, the photo-electrochemical response of samples annealed at 800 °C was also investigated and representative  
22 results are reported in Figure 12 for samples deposited at 5, 10 and 15 Pa (i.e. see black bars). Extremely low activity  
23 was found in this case. As a matter of fact very low values of photocurrent density (i.e. close to 10 μA cm<sup>-2</sup> at 0.5 V)  
24 were measured.

25  
26 Finally, photoelectrochemical tests were also carried out in the presence of ethanol, ethylene glycol or glycerol. For this  
27 purpose, the behaviour of the sample prepared at 5 Pa of oxygen (i.e. for the morphology that had shown the best  
28 performances) and annealed at 500 °C (mass = M) was investigated. Figure 13 shows the results in terms of the  
29 parameter  $\gamma$  evaluated as ratio between the photocurrent values obtained at 0.5 V with and without the organics as a  
30 function of their volume fraction. Accordingly, when  $\gamma > 1$ , it accounts for the performance gain due to the presence of  
31 the organic compounds.

1 As it clearly appears from Figure 13, all the investigated organic compounds improves the PEC performances which is  
2 mainly attributed to the great increase of charge separation efficiency since they act as sacrificial electron donor by  
3 consuming photogenerated holes and/or oxygen, thus lowering the electron-hole recombination and/or H<sub>2</sub>-O<sub>2</sub> back  
4 reaction, i.e. the most important reactions for decreasing the light-to hydrogen conversion efficiency [60]. According to  
5 several literature reports [61-64] the photo performances gain using ethanol as scavenger is the lowest if compared to  
6 ethylene glycol and glycerol because of the different chemico-physical properties of the alcohols (e.g. number of  $\alpha$ -H  
7 and OH groups, the proportion between carbon and hydroxyl groups number, alcohol polarity and their standard  
8 oxidation potentials). However, specific optimum concentration values were found for each organic compound. In the  
9 case of ethanol the increase of photo response is evident at the lowest investigated concentration (i.e. 5 vol.%) and then,  
10 according to the literature [65, 66] it stabilizes at higher concentrations. The same saturation effect is observed in the  
11 case of ethylene glycol. Besides, in the case of glycerol, the highest performances are obtained with very low  
12 concentrations of the sacrificial agent (i.e. 2 and 3 vol.%) while further concentration increase has adverse effect  
13 resulting in a photoresponse even lower (i.e.  $\gamma < 1$ ) than the pure KOH solution. This may be explained considering that  
14 the solution becomes very viscous which is expected to negatively affect light penetration and/or electrolyte ions  
15 transport/diffusion.

16  
17 The bulk of the above results reveals a strong dependence of the photoelectrochemical performances on samples  
18 structure, morphology and multiscale organization, as well. A tentative explanation for the observed trends in  
19 photocurrent performances as a function of deposition pressure and annealing treatment can be proposed, in relation to  
20 the accessible active surface (depending on total surface area and thus on nanoscale porosity), carrier recombination  
21 (affected by degree of crystallinity and grain boundaries) and electrical transport (which is expected to depend on the  
22 film connectivity, vertical or quasi-1D morphology and crystallinity). As for morphology, we found that 5 Pa deposition  
23 pressure corresponds to an optimum condition for the film performance. More in particular, for samples annealed at  
24 500°C, the photocurrent response was found to increase by moving from 3 to 5 Pa O<sub>2</sub> pressure, whereas there was a  
25 drastic decrease in performance associated with the samples deposited at higher O<sub>2</sub> pressures, i.e. 10 and 15 Pa O<sub>2</sub>. This  
26 trend can be ascribed to the peculiar morphology of PLD grown samples in the 3-15 Pa range. As previously discussed,  
27 the deposition background gas pressure strongly affects the TiO<sub>2</sub> film growth mechanisms and its final porosity. In fact,  
28 while at the lowest pressure (i.e. 3 Pa) a 500 nm thick, dense and compact film develops, the increasing deposition  
29 pressure in the 5-15 Pa range allows a vertically oriented, quasi-1D organization (from a columnar-like to a hierarchical  
30 tree-like nanostructure) with structures reaching more than 1  $\mu$ m in length. As a consequence, since the same mass was  
31 deposited for each sample, the increasing deposition pressure leads to a parallel decrease in film density, i.e. to an

1 increase in film porosity and thus in the available active surface area. On this regard, it was found that the BET specific  
2 surface area of films deposited at 5 Pa O<sub>2</sub> after thermal treatment at 500 °C was around 25 m<sup>2</sup> g<sup>-1</sup>, with a pore size  
3 distribution in the range from a few nm to ~100 nm. This surface area value is representative also of films annealed at  
4 650 °C, since SEM shows that no significant change in morphology occurs at this temperature, while annealing at 800  
5 °C results in a strong coalescence and, presumably, in a strong decrease of the available surface.

6 In a previous work [32], it was shown that, as the deposition pressure increases, specific surface area increases while  
7 density decreases, so that the *roughness factor*, i.e. the ratio between the available material surface and the geometrical  
8 footprint of the film, has an optimum value for intermediate pressure conditions. In our case, by knowing film density,  
9 thickness and specific surface, it is possible to evaluate the roughness factor: in the case of films deposited at 5 Pa we  
10 calculated a *roughness factor* per unit thickness around 50 μm<sup>-1</sup> (i.e. 50 cm<sup>2</sup> of active surface for a film 1 μm thick and  
11 with a footprint of 1 cm<sup>2</sup>).

12 On this basis, it is not surprising that samples deposited at 3 Pa O<sub>2</sub> show a lower photoactivity. In fact, in order to  
13 achieve high photoelectrochemical performances, a large surface area is desired along with suitable electronic features  
14 (e.g. adequate band edge positions and rapid charge separation properties): however, in the case of sample deposited at  
15 3 Pa O<sub>2</sub> a compact TiO<sub>2</sub> film is obtained with small porosity (18%) and thus low surface area. Conversely, the enhanced  
16 performances observed for the sample deposited at 5 Pa O<sub>2</sub> could be reasonably ascribed to the larger surface area  
17 which entails the availability of an increased number active sites for the reaction. Moreover, it may be argued that a  
18 more open structure with vertical void channels, typical of quasi-1D nanomorphologies obtained with the increased  
19 deposition pressure, can offer the advantage of better **electrolyte ions** transport/diffusion allowing the whole surface to  
20 be active in the photoelectrochemical process. **This was confirmed by CV and EIS results, where both the accessibility  
21 of the active sites by the electrolyte ions and the high charge transfer capacity were indicated as beneficial in  
22 determining the high performances of sample deposited at intermediate pressure (i.e. 5 Pa).**

23 On the other hand, the significant photoresponse decrease observed for samples deposited at the highest deposition  
24 pressures (i.e. 10 and 15 Pa O<sub>2</sub>) could be tentatively ascribed to the higher recombination losses as a consequence of the  
25 excessive thickness and more open morphology of tree-like structures, i.e. lack of connectivity (see the discussion  
26 below). **In addition, according to CV and EIS measurements, both slow charge transfer properties and diffusive  
27 limitations may explain the low photoelectrochemical response observed for samples deposited at high temperatures.  
28 Besides, possible effect of the different crystalline structure (a mixture of anatase/rutile for sample deposited at 10 and  
29 15 Pa O<sub>2</sub>) could not be completely ruled out even though it sounds unlikely. In fact several works reported that mixtures  
30 of anatase/rutile are more active than pure rutile or anatase in photocatalytic reactions since the anatase/rutile phase  
31 junction is supposed to improve charge carriers separation and their life-time. [67-70]**

1 Once the structure/morphology of the material has been optimized, it was found that the increase of the film thickness  
2 does not correspond to a monotonic increase in the photocurrent, even though, of course, the total surface area  
3 increases. Possible explanations for this behaviour include non-optimized carrier transport for very high thicknesses. In  
4 addition, several reports focused on nanotubular TiO<sub>2</sub> photoanodes [71-74] or other TiO<sub>2</sub> nanostructures [20,75],  
5 reported the existence of a critical thickness value which has been explained as a result of an optimum balance between  
6 light absorption and charge carriers life-time. Accordingly, for films with low thickness as in the case of mass-0.5M  
7 sample, the amount of the material is likely too low and the light absorption too weak as well, thus leading to low  
8 efficiencies. Otherwise, for films with too high thickness, as in the case of mass-2M sample, the long transport distance  
9 for charge carriers may lead to undesirable recombination phenomena. In addition, mass-transport limitations at the  
10 electrode/electrolyte interphase could be invoked to explain the inefficiencies observed for the longer hierarchical  
11 treelike structures, e.g. leading to a minor electrolyte ions infiltration and limiting the true active surface only to the top  
12 part of the film.

13 Concerning the effect of thermal treatments, the increased photoelectrochemical performances observed for samples  
14 annealed at 650 °C can be related to the efficient sintering between nanoparticles, that can reduce amorphous regions or  
15 grain boundaries and consequently can ensure a slightly higher degree of crystallinity. This likely improves conductivity  
16 and charge transport and also favours a probable defect healing (e.g. at grain boundaries) which may reduce carrier  
17 recombination. On the contrary, for films annealed at 800 °C the reduction in active surface, resulting from the strong  
18 degree of coalescence, probably plays a major role, resulting in a negligible photocurrent.

19 As a final point, the photoresponse was further strengthened with the presence of organic sacrificial reagents who  
20 served as hole scavengers. In particular, the performance gain observed in the presence of very low amounts of glycerol  
21 is particularly attractive. In fact, glycerol is the major byproduct of biodiesel production and its photoelectrochemical  
22 re-utilization is of great industrial interest in order to improve the global biodiesel economy [76, 77].

## 23 **Conclusions**

24 Quasi-1D and tree-like hierarchical nanostructured TiO<sub>2</sub> films were prepared by Pulsed Laser Deposition (PLD) and  
25 evaluated as potential photoanodes for the photoelectrochemical (PEC) water splitting reaction.

26 In particular, the photoelectrochemical responses have been discussed as a function of the different material  
27 morphologies and structures, which were tailored by varying the preparation conditions.

28 At first, samples were prepared by changing the oxygen pressure (in the range 3-15 Pa): it was found that film growth  
29 can be tuned at the nanoscale from compact/dense films to columnar/vertically oriented or hierarchical porous  
30 nanostructures. In relation to optimized values of density/surface area, crystallinity and electron transport, the best

1 photoelectrochemical performances were associated with the sample prepared using 5 Pa of oxygen. In particular,  
2 according to CV and EIS analysis, performed both in the dark and under illumination, its accessibility by the electrolyte  
3 ions and its charge transfer capacity were indicated as crucial in determining its high photoresponse.

4 The effect of the variation in the mass of deposited material, that leads to an increased thickness of the catalytic layers,  
5 suggested the existence of an optimal thickness value that likely improves the electron transfer. Of note PLD samples  
6 showed a photo-activity even higher (i.e. depending on thickness) than TiO<sub>2</sub> nanotubular arrays prepared by anodic  
7 oxidation, but presented a lower value of  $V^*$  at which the maximum electrical yield may be reached.

8 The study of the effect of the annealing temperature showed that the photoelectrochemical response increases for  
9 samples annealed at 650 °C, indicating the importance of crystallinity and structure connectivity.

10 The set of results indicates that the TiO<sub>2</sub> nanostructures prepared by reactive pulsed laser deposition (PLD) can be  
11 considered of practical interest for photoelectrochemical water splitting applications. In particular, open morphologies  
12 characterized by relevant nanoscale porosity and by a vertically oriented morphology have shown promising results  
13 achieving photocurrent efficiencies up to 8%, under UV irradiation.

14 Conversely, tree-like nanostructures (i.e. more open morphologies prepared at 10 and 15 Pa O<sub>2</sub>) showed lower PEC  
15 water splitting activities, possibly due to the occurrence of higher recombination losses as a consequence of their  
16 excessive thickness.

17 Eventually, the use of organic sacrificial reagents (i.e. ethanol, ethylene glycol or glycerol) has been proved to be  
18 exploitable to improve PLD photoanodes performances.

19 Further optimization of the material structure-morphology, and possible routes for enhancing the response to visible  
20 light (e.g. doping, sensitization) offer future opportunities for improving PEC water splitting devices based on  
21 nanostructured TiO<sub>2</sub> films prepared by Pulsed Laser Deposition.

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**Tables captions**

**Table 1.** Circuit parameters obtained by fitting the experimental impedance results with the selected equivalent circuit for PLD samples deposited at 3, 5 and 10 Pa. Data obtained under dark conditions at -0.7V.

**Table 2.** Circuit parameters obtained by fitting the experimental impedance results with the selected equivalent circuit for PLD samples deposited at 3, 5 and 10 Pa. Data obtained under illumination (365nm wavelength) at 0.5V.

	<b>3 Pa</b>	<b>5 Pa</b>	<b>10 Pa</b>
$C_1 (C)$	1.52E-07	1.29E-07	2.12E-07
$R_1(\Omega)$	20.78	20.08	15.34
$\tau_1 (s)$	3.16E-06	2.58E-06	3.26E-06
$Q_2 (S s^n)$	4.53E-05	1.00E-04	9.49E-05
$n_2$	0.6874	0.6608	0.6786
$R_2(\Omega)$	2.23E+04	793.4	1.16E+04
$\tau_2 (s)$	1.02	0.02	1.15
$C_3 (C)$	3.03E-05	1.14E-04	6.80E-05
$R_3 (\Omega)$	43.11	1462	149.3
$\tau_3 (s)$	0.0013	0.1665	0.0102

**Table 1**

	<b>3 Pa</b>	<b>5 Pa</b>	<b>10 Pa</b>
$Q_1(S s^n)$	6.54E-08	1.18E-07	1.05E-07
$n_1$	1	0.95	1
$R_1(\Omega)$	24.32	24.61	21.56
$\tau_1(s)$	1.59E-06	1.48E-06	2.26E-06
$Q_2(S s^n)$	2.27E-05	1.88E-05	3.36E-05
$n_2$	0.78	0.81	0.86
$R_2(\Omega)$	9608	6910	5135
$\tau_2(s)$	0.14	0.08	0.13
$Q_3(S s^n)$	7.45E-06	6.68E-06	1.03E-05
$n_3$	0.97	1	0.92
$R_3(\Omega)$	1.02E+05	2.58E+05	2.74E+05
$\tau_3(s)$	0.75	1.72	3.11

**Table 2**

## Figures captions

**Fig 1.** SEM images of as deposited PLD grown TiO<sub>2</sub> photoanodes produced with mass=0.5M and at different background gas pressure: a=3 Pa, b=5 Pa, c=10 Pa, d=15 Pa O<sub>2</sub>.

**Fig 2.** Film density variation (black squares and dotted line) and the related film porosity (red circles and solid line) of as deposited PLD grown TiO<sub>2</sub> photoanodes produced at different background gas pressure (mass=0.5M).

**Fig 3.** SEM images showing the effect of thermal treatment on PLD grown TiO<sub>2</sub> films deposited at 5 Pa and 10 Pa O<sub>2</sub> (mass=0.5M).

**Fig4.** Raman spectra of a compact film grown at 5 Pa O<sub>2</sub> (left) and a porous film grown at 10 Pa O<sub>2</sub> (right), as deposited (on glass substrate) and after annealing at 500, 650 and 800°C (on crystalline silicon substrate). Raman peaks related to anatase (rutile) phase are indicated by A (R). Silicon Raman peak at 521 cm<sup>-1</sup> is indicated with a dashed line in the spectra of annealed films.

**Fig 5.** SEM images of the annealed TNT photoanode: top-view (a); cross-view (b).

**Fig. 6.** EIS results measured under dark conditions at -0.7V in 0.1M KOH for samples deposited at 3, 5 and 10 Pa pressure (annealed at 500°C, mass=0.5M): Nyquist plots

**Fig 7.** Comparison of reductive voltammetric scan performed under dark conditions in ferro/ferricyanide solution over samples deposited at 3, 5 and 10 Pa pressure (annealed at 500°C, mass=0.5M). Inset: example of whole voltammetric scan (potential scan rate 100 mV/s).

**Fig 8.** Current-potential response of the PLD grown TiO<sub>2</sub> photoanodes. Fig. 8a: Dark conditions (curve a); samples produced at 5 Pa pressure annealed at 500°C (curve b: mass=0.5M; curve c: mass=M; curve d: mass=2M), 650°C and 800°C (curve e and f (mass=0.5M)). Fig. 8b: samples produced at 3 Pa pressure, annealed at 500°C (curve a: mass=0.5M; curve b: mass=M ) and 650°C (curve c: mass=0.5M). Fig. 8c: samples produced at 10 Pa pressure (mass=0.5M), annealed at 500, 650 and 800°C (curves a, b and c). Fig. 8d: samples produced at 15 Pa pressure



(mass=0.5M), annealed at 500, 650 and 800°C (curves a, b and c). Current-potential response of the TNT photoanode (Fig. 8b, curve d).

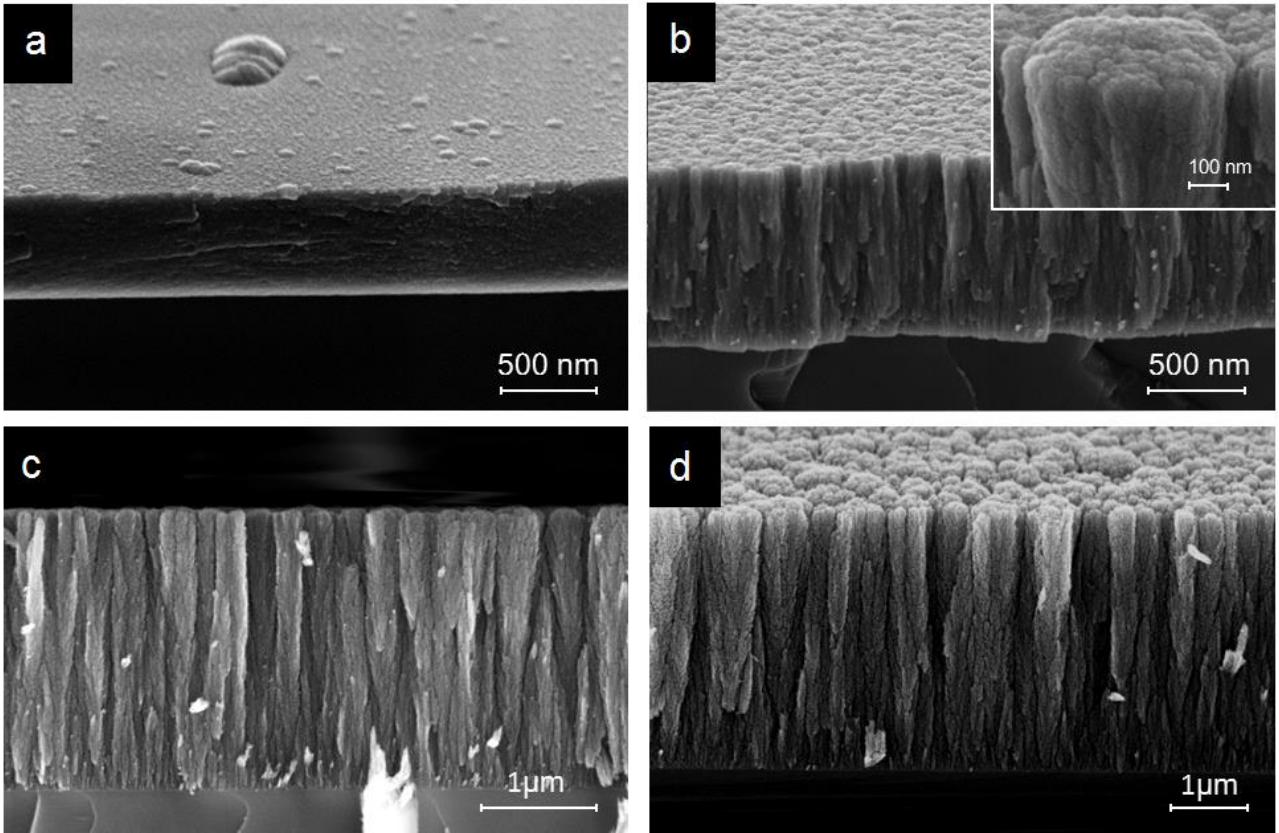
**Fig 9.** Photoelectrochemical behaviour for PLD grown TiO<sub>2</sub> photoanodes produced at different background pressure and annealed at 500 °C (White bars: mass=0.5M; Brown bars: mass=M; Gray bars: mass=2M). a: photopotential on-set; b: photocurrent densities measured at 0.5 V.

**Fig 10.** EIS results measured under illumination (365nm wavelength) at 0.5V for samples deposited at 3, 5 and 10 Pa pressure (annealed at 500°C, mass=0.5M): a) phase angle (empty symbols) and modulus (solid symbols) Bode plots; b) Nyquist plots

**Fig 11.** Photoconversion efficiency as a function of the applied potential. a: Effect of the background pressure for the PLD grown TiO<sub>2</sub> photoanodes annealed at 500 °C (mass=0.5M); b: Effect of thickness for the PLD grown TiO<sub>2</sub> photoanodes produced at 5Pa (annealing temperature = 500 °C; corresponding thicknesses reported in the figure) and photoconversion efficiency for the TNT photoanode); c: Effect of thickness for the PLD grown TiO<sub>2</sub> photoanodes produced at 3 Pa (annealing temperature = 500 °C; corresponding thicknesses reported in the figure); d: Effect of the background pressure for the PLD grown TiO<sub>2</sub> photoanodes annealed at 650 °C (mass=0.5M)

**Fig 12.** Photoelectrochemical behaviour for the PLD grown TiO<sub>2</sub> photoanodes produced at different background pressure and annealed at 650 °C (With bars) and 800 °C (Black bars): photocurrent densities measured at 0.5 V.

**Fig 13.** Photoelectrochemical behaviour in the presence of organic sacrificial reagents in terms of performance gain  $\gamma$  evaluated as ratio between the photocurrent values obtained 0.5 V with and without the organics as a function of their volume fraction (PLD grown TiO<sub>2</sub> photoanodes deposited at 5 Pa (mass=M) and annealed at 500 °C)



**Fig 1.**

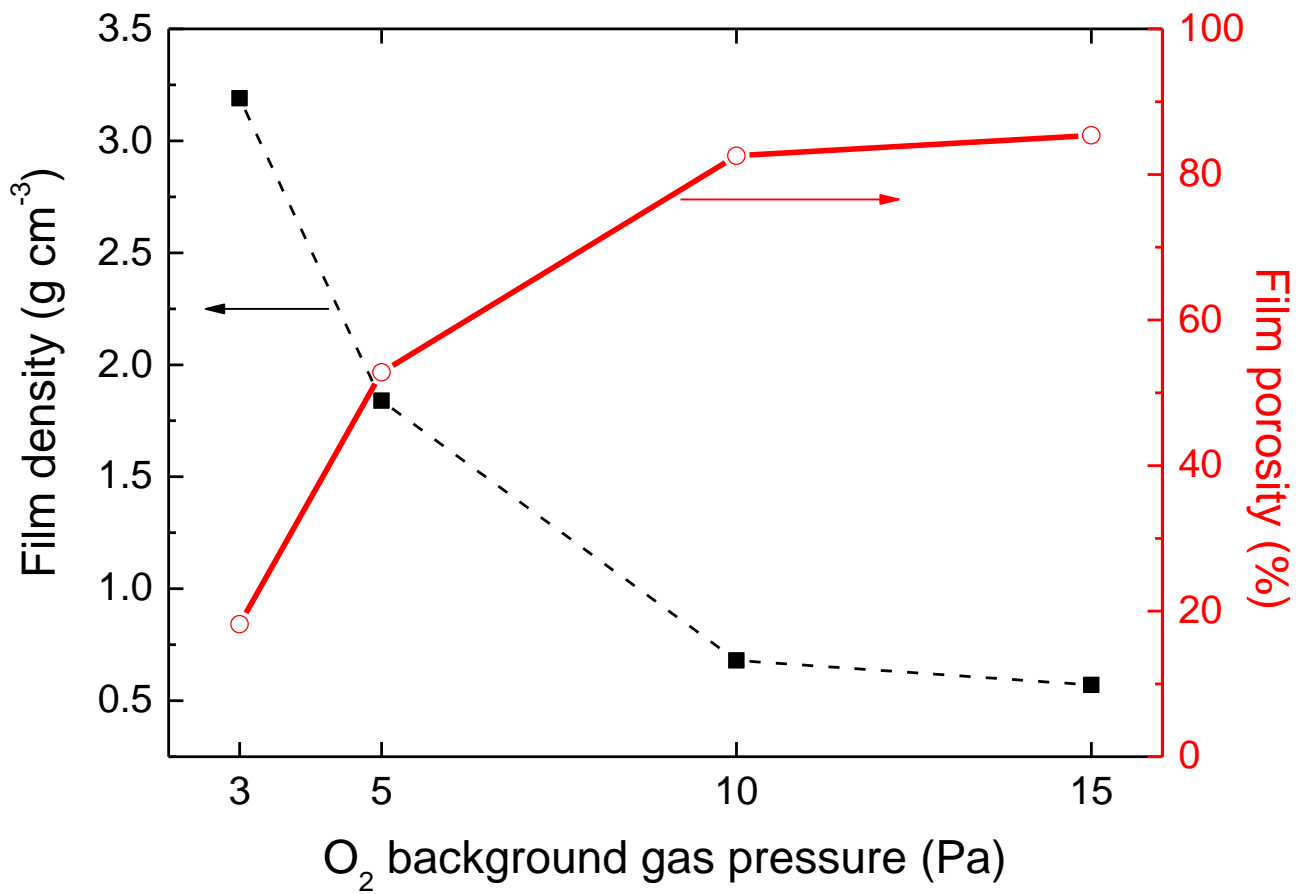
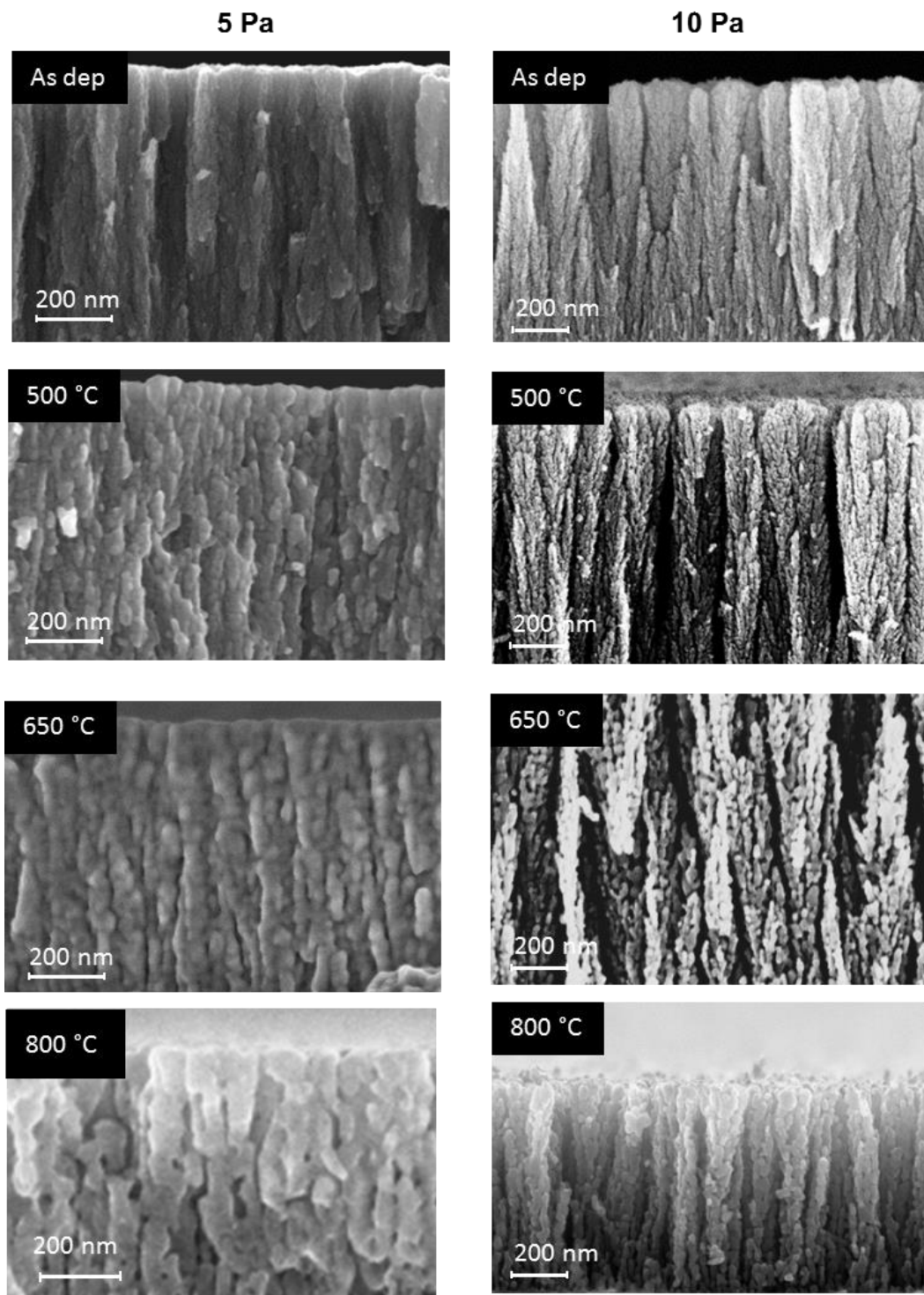


Fig 2.



**Fig 3.**

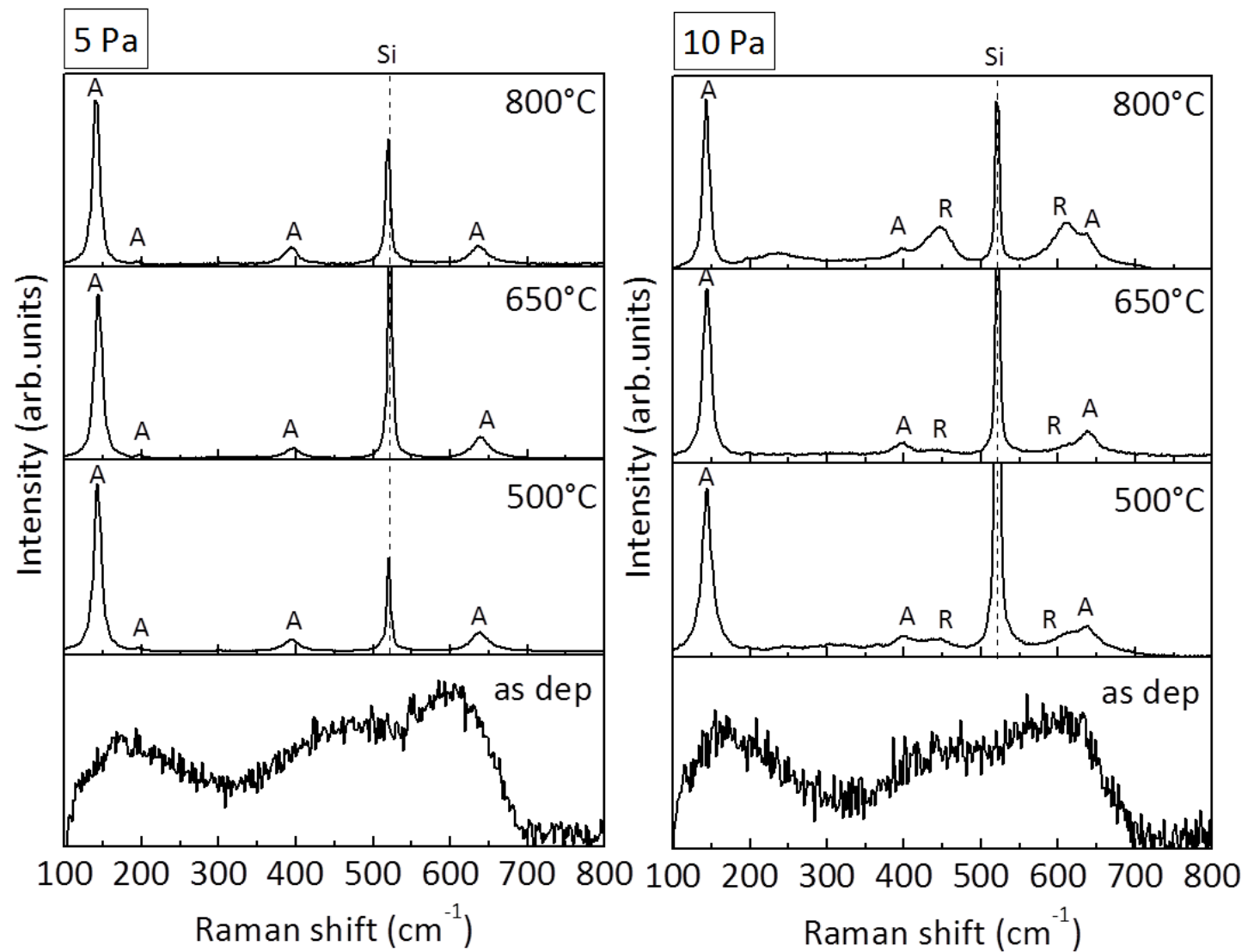
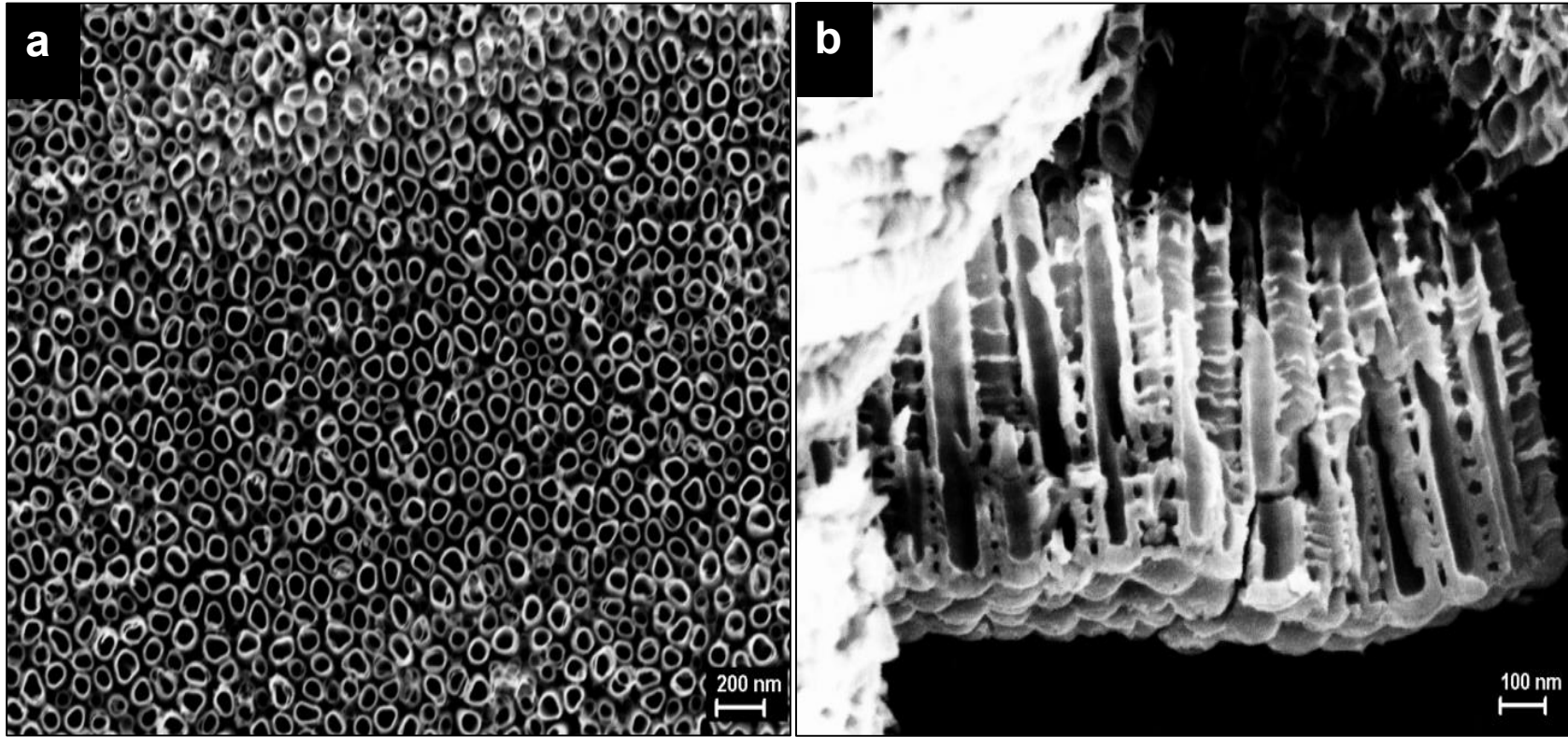
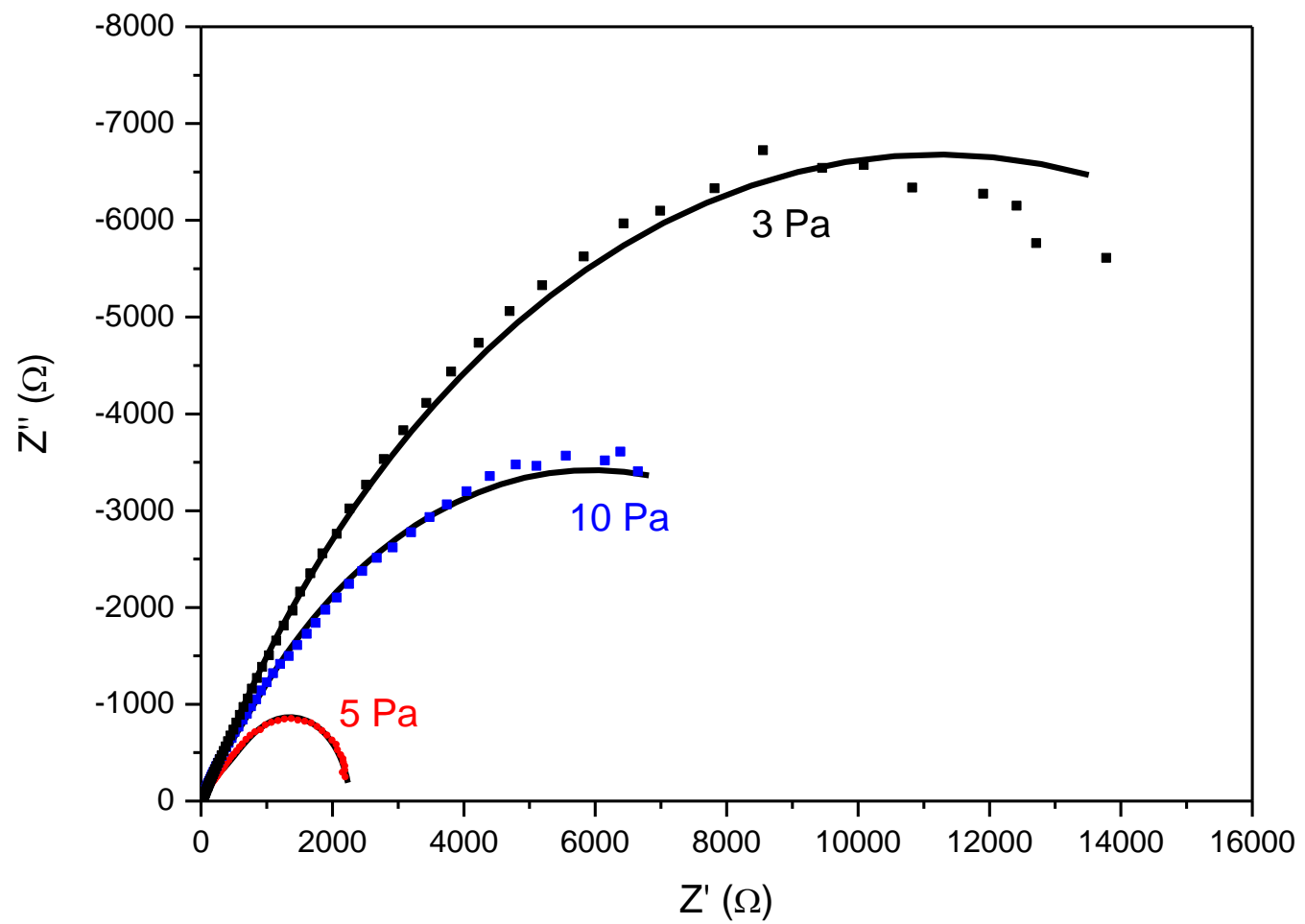


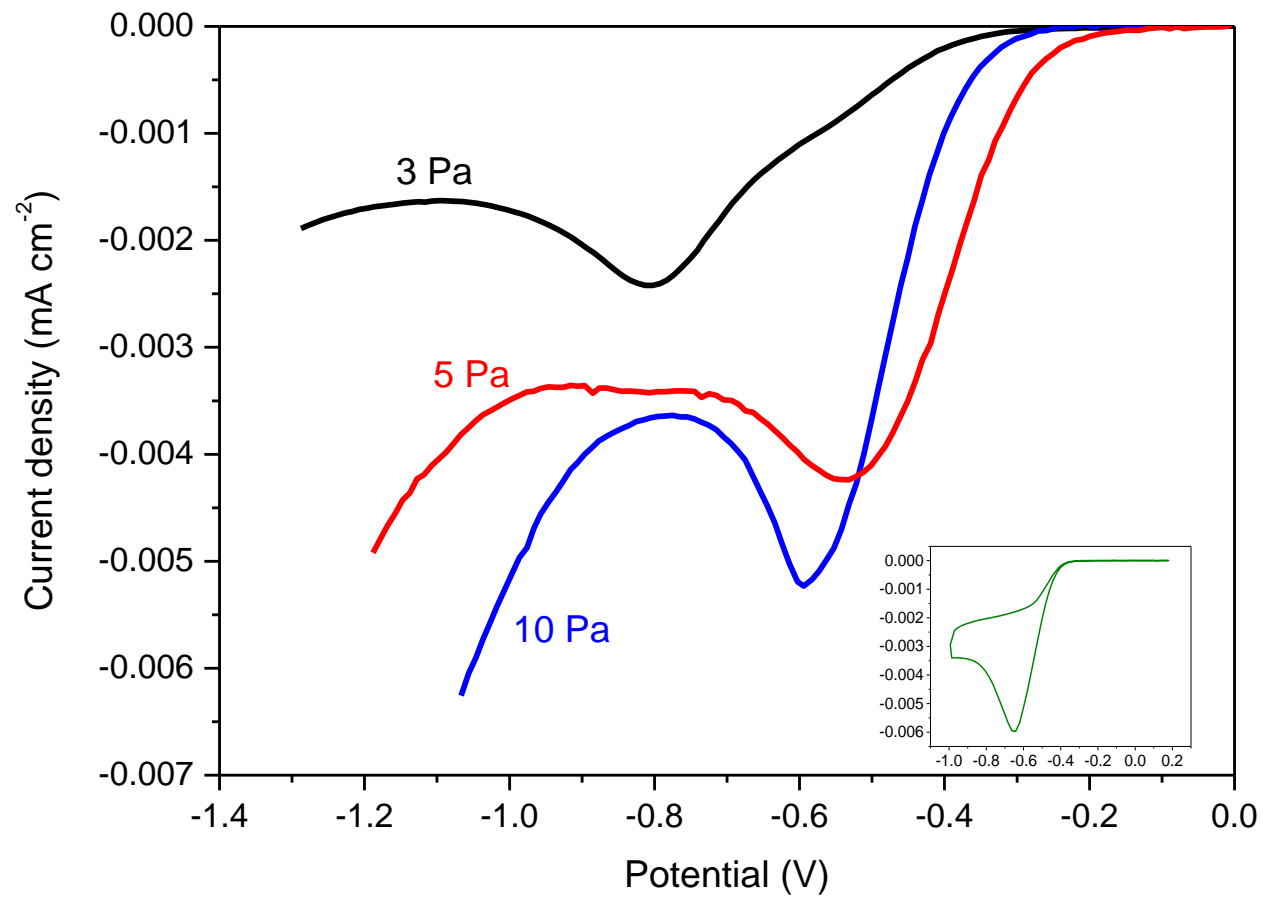
Fig 4.



**Fig 5.**

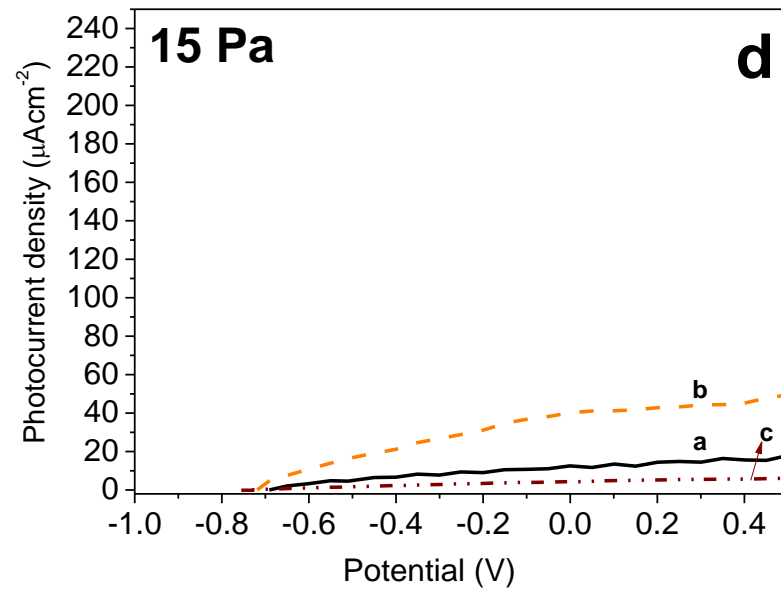
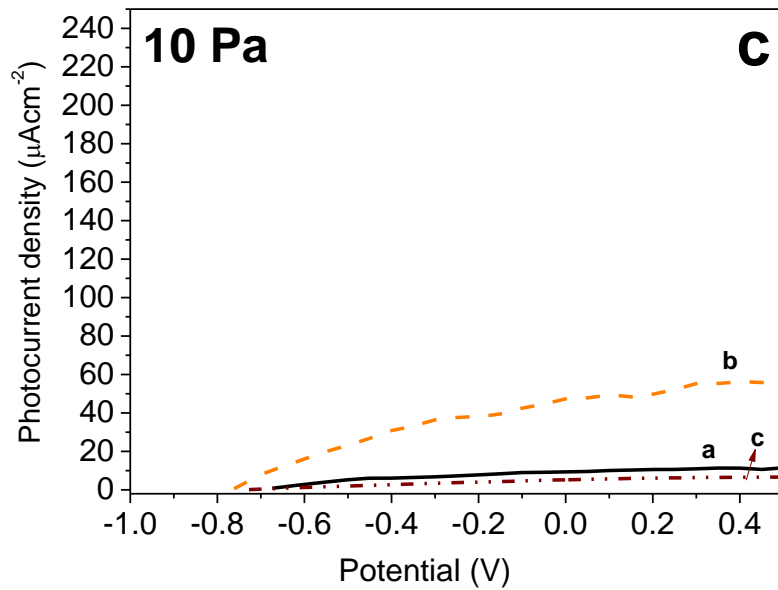
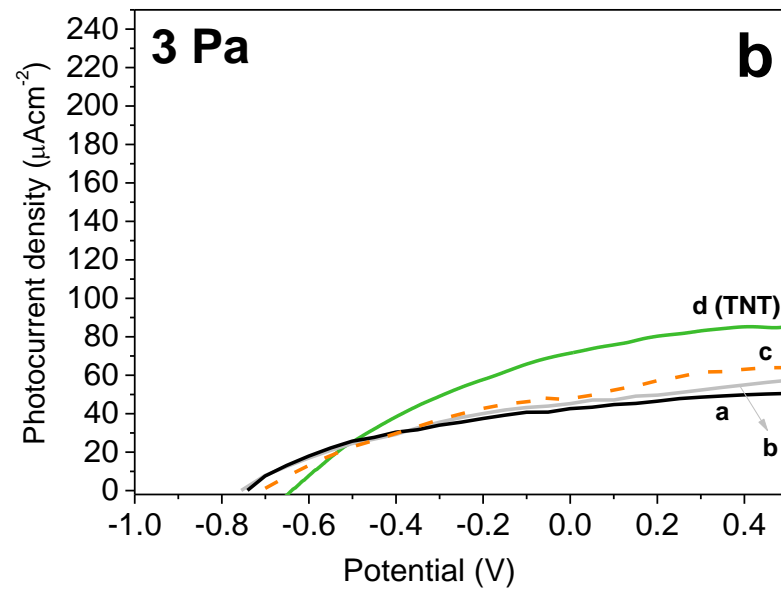
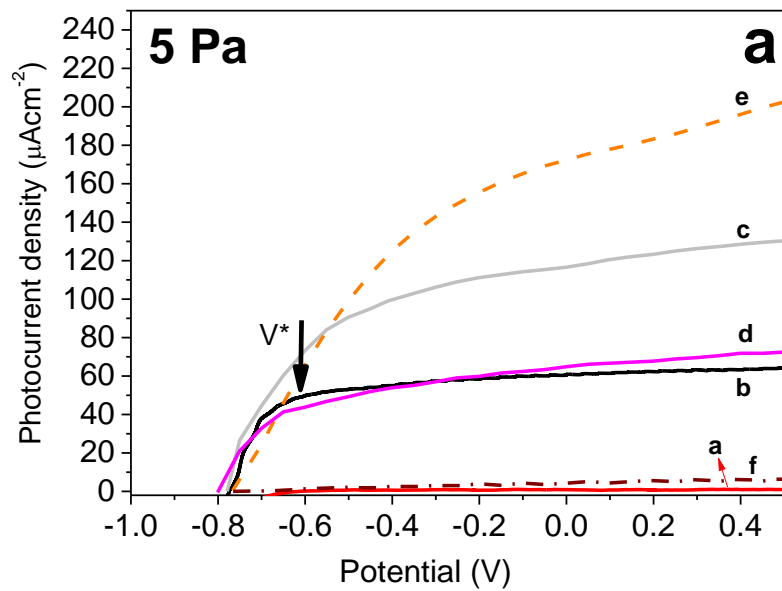


**Fig 6.**



**Fig. 7**





**Fig 8.**

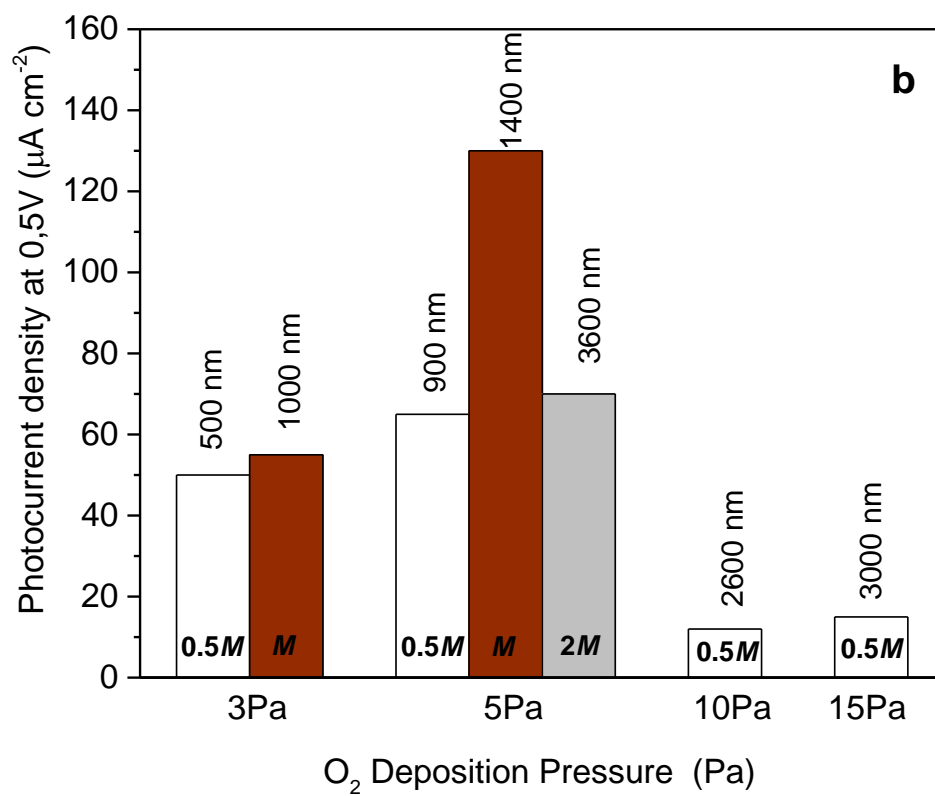
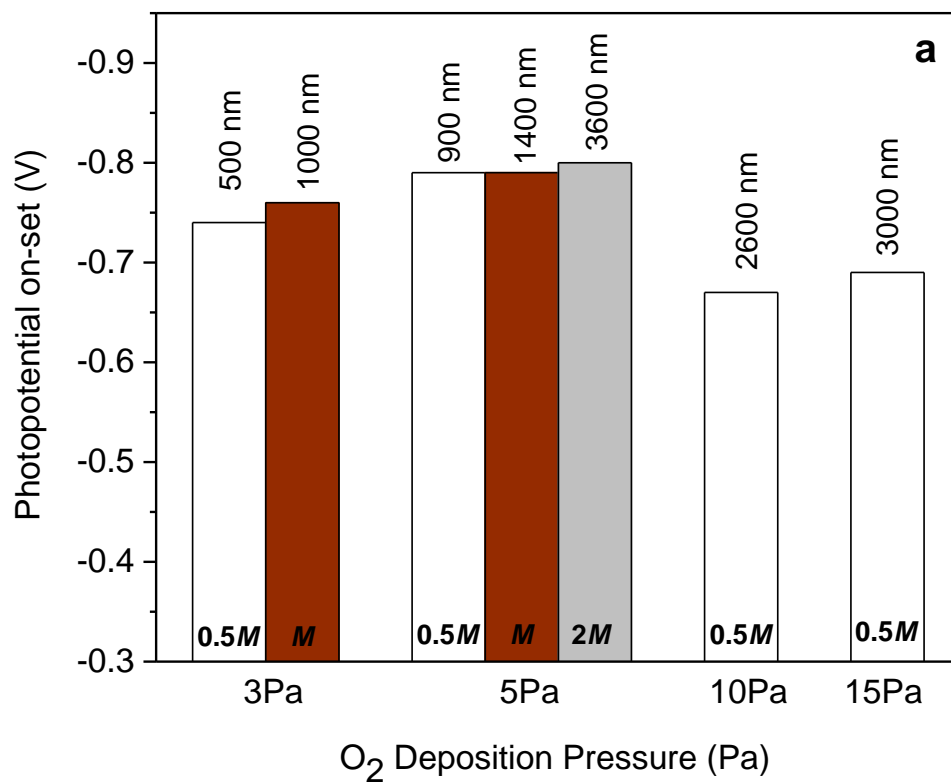
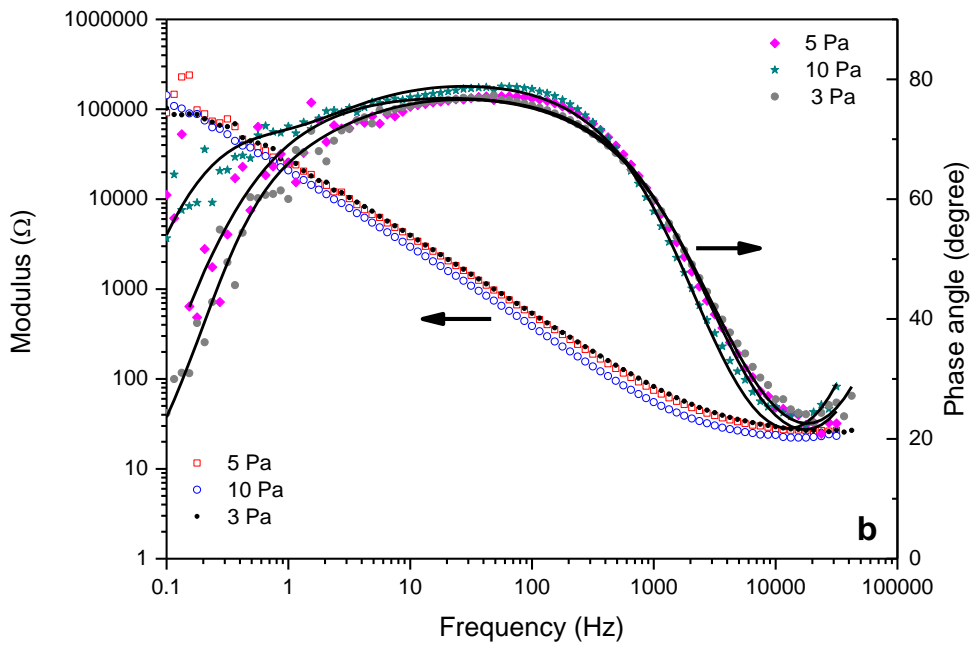
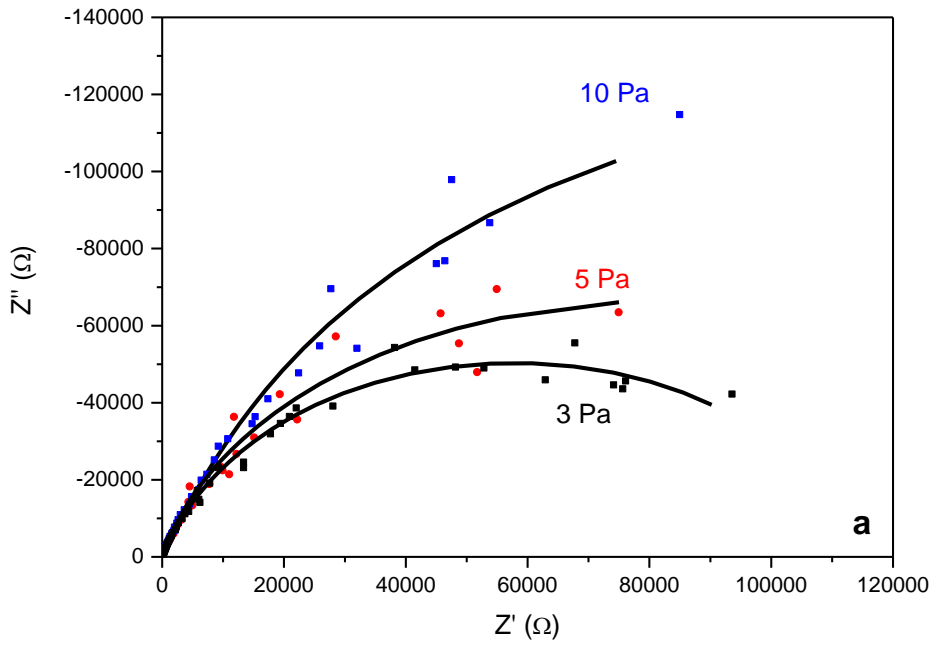
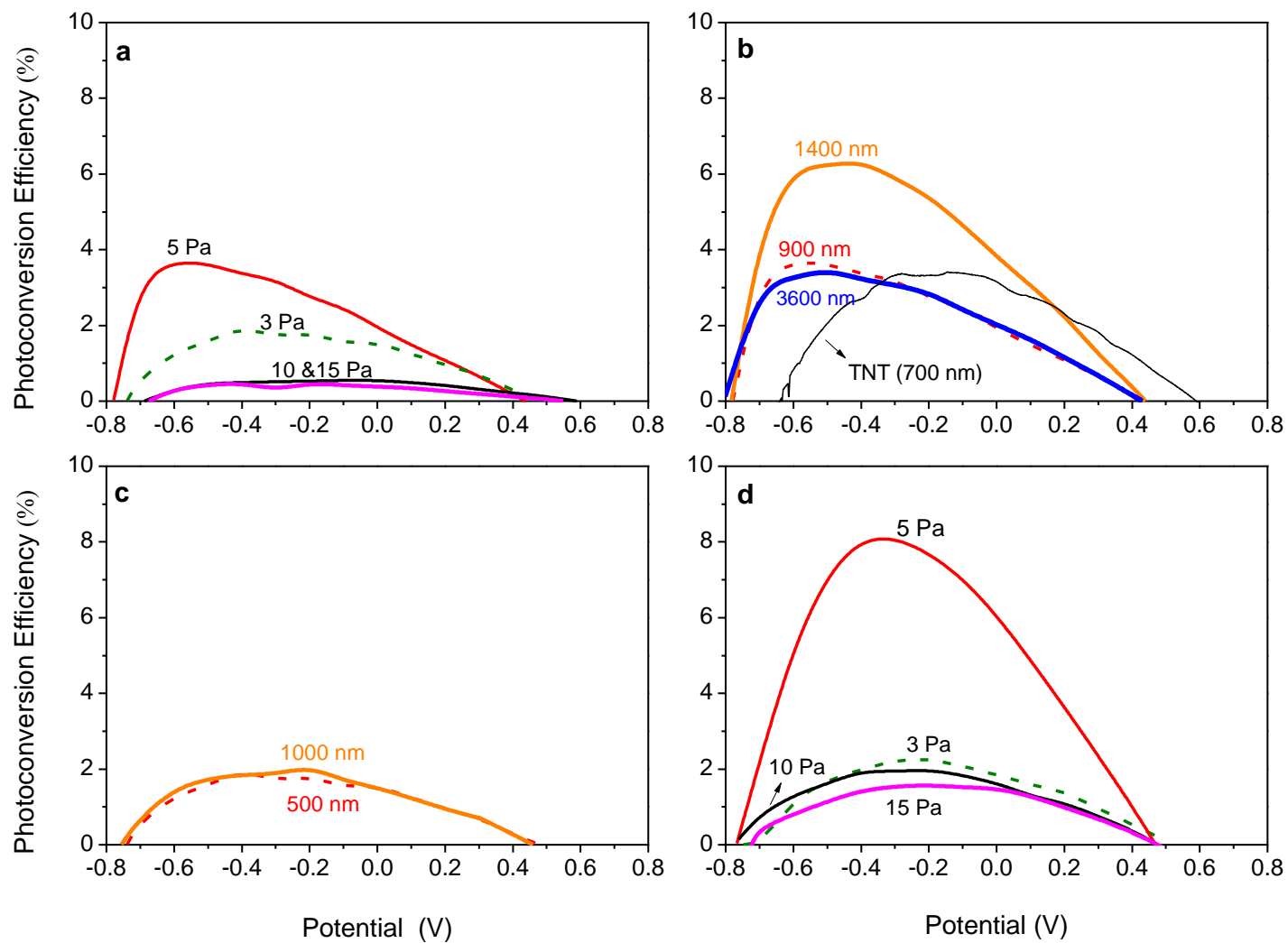


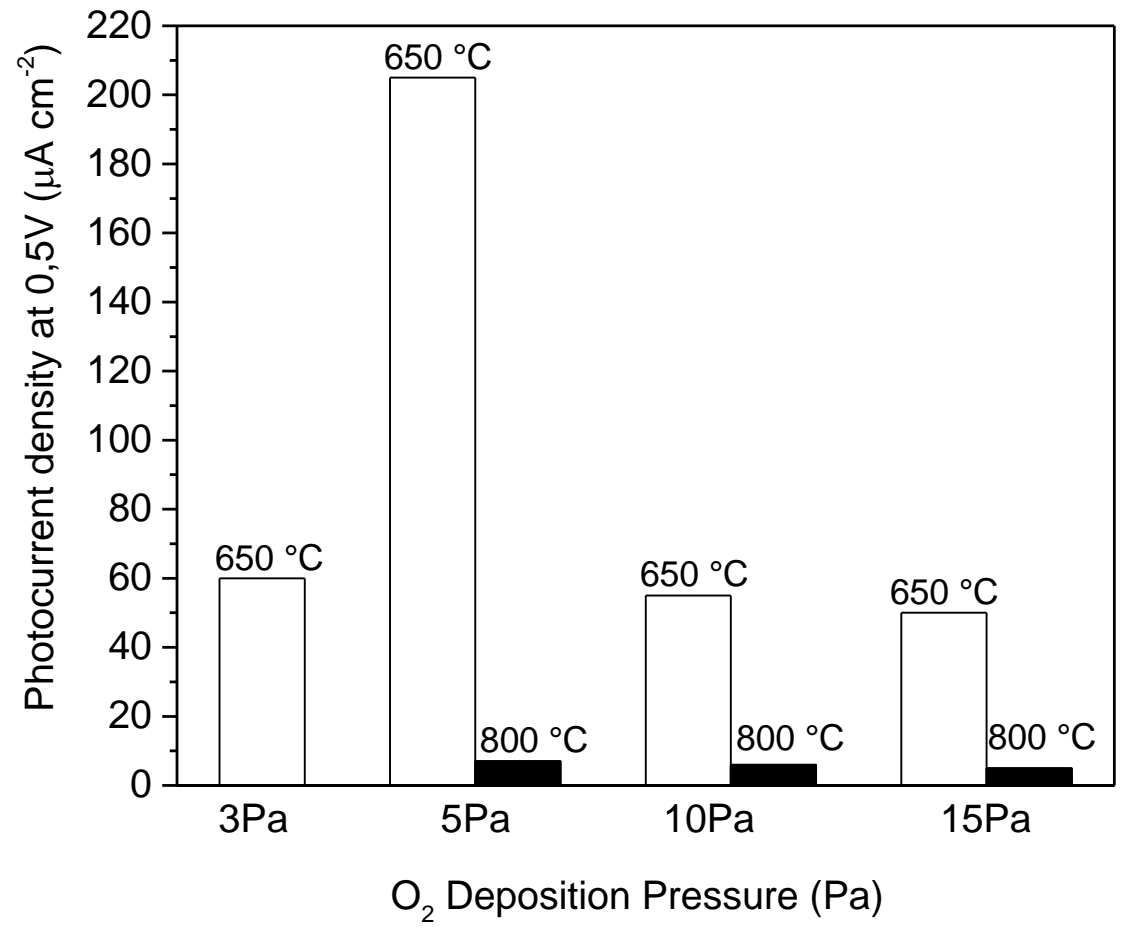
Fig 9.



**Fig 10.**



**Fig 11.**  
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**Fig 12.**

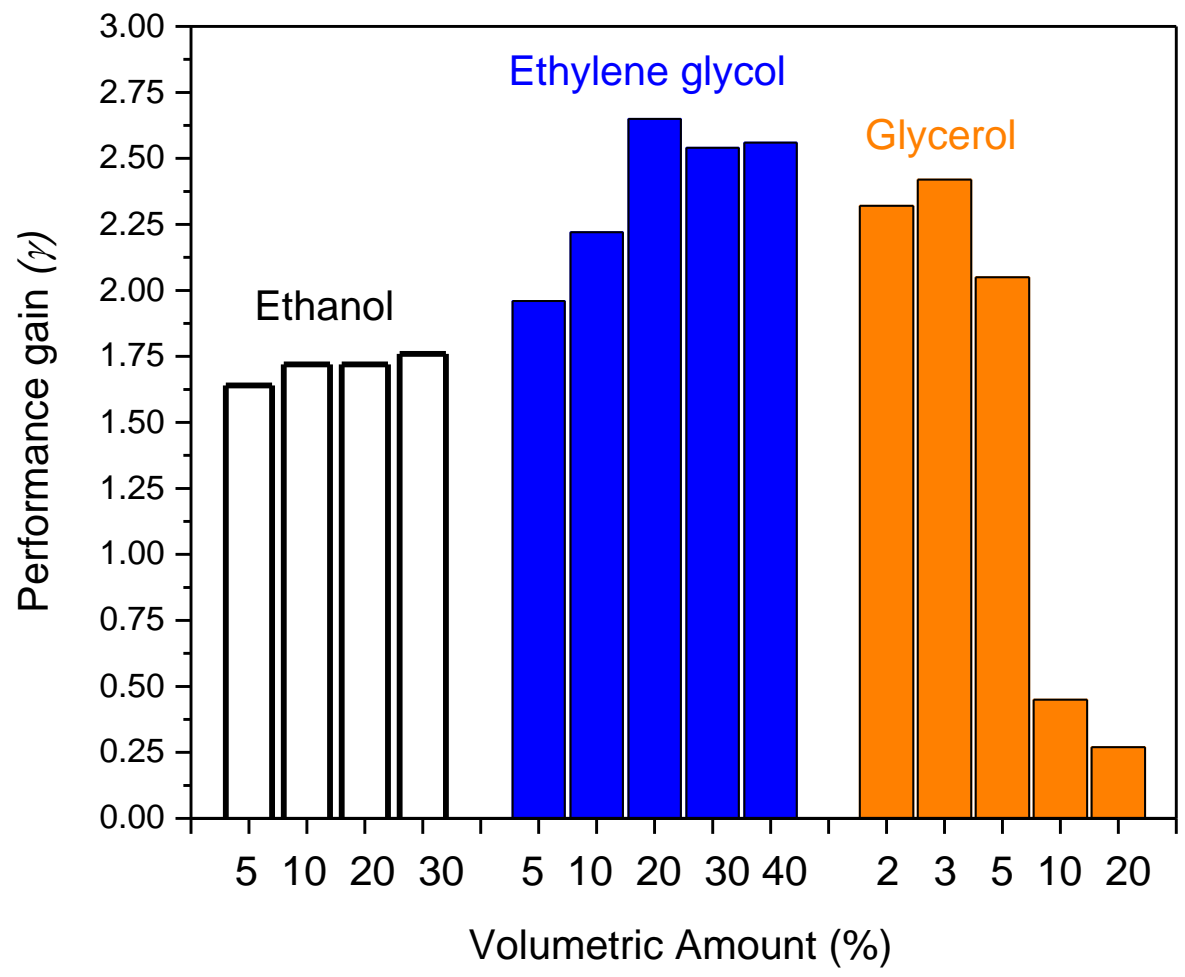


Fig 13.