

Synthesis and characterization of single-crystal TiO₂ Nanowires by thermal oxidation of Ti foil

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Abstract

TiO₂ nanowires (NWs) can improve the advantageous photocatalytic properties of TiO₂ by increasing the active surface area. Here we investigate the synthesis of TiO₂ NWs by thermal oxidation, studying the role of temperature, annealing time, and gas flow rates. The optimal thermal growth condition was found to be 800°C, 4h in a mixed gas flow of Ar and O₂.

Morphological and structural characterizations, carried out by scanning and transmission electron microscopy (SEM, TEM), and X-Ray diffraction (XRD), indicated a TiO₂ rutile monocrystalline structure of the nanowires. An in situ thermal growth analysis was performed by means of an environmental SEM, providing additional insights on the TiO₂ NWs growth dynamics.

The photocatalytic properties were studied by using the degradation rate of Methylene Blue under UV light. TiO₂ NWs revealed a 70% improvement of the degradation rate compared to a reference TiO₂ bulk sample. Moreover, NWs were additionally annealed in forming gas (5%H₂ in N₂) in order to promote the formation of oxygen vacancies and an increase of the carrier density. Indeed, the photocatalytic activity of the NWs treated in forming gas, was 3 times higher than the one of the reference TiO₂ bulk sample. The photonic efficiency and the quantum efficiency, also showed an increase versus bulk TiO₂ of about 20% in the presence of NWs, and of about 100% with the forming gas annealing. Moreover, this increase in the photocatalytic activity after the forming gas annealing correlates also with the disappearance of a deep level recombination center as observed by deep level transient spectroscopy.

1. Introduction

Titanium dioxide or titania (TiO_2) is a well known material with increased interest since the pioneering work of Fujishima and Honda in 1972 [1], which demonstrated its advantageous photocatalytic properties. Titania is an earth abundant material with various advantageous features, such as optimal photo-catalytic properties, reasonable optical and electronic properties, long lifetime of excited electrons, hydrophobicity, non-toxicity, excellent long-term chemical stability, environmental safety, high corrosion resistance and relative low cost [2, 3]. TiO_2 is also widely applied in many sectors of industry like cosmetic, paints, food, and as a self-cleaning and whitening agent. On the other hand, its large band gap (~ 3 eV) enables TiO_2 to absorb only in an UV range of the solar spectrum.

Titania occurs in three main crystalline phases: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic); among them, Rutile appears the most stable one [2].

TiO_2 has been used in a range of applications, while showing particular promise in photo catalysis, photovoltaic, chemical sensing, and optical devices. Specifically, in water purification, it is widely employed as it can degrade organic compounds (e.g. bacteria and pharmaceutical pollutants) that are exposed to UV light. Since this photo catalytic process is a surface mechanism, it can be made more efficient by increasing the surface area in contact with water. Therefore, synthesizing TiO_2 nano structures on the surface of the same material can boost this degradation process.

The focus of this paper is the study of the particular structures called nanowires (NWs) of TiO_2 , for applications in water purification. The NWs structure can also have further advantages such as the fact that can be used to create nano-membranes to be applied both for water filtration and purification [4, 5]. Literature works reported several methods for the synthesis of TiO_2 NWs such as hydrothermal process [6], chemical vapor deposition [7] and thermal oxidation [8, 9, 10, 11].

In this work, we focus on the growth of NWs by thermal oxidation; Vapour-Liquid-Solid (VLS) and Vapor-Solid (VS) are reported as growth mechanisms for TiO_2 NWs [8]. Thermal methods allow producing TiO_2 NWs with low chemical contaminations in the stable phase of rutile. Synthesis mechanism is still controversial and a systematic study as a function of annealing parameters is lacking. Moreover, NWs can be grown on a solid substrate offering the possibility to perform an experimental investigation of their electrical properties with conventional and well-established spectroscopic characterization techniques. Defects in TiO_2 can affect the photocatalytic activity, so it is important to correlate the several properties of the material in a systematic framework of characterizations. In this work, we varied temperature, annealing duration, gas content and flow during the annealing in order to

determine the process conditions, which optimize the NWs production in terms of NWs length, density and structure. Scanning Electron Microscopy with *in situ* annealing helped to understand the transition between the growth of NWs and the concurrent large grain TiO₂ structures as a function of temperature and time. The photocatalytic activity and the electrical properties of the NWs were also investigated by using the dye degradation method of methylene blue and Deep Level Transient Spectroscopy (DLTS), respectively. In particular, it has been reported [12, 13] that an atmosphere of H₂ in N₂ can increase the photoefficiency of TiO₂ by the formation of oxygen vacancies, which increase the shallow donor density, promoting the conductivity and improving the charge collection. We used an additional annealing in forming gas (a mixture of H₂ and N₂ gas) in order to investigate the effect on the TiO₂ electrical properties.

2. Experimental

2.1 Materials preparation

The samples used as substrate for the growth of TiO₂ NWs were Ti foils, with thickness of 0.13 mm and 0.25 mm and purity $\geq 99.99\%$ (Sigma Aldrich). Each sample was cut by diamond saw in pieces of about 1x1 cm² and cleaned via ultra-sonication in acetone for 30 min and in isopropyl alcohol for 15 min. Afterwards, a thin layer of Au with thickness in the range of 3-5 nm, was deposited on the sample surface by means of an RF (60 Hz) Emitech K550X sputter. The deposition occurred in Ar flow at a plasma current of 10 mA for 1 to 3 min, with a chamber pressure of 0.02 mbar and using an Au target of 99.999% purity. Then, in order to synthesize the TiO₂ NWs, the thermal oxidation process was applied by annealing in a carbolite horizontal furnace at temperatures between 700°C and 1000°C, for 1 to 4 hours in a mixed gas flow of argon (1.5 – 10 lpm) and oxygen (5 – 1 lpm). Some samples were additionally annealed in forming gas (a mixture of nitrogen and hydrogen at 5%) at 500°C for 2h.

For the *in situ* thermal growth, an Au film was deposited on the Ti foil surface, following the same procedure already reported for the other samples. Then, the sample was inserted in the SEM furnace placed inside the SEM chamber and annealed at 1000°C in water vapour atmosphere at 500 Pa. The *in situ* SEM annealing was performed using a FEI Quanta 200 FEG Environmental-SEM.

2.2 Characterization

The morphology was analysed by Scanning Electron Microscopy (SEM) using a Gemini field emission SUPRA 25 of Carl Zeiss, in plan-view and cross-section. The structure was investigated with

X-Ray Diffraction (XRD) by means of a Bruker D-9000 diffractometer with Cu K α . The Au thickness was determined by Rutherford Backscattering Spectrometry (RBS) with 2 MeV $^4\text{He}^+$ beam and 165° scattering angle. Transmission Electron Microscopy (TEM) was performed by using a microscope Jeol 2010F with a camera Gatan Orius 2k/2k at an acceleration voltage of 200 keV.

For the electrical measurements, 100 nm thick Au contacts were deposited on the TiO₂ NW samples and on a single crystal (rutile) bulk TiO₂ sample for comparison. The depositions were made by thermal evaporation through a shadow mask and the contacts displayed a Schottky behavior with about one order of magnitude (or more) in current rectification between +1 V in forward and -1 V in reverse bias. The DLTS measurements were carried out in the temperature interval of 50 to 300 K using a refined version of the setup described in Ref.X [B.G. Svensson, K.H. Rydén, and B.M.S. Lewerentz, J. Appl. Phys. **66**, 1699 (1989).J]; the quiescent reverse bias used was -1 V together with 1 V filling pulse of 50 ms duration.

2.3 Photocatalytic experiment

The study of the photo-catalytic properties was carried out following the international standards ISO 10678:2010 [14, 15]. We monitored the degradation of a common dye, the methylene blue (MB), in a water solution under UV light.

First, the sample was preconditioned: it was exposed to UV light (TL 8W BLB 1FM Philips lamp, in the wavelength range of 350-400 nm with a stable irradiance of 1.1 mW/cm² at the sample surface), in order to clean the surface from any organic contaminant, which could affect the measurements. Then, the sample was placed in a cuvette filled with the MB water solution (2 ml at $\sim 10^{-5}$ M) and kept in dark. In this way the dye degradation was monitored in dark for about 12 h until saturation (variation $< 1\%$ hour⁻¹); after this step, the decrease of MB concentration due to the physical absorption of the dye by the sample surface can be considered negligible. Afterwards, the cuvette with the MB and the sample was covered with a quartz glass to prevent the solution evaporation, and irradiated with the same UV light employed for the preconditioning step; the experiment was carried out at room temperature condition and in air. Meanwhile, we monitored the MB degradation by measuring the absorbance of the solution, which is proportional to the MB concentration according to the Lambert-Beer law [16]. During 3 hours we measured every 20 min the absorbance at the wavelength of 664 nm, where the main absorbance peak of MB occurs, by means of a spectrophotometer (Lambda45, Perking-Elmer) in the wavelength range of 500-750 nm. With these values, normalized to the macroscopic area, we could calculate the pseudo-first order photocatalytic

rate constant or degradation rate of our sample, following the degradation kinetics law. We also performed all the mentioned processes in parallel with a cuvette containing only the MB solution, in order to have a control reference measurement.

In addition, measurements of the samples reflectivity were carried out by means of a Lambda 40 Perking-Elmer spectrophotometer, in order to evaluate the fraction of photons that are not reflected and that are actually involved in the photocatalytic process.

3. Results and Discussion

3.1 NWs synthesis on Ti foil

TiO₂ NWs on Ti foil were synthesized using different annealing times (1 to 4 hours), temperatures (700°C to 1000°C) and flow rates (various O₂/Ar mix). The effect of the annealing temperature was investigated by thermally processing Ti foils samples at 700°C, 800°C, 900°C and 1000°C. Temperatures below 700°C showed poor growth of NWs.

Figure 1 reports the SEM plan-view images of samples annealed at 700°C (fig.1.a and e), at 800°C (fig.1.b and f), at 900°C (fig.1.c and g) and at 1000°C (fig.1.d and h). The images in fig.1.a) to d) refer to samples annealed for 1 hour, while 4 hours annealing was applied to the foils reported in fig.1.e) to h). The results indicate that increasing the temperature above 700°C, the growth kinetics is strongly improved. Indeed, at 700°C very few NWs were grown, and they are characterised by a maximum length of 200-300 nm (fig.1.a). Already at 800°C (fig.1.b), the growth improvement was well visible: the NWs density increased and the maximum length went up to 2-3µm. Au nanoparticles are present on top of the nanowires, indicating that the growth mechanism corresponds to the Vapour-Liquid-Solid (VLS) process, that is well-known in the literature particularly for the synthesis of silicon nanowires [17]. This means that nanowires are formed because of the unidimensional growth that is catalysed by the Au nanoparticles laying on the surface. First, Au nanoparticles are formed on the substrate surface because of a de-wetting process [18]. Second, Ti atoms diffused from the substrate into the Au drops and precipitated. Since several NWs show a larger bottom section with respect to the top, VLS could not be the proper mechanism, but it could be referred to as a diffusion mediated growth. Being in oxygen atmosphere, TiO₂ formed and the TiO₂ nanowire elongated along a main growth direction. Furthermore, several nanowires present a change of direction within their structures, even with very sharp edges. This effect is probably due to the presence of an extended defect in the crystallographic structure of the nanowire. Indeed, as for a polycrystalline growth [19], the nucleation of a crystallographic defect can act as an instability and lead to an abrupt change of crystal structure that – in the nanowire – is observed like a sharp change of the main growth direction.

Increasing the annealing temperature to 900°C (fig.1.c), the synthesized structures stay very similar to the ones processed at 800°C. An increase of the average length of the NWs up to 4-5µm is just observed.

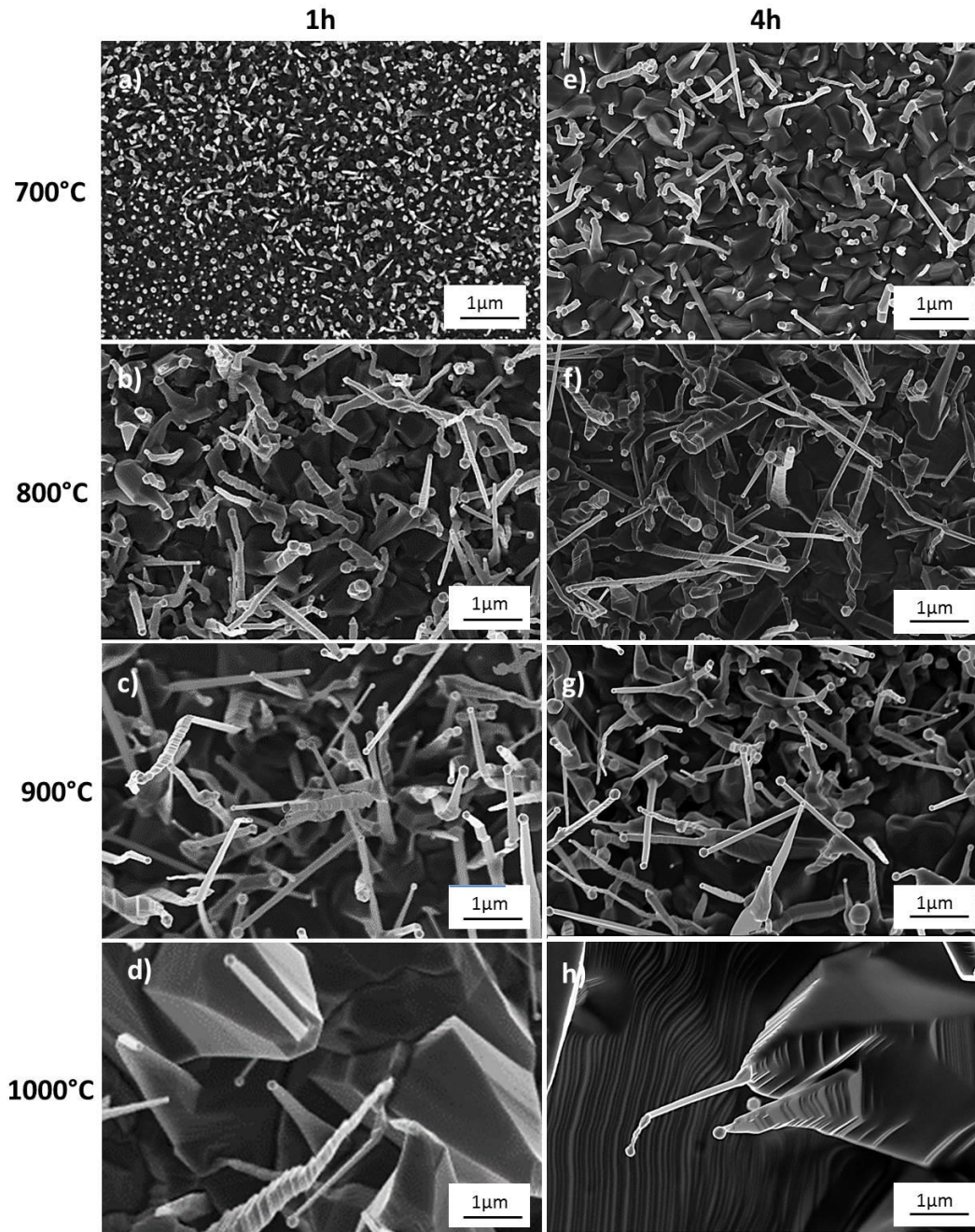


Figure 1 - SEM plan view of TiO₂ NWs growth at different temperatures: a) and e) at 700°C, b) and f) at 800°C, c) and g) at 900°C, d) and h) at 1000°C. Annealing time of 1h was applied for the samples a) to d), and 4h for samples e) to h).

A different effect was obtained by annealing at 1000°C, where the NWs growth mechanism occurred in competition with microcrystal grain formation, as showed in the SEM image of fig.1.d.

It is important to mention that the samples processed at annealing temperatures higher than 800°C, resulted to be fragile and friable at the macroscopic level, hence not optimal for applications.

Fig.1e) to h) show the samples obtained after increasing the annealing time to 4 hours. In particular, a comparison of fig.1a) and e) show that at 700°C the nucleation is improved (higher density of NWs) together with the length and the diameter of the nanostructures. At 800° and 900°C we observe an increase in the average NWs length. This is due to the fact that the nucleation is fully activated at temperatures higher than 700°C, therefore longer annealing time only favour the growth of NWs in length. Fig.1h (sample processed at 1000°C, 4h) shows that the competitive mechanism of micrograins nucleation prevails over the NWs growth, since the grains increased in size while the NWs are shorter and set on the top of the grains. In the following, mainly the Ti foil annealed at 800°C for 4 hours is studied, considered as the optimal sample.

The growth direction of nanowires has no specific orientation with respect to the substrate. Epitaxial growth was observed for Si VLS nanowires on a single crystal substrate [17]. This is not the case for oxides, moreover the substrate foil has a polycrystalline structure.

Several nanostructures are formed during the annealing process. The SEM plan view images of fig.2 show that it is possible to find structures such as ribbons, facet nanowires, spikes, rods, either with or without the Au drop on the top. However, the predominant structure is the facet nanowire with gold on its tip, as also illustrated by the images in fig.1. In fig.2 (bottom images), it is also possible to better appreciate the morphology of the NWs Au caps, which do not show a spherical shape but a more facet one. This indicates again that the growth process is not properly VLS where the Au nanoparticles typically present a spherical smooth surface, having passed through the liquid phase. Once again, the growth mechanism could be referred to a diffusion mediated growth or to a Au catalyzed VS mechanism, where the Au nanoparticles remain in their solid phase and take that facet structure. Furthermore, a pure VLS mechanism with Au as catalyzer is difficult to predict for TiO₂ NWs since the Au-Ti phase diagram does not exhibit a single eutectic point such as the Au-Si one [17].

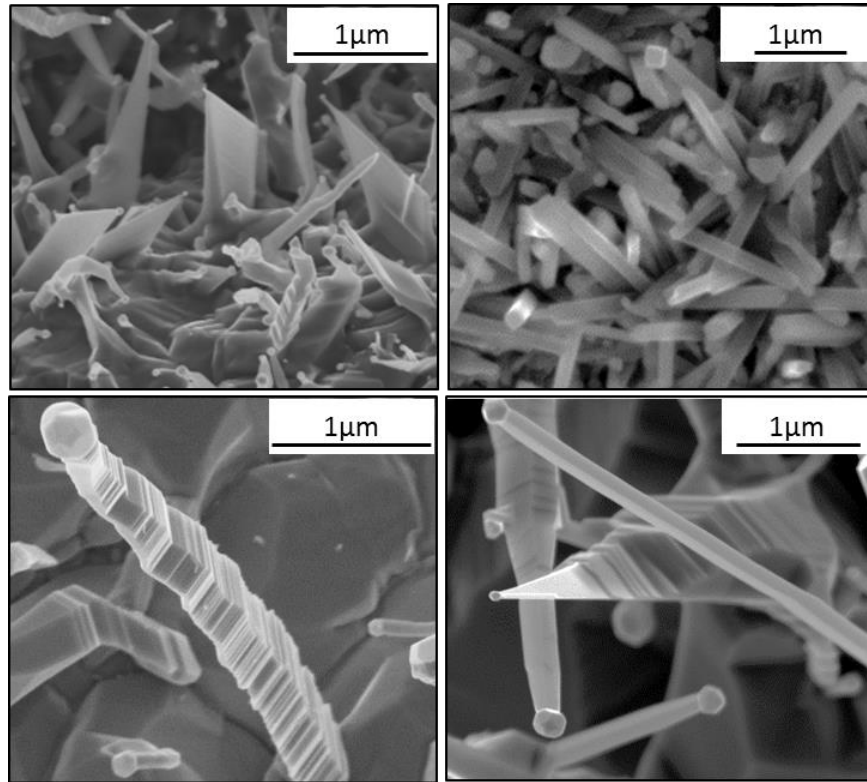


Figure 2 – SEM plan view of different TiO₂ nanostructures grown during the thermal oxidation process of a Ti foil.

In order to investigate the nucleation mechanism in relation to the different synthesis parameters, such as gas carrier flow and oxygen content, we prepared a set of samples processed with different gas flow in the furnace chamber at the annealing temperature of 700°C, which is the threshold temperature for the activation of the nucleation process.

Figure 3.a) shows the high resolution SEM plan-view images of the annealed sample for 4 h at low Ar flow (1lpm). The Ar gas used for this experiment was pure at 99.999%, so the oxygen contamination is negligible within the range of the experimental set up. TiO₂ grains are well distinguished on the sample surface and some of them have an elongated shape on their top that indicates the formation of a NW with a large base (inset of fig.3a). Au nanoparticles are well separated from each other, indicating that de-wetting occurred. Some Au nanoparticles appear to evolve in a dendritic shape as shown in the SEM image of the inset of fig.3a. This effect was reported for Au de-wetting on oxide substrate and it is related to the fast temperature quenching of the annealing process [20]. NWs appear only in few spot with very small area ($\sim\mu\text{m}^2$). In particular, these few NWs nucleated without the VLS process but in rod-shape since the Au nanoparticles are not visible on the top. This kind of growth mechanism was reported in the literature for other metal oxides NWs, and it is promoted by the presence of surface

roughness or defects in the substrate [21]. Since the substrate is a Ti foil, this growth mechanism is randomly induced on the surface. The uniformity of NWs over the full sample area was indeed very poor in this condition, since NWs can only be detected in small bunches as the one shown in fig.3a. In fig.3.b, it can be observed that the increase of Ar flow (to 15lpm) favours the NWs growth in some larger spots of the sample with respect to the low gas flow condition (fig.3a). However, the distribution over the full sample area is still poor, as observed in the insert of Fig. 3.b, where the bright zones contain NWs. Therefore, we investigated how to improve a uniform density distribution of NWs. We observed that an increase of oxygen content was effective to promote a uniform growth. Figures 4 a), b) and c) report the SEM images of samples annealed at 700°C for 1 h with different mix of argon and oxygen flow. The NWs distribution is uniform over the full size of the sample (fig.4d). However, the effect of Ar/O₂ ratio in this range of gas flow does not provide a remarkable effect in terms of NWs density increase. The optimal gas condition was then set to 7.5 lpm of oxygen and 10 lpm of argon, based on the experimental results of NWs growth.

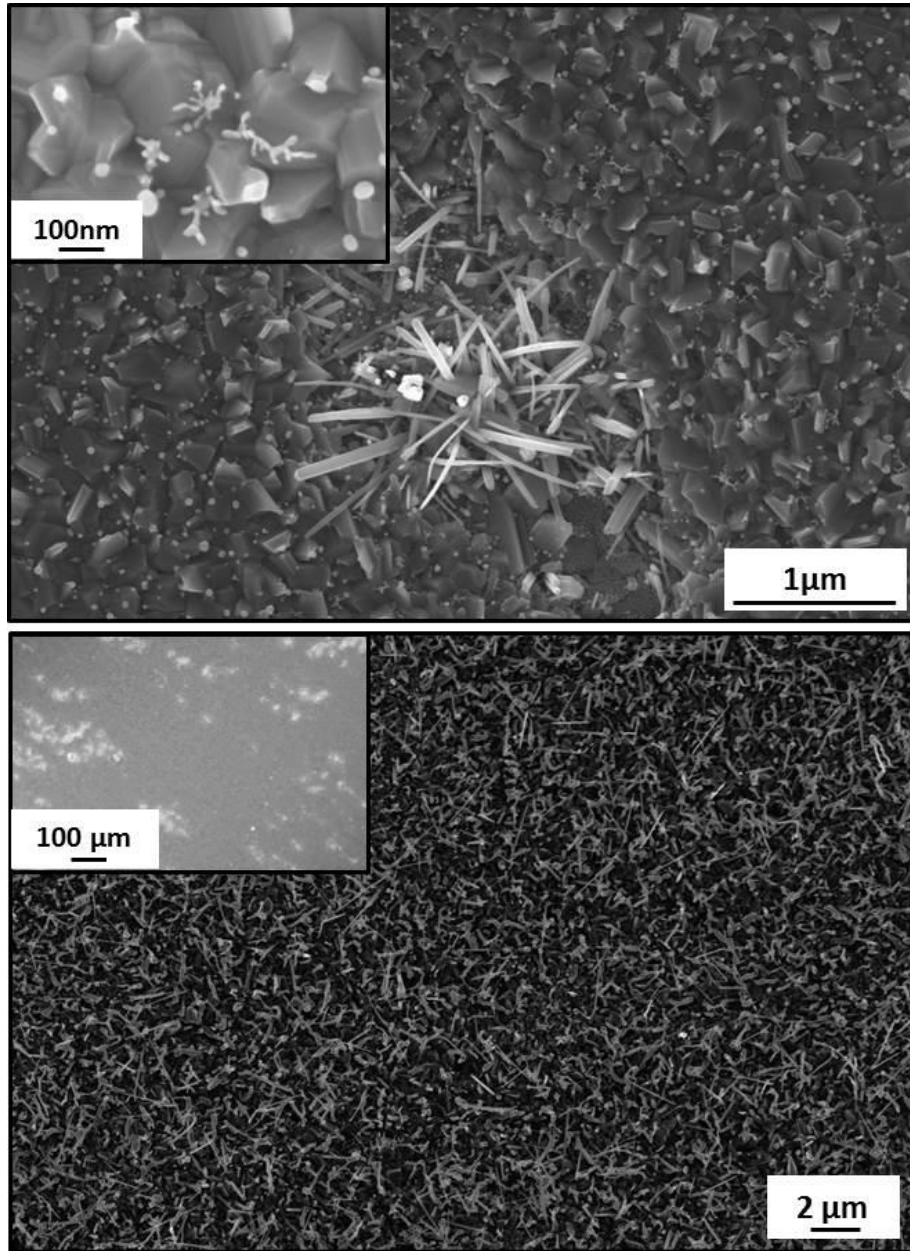


Figure 3 – SEM plan view of TiO₂ foil with a 3nm of gold layer deposited on the surface, annealed at 700°C for 4h with a) a low Ar flow of 1 lpm and b) an high Ar flow of 15 lpm. Bright zones in the insert of b) contain NWs.

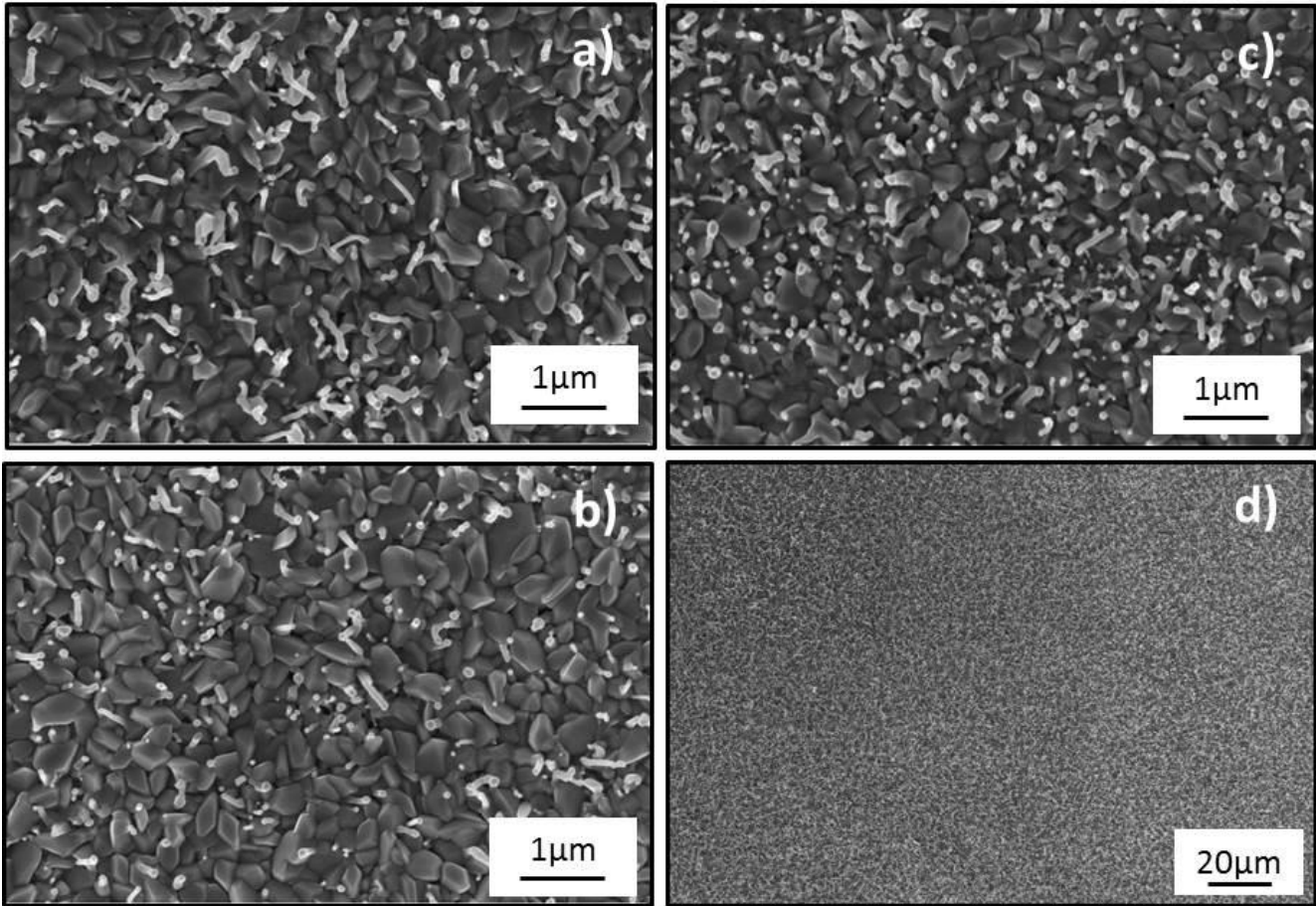


Figure 4 - SEM plan views of TiO₂ samples annealed at 700°C for 1 h with different argon and oxygen flows: a) O₂ 1.5 lpm and Ar 10 lpm; b) O₂ 5 lpm and Ar 10 lpm; c) O₂ 10 lpm and Ar 5 lpm; d) O₂ 7.5 lpm and Ar 10 lpm (optimal flow) view at low magnification.

The structure of the TiO₂ NWs has been analysed by XRD and the results are shown in fig.5. The TiO₂ signals are always found to be rutile phase which is reported to be the most stable structure upon annealing at temperatures higher than 600°C [22]. The most intense peak is represented by the (110) orientation that is reported to be the most thermodynamically stable in the rutile TiO₂ structure [2]. The signals associated to gold are also present, and they are due to the Au nanoparticles formed on top of the NWs.

Figure 6 shows the TEM analysis performed on TiO₂ NWs isolated from the substrate. The diffraction pattern indicates that the NWs are pure TiO₂ monocrystalline. In diffraction conditions we were able to identify the crystal orientations of TiO₂ rutile associated with the (110) and (200) planes. The NW has a quite uniform diameter of about 200 nm, which shrinks in the highest third part of the NW down to about 120 nm just at the bottom of the Au cap. In the inset of fig. 6 the crystal planes are clearly distinguishable.

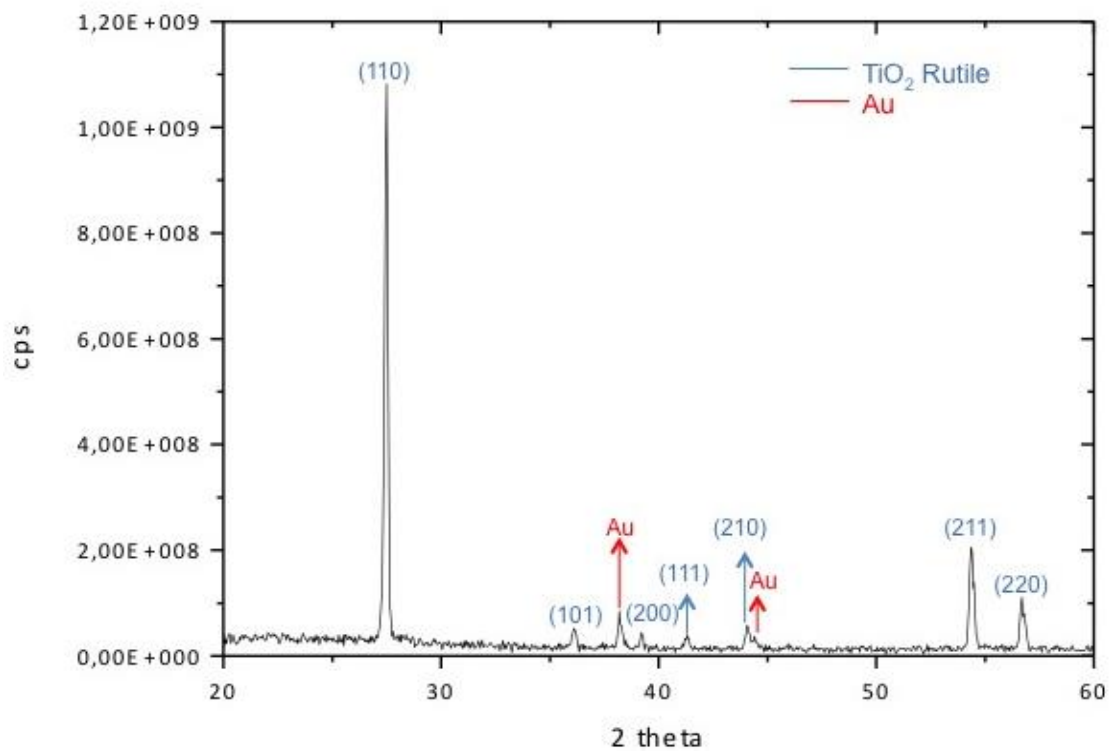


Figure 5 - XRD analysis of TiO₂ NWs synthesized by thermal oxidation.

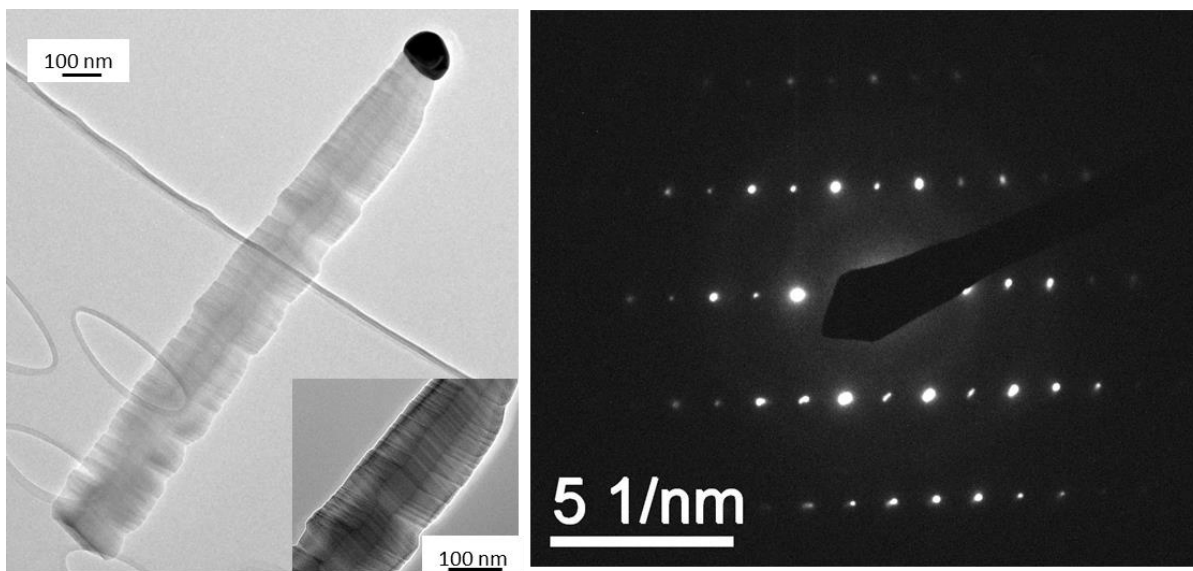
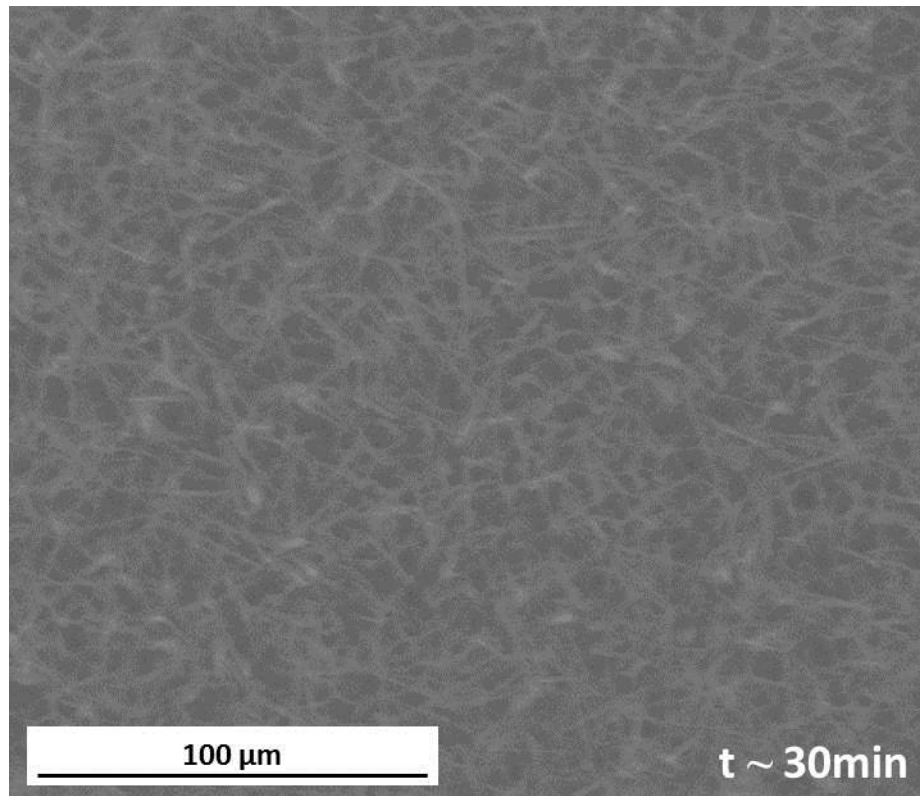


Figure 6 – TEM image of a TiO₂ NW and its diffraction pattern.

3.2 *In situ thermal growth*

In order to investigate in more detail the growth mechanism of the NWs, an *in situ* thermal growth was performed by means of an environmental SEM on a Ti foil substrate, coated with Au thin film, as described in section 2.1. The sample was inserted in the SEM furnace placed inside the SEM chamber and annealed at 1000°C in water vapour atmosphere at 500 Pa. The SEM detector showed that as soon as we started the annealing, an explosive growth of NWs occurred (length of about ~ 30 µm) at the sample surface. The main growth occurred during this initial stage and fig.7 reports a representative SEM plan view of the sample after about 30 min annealing.

Figure 7 – SEM plan view images of TiO₂ NWs synthetysed by *in situ* thermal growth



at 1000°C in water vapour atmosphere at 500 Pa, at an annealing time of about 30 min.

Applying a lower annealing temperature of 800°C with the same conditions of atmosphere and pressure, the growth process is slower and the NWs growth dynamics was possible to monitor as a function of time. It was possible to obtain SEM images on average every 2 minutes for a total annealing time of 2 hours and 15 minutes (*in situ video available as supplementary information*).

Fig.8 reports six representative images of a sample area near the edge, obtained when the annealing was just started (fig.8 a), and then after different annealing times, i.e. 20 min (fig.8 b), 40 min (fig.8 c), 1 h (fig.8 d), 1h 45 min (fig.8 e) and 2h 15 min (fig.8 f). During the first 20-40 minutes (fig.8 b and c), there is higher rate of growth of NWs in length and density, with dimension up to 10-20 μm in length and up to $\sim 10^2$ nm in diameter. During the following hour (fig.8 d and e), the NWs tend to shorten and become wider in their base, creating more wide rods/grains shapes, with width and length both of a few microns.

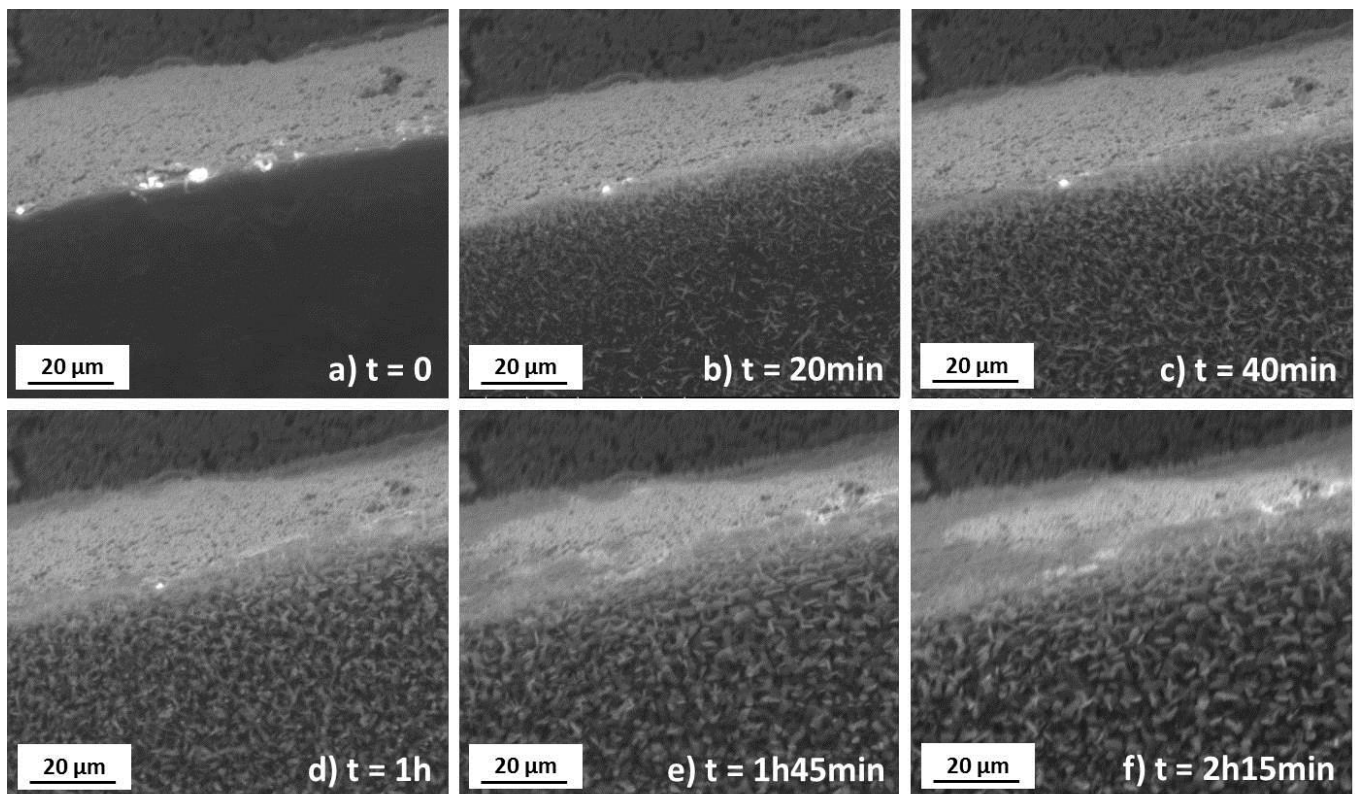


Figure 8 – SEM plan view images of TiO₂ NWs synthetysed by in situ thermal growth at 800°C in water vapour atmosphere at 500Pa, at the beginning of the annealing (a) and after an annealing time of 20 min (b), 40 min (c), 1 h (d), 1h 45 min (e) and 2h 15 min (f).

This is in agreement with the study of Perez [23] that reports an increased oxidation rate of Ti for short times in water vapour; while, as the annealing time increases, the oxidation rate decreases and the formation of dense oxide scales is observed. Motte et al. [24] also reported an higher oxidation rate of Ti for short time of annealing under water vapour.

3.3 Photocatalytic properties

The analysis of photo-catalytic activity of the synthesized NWs is illustrated in Figure 9. The plot shows the values of the logarithm of the absorbance at 664 nm normalized to the initial value at $t=0$ s and to the macroscopic area of each sample; the lines represent the fits with linear regression. The reported data refers to the following samples: MB reference solution without any TiO_2 sample (blue downward triangles); TiO_2 reference foil without NWs (green upward triangles); TiO_2 foil with NWs (black squares); TiO_2 foil with NWs and additional annealing in forming gas at 500°C for 2h (red circles). The TiO_2 reference sample without NWs was processed with the same annealing treatment as the NWs sample but without gold previously sputtered on its surface. The negative slope of the lines (not considering the MB reference solution), confirm a decrease with time of the absorbance and therefore of the MB concentration; this indicates that the TiO_2 photocatalysis reaction, i.e. the degradation of the dye, took place. This slope represents the pseudo-first order photocatalytic rate constant (or degradation rate) of the photo-catalysis reaction per unit of area. The inset of fig.9 shows more clearly the degradation rate (K) of the samples per unit area (A) normalised to the degradation rate of the TiO_2 reference sample without NWs. The histogram illustrates that the sample with TiO_2 NWs shows an increase in the degradation rate of almost 70% compared to the one of the reference TiO_2 foil without NWs. Moreover, an additional thermal treatment in forming gas results in a further improvement of the degradation rate, which is almost 3 times higher compared to the one of the reference TiO_2 foil and almost doubled versus the one of the TiO_2 NWs sample. These results indicate that the presence of NWs gives a considerable contribution to the photocatalytic properties of the material. Furthermore, they suggest that the annealing in H_2 atmosphere acted on the TiO_2 NWs sample increasing the carrier density [12, 13] and so the surface degradation reactions.

The mean photonic efficiency of the MB degradation (ζ_{MB}) was calculated as indicated in the international standards ISO 10678:2010 [14]:

$$\zeta_{\text{MB}} = \frac{P_{\text{MB}}}{E_{\text{P}}} \times 100$$

where P_{MB} is the photoactivity, corresponding to the average degradation rate calculated during the UV irradiation; E_{P} is the mean photon UV-radiation intensity from the lamp used during the MB experiment.

ζ_{MB} refers to the efficiency of the photons in the process of MB degradation, considering the total light incident on the sample. The resulting efficiencies for the three samples are reported in Table 1. The NWs sample showed an increased photon efficiency of 25% compared to the TiO_2 sample

without NWs. Moreover, the NWs annealed in forming gas, revealed an even higher photon efficiency, doubled with respect to the ζ_{MB} of the reference TiO₂ foil. Another significant parameter to take into account is represented by the quantum efficiency of the MB degradation (Φ_{MB}), which considers only the effect of the absorbed photons (or not reflected) [25].

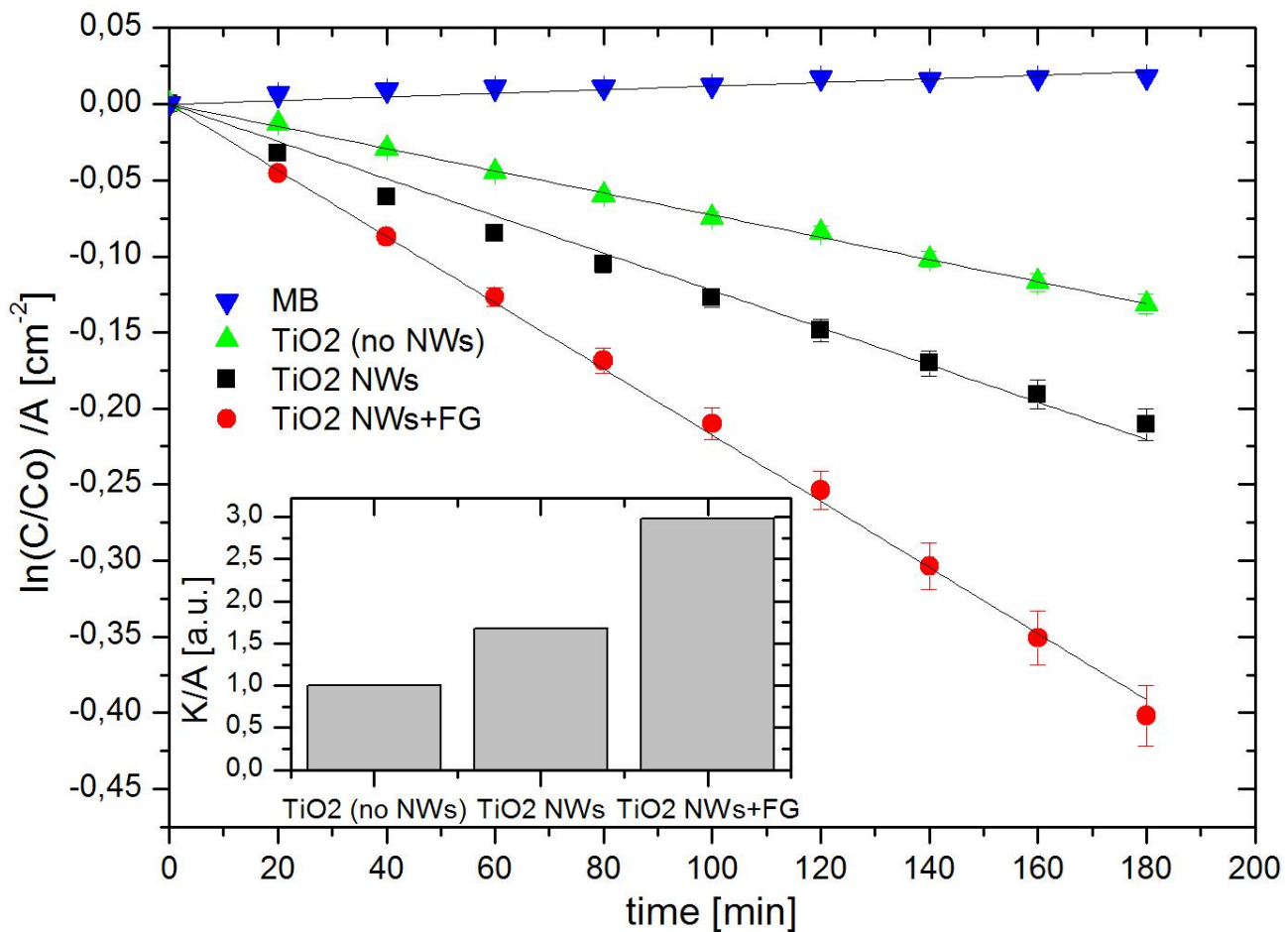


Figure 9 – Photocatalytic activity of various samples: MB reference solution without any TiO₂ sample (blue downward triangles); TiO₂ reference foil without NWs (green upward triangles); TiO₂ foil with NWs (black squares); TiO₂ foil with NWs and additional annealing in forming gas (FG, red circles). Inset: degradation rate per unit area (K/A) of the samples normalised to the K/A obtained from the TiO₂ reference foil without NWs.

For this purpose, the reflectance of the three studied samples was measured and it is here reported in fig.10 together with the spectra of the UV lamp employed for the MB photocatalytic degradation measurements. The quantum efficiencies were then calculated by using these values of reflectance in the spectra of the UV lamp used in our MB experiment (table 1). The obtained Φ_{MB} values showed

again an improvement with the presence of the NWs of almost 20% compared to the reference TiO₂ foil; this increase went up to 90% in the case of NWs treated with the forming gas.

These improvements in efficiencies further confirm the positive effect of the nanowires structures and of the additional forming gas treatment, in the photocatalytic properties of the TiO₂ material. Such results can provide a good upgrade in several sectors of application of TiO₂.

Table 1 – Photocatalytic and efficiency parameters of the studied samples.

| | TiO ₂ (no NWs) | TiO ₂ NWs | TiO ₂ NWs+FG |
|---------------------------|---------------------------|----------------------|-------------------------|
| K/A [a.u.] | 1 | 1.67 | 2.98 |
| ζ_{MB} [%] | 0.0095 ± 0.0009 | 0.012 ± 0.001 | 0.019 ± 0.001 |
| Φ_{MB} [%] | 0.011 ± 0.001 | 0.013 ± 0.001 | 0.021 ± 0.001 |

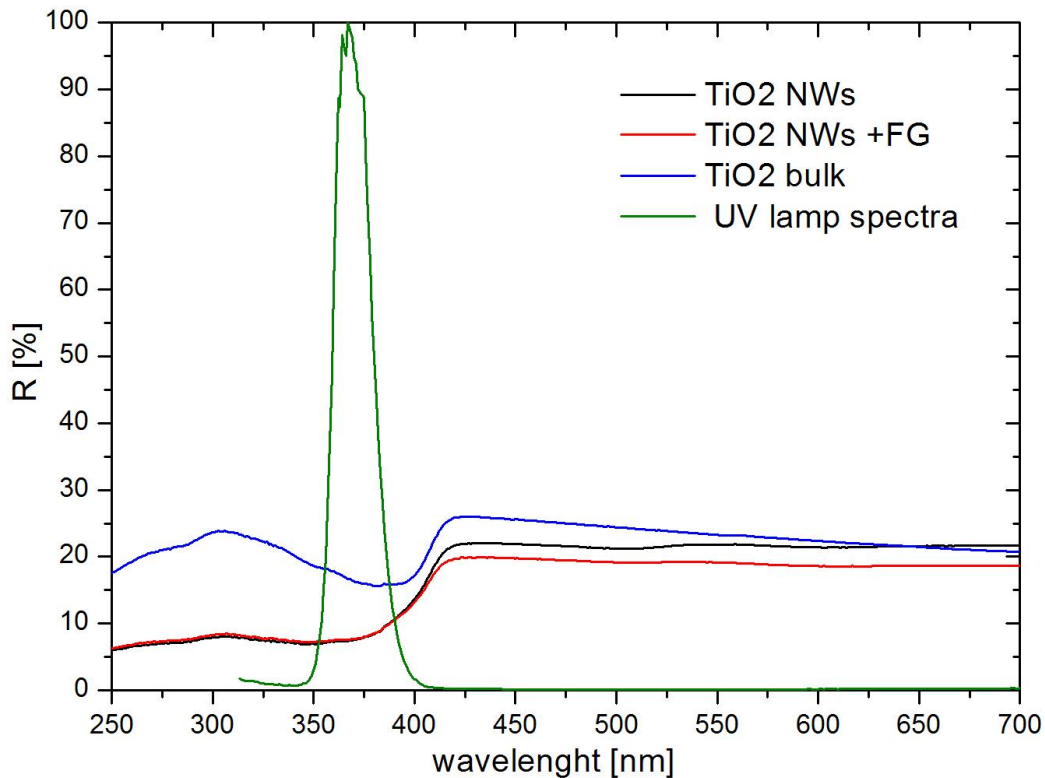


Figure 10 – Reflectance of the three studied sample and spectra of the employed UV lamp.

3.5 Electrical properties by Deep Level Transient Spectroscopy

Figure 11 shows DLTS spectra of two TiO₂ NW samples, one as-grown and one subjected to post-growth treatment in FG similar to that for the samples in Fig.9. Further, the spectrum of an as-grown TiO₂ sample without NWs is also included for comparison. Four peaks are clearly resolved occurring at ~55 K, ~110 K, ~188 K and >320 K, respectively, and they are labelled E₁, E₂, E₃ and E₄. The E₄ peak was not possible to cover fully because of the high conductance of the Schottky contacts at temperatures above 320 K. The corresponding energy positions extracted from six DLTS spectra, recorded simultaneously during one temperature scan and with rate windows between (20 ms)⁻¹ and (640 ms)⁻¹, are given in Table 2. The apparent electron capture cross sections of the levels, obtained by extrapolation of the Arrhenius plots of their emission rates, are also included in Table 2. The spectra of the ‘no NW sample’ and the as-grown ‘NW sample’ are similar both in shape and amplitude of the four peaks. However, the ‘NW + FG sample’ exhibits a considerably higher amplitude of the shallow E₁ peak than the other samples while the E₂, E₃ and E₄ peaks are substantially weaker. This holds especially for the deep E₄ peak which has vanished and the spectrum displays negative values above ~275 K presumably caused by hole injection. The loss of the E₄ level after the FG treatment can be correlated with the increase in photocatalytic activity of the ‘NW + FG’ sample in Fig.9. As mentioned above, the position of the E₄ level cannot be determined from the present data but it is estimated to be located at least 0.6 eV below E_C assuming a capture cross section with a typical value of ~10⁻¹⁵ cm². Hence, E₄ can be anticipated to act as a competing charge carrier recombination center suppressing the catalytic effect of the photon-induced electron-hole pairs.

The identity of the E₁, E₂, E₃ and E₄ levels is not known and previous DLTS data in the literature on deep levels in TiO₂ NWs are scarce (if any). In fact, this holds also for mono-crystalline TiO₂ bulk material where the recent amount of DLTS reports is very limited. An early study by Duckworth et al. [C.N. Duckworth, A.W. Brinkman and J. Woods, Phys. Stat. Sol, (a) **75**, K99 (1983)] showed the presence of a level at ~E_C-0.4 eV in Nb-doped rutile samples. This level is possibly identical to the E₃ level in our samples, and Duckworth et al. discussed a tentative assignment to the oxygen vacancy. Regarding the E₄ level, it is tempting to make an association with a defect of dangling bond character being passivated by hydrogen during the FG annealing. However, further work needs to be pursued in order to confirm this speculation.

Table 2 – Energy level positions and apparent electron capture cross sections of the E_1 , E_2 , E_3 and E_4 levels

| Level | $E_C - E_T$ [eV] | σ [cm^2] |
|-------|------------------|----------------------------|
| E_1 | 0.11 | $\sim 10^{-14}$ |
| E_2 | 0.30 | $\sim 10^{-13}$ |
| E_3 | 0.45 | $\sim 10^{-14}$ |
| E_4 | >0.6 | - |

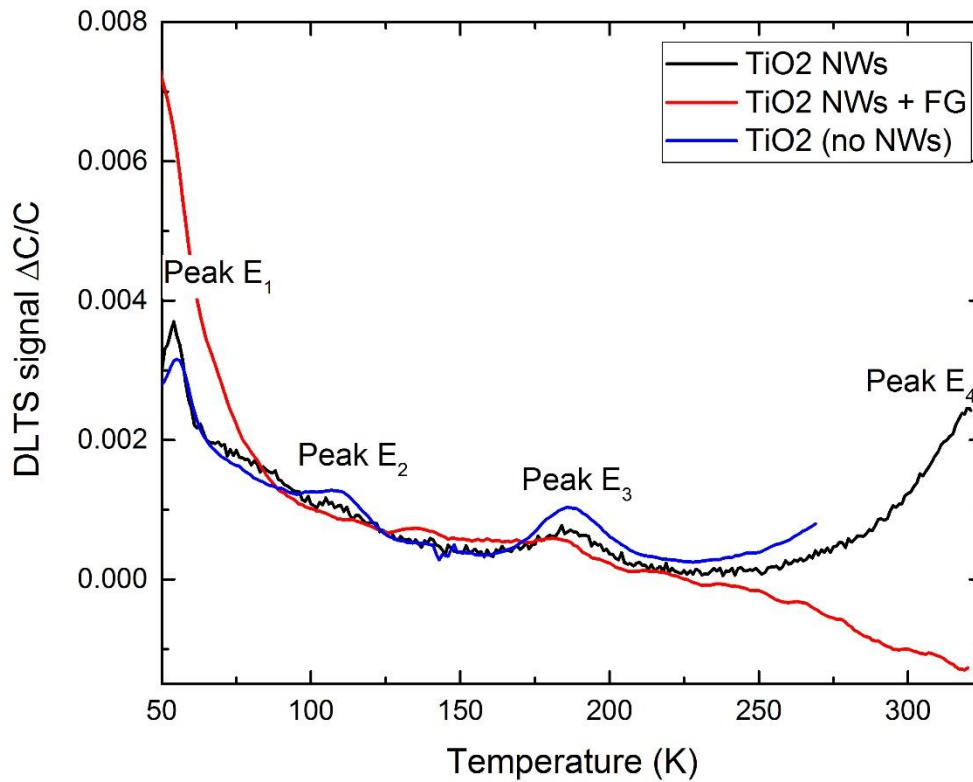


Figure 11. DLTS spectra between 50 and 325 K for three different samples; ‘TiO₂ NW’ (as grown), ‘TiO₂ NWs + FG’, and a TiO₂ sample without NWs. Reverse bias = -1V, filling pulse = +1V, and rate window = $(640 \text{ ms})^{-1}$.

4. Conclusions

Thermal oxidation synthesis of TiO₂ NWs was performed on substrates of TiO₂ foils coated with a thin layer of Au (3-5 nm). Annealing at temperature below 700°C for 1h revealed very rare and short NWs. With increasing temperature, the NWs grew in length and in density. At 1000°C, a mechanism of micrograins growth appeared in competition with the NWs evolution. Increasing the annealing time to 4h amplified the effect obtained for 1h. Besides, samples annealed at temperature higher than 800°C became macroscopically friable. Hence, the optimal growth parameters were set at 800°C and 4h. Concerning the annealing atmosphere, an increase in gas flow rates improved the nanowires coverage, while varying the mixture of Ar and O₂ did not give relevant changes. The optimal gas condition was 7.5 lpm of oxygen and 10 lpm of argon. XRD measurements of the NWs revealed a TiO₂ rutile crystalline phase with a main peak from the (110) orientation. TEM analysis indicated that the NWs are pure TiO₂ monocrystalline. In situ thermal growth in water vapor atmosphere at 800°C for about 2h, showed that the rate of NWs growth in length and density was higher in the first 20-40 minutes (length up to 10-20 μm); subsequently the oxidation rate decreased and the NWs tend to shorten and became wider in their base, creating more wide rods/grains shapes (length of few μm).

The analysis of the photocatalytic properties of the TiO₂ NWs showed a degradation rate 70% higher compared to the one of a reference TiO₂ bulk sample. The photocatalytic activity of the NWs treated with forming gas, was 3 times higher than that of the reference bulk TiO₂ sample. Photonic efficiency and quantum efficiency of the MB degradation were also deduced and showed an increase relative to the reference bulk TiO₂ sample of about 20% for the NWs sample, and of about 100% for the NWs annealed in forming gas. According to DLTS measurements of the NW samples, the annealing in forming gas leads to a reduction of deep level recombination centers competing with the photocatalytic processes. These increases in efficiency indicate the positive contribution of the NW structures and of the additional forming gas treatment, to the photocatalytic activity of TiO₂. These results are, indeed, promising for applications of TiO₂ where nanowires are required, like for examples photocatalytic membranes or filters.

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Reference

- [1] Fujishima A and Honda K, *Nature* 238 (1972) 37-38.
- [2] Fujishima A, Zhang X, Tryk D A, *Surf. Sci. Rep.* 63 (2008) 515-82.
- [3] X. Chen, S. S. Mao, *Chem. Rev.* 107 (2007) 2891.
- [4] X. Zhang, T. Zhang, J. Ng and D.D. Sun, *Adv. Funct. Mater.* 19 (2009) 3731.
- [5] A. Hu, X. Zhang, K. D. Oakes, P. Peng, Y. N. Zhou, M. R. Servos, *J. Hazard. Mater.* 189 (2011) 278.
- [6] H. Yin, G. Ding, B. Gao, F. Huang, X. Xie, M. Jiang, *Mater. Res. Bull.* 47 (2012) 3124.
- [7] J. M. Baik, M. H. Kim, C. Larson, X. Chen, S. Guo, A. M. Wodtke and M. Moskovits, *Appl. Phys. Lett.* 92 (2008) 242111.
- [8] B. Dinan, S. A. Akbar, *Funct. Mater. Lett.* 2 (2009) 87.
- [9] J. M. Wu, W.-T. Wu and H.C. Shih, *J. Electrochem. Soc.* 152 (2005) G613.
- [10] J.-C. Lee, K.-S. Park, T.-G. Kim, H.-J. Choi and Y.-M. Sung, *Nanotechnology* 17 (2006) 4317.
- [11] B. Dinan, D. Gallego-Perez, H.Lee, D. Hansford, S.A. Akbar, *Ceram. Int.* (2013).
- [12] C. Fàbrega, T. Andreu, F. Guell, J.D. Prades, S. Estradé, J.M. Rebled, F. Peirò and J.R. Morante, *Nanotechnology*, 22 (2011) 235403.
- [13] G. Wang, H. Wang, Y. Ling, Y. Tang, X. Yang, R. C. Fitzmorris, C. Wang, J. Z. Zhang and Y. Li, *Nano Lett.*, 11 (2011) 3026-3033.
- [14] *Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue. ISO 10678:2010(E)*. International Organization for Standardization (2010). Switzerland.
- [15] A. Mills, C. Hill and P. K. J. Robertson, *J. Photochem. Photobiol. A.* 237 (2012) 7.
- [16] AD. McNaught, A. Wilkinson, *Compendium of Chemical Terminology, 2nd edition*. Oxford: Blackwell; 1997.
- [17] Wagner R. S., Ellis W. C., *Appl. Phys. Lett.* 4 (1964) 89.
- [18] C.V. Thompson, *Annu. Rev. Mater. Res.* 42 (2012) 399.
- [19] L. Romano, V. Privitera, C. Jagadish, *Defects in Semiconductors, 1st Edition*. Multi-volume: Semiconductors and Semimetal. Elsevier, 2015.ISO 10678:2010.

- [20] F. Ruffino, L. Romano, G. Pitruzzello, M. G. Grimaldi, *Appl. Phys. Lett.* 100 (2012) 053102.
- [21] M. Chen, Y. Yue, and Y. Ju, *J. Appl. Phys.* 111 (2012) 104305.
- [22] D. A. H. Hanaor, C. C. Sorrell, *J. Mat. Sci.* 46 (2011) 855.
- [23] P. Perez, *Corrosion Sci.* 49 (2007) 1172.
- [24] F. Motte, C. Coddet, P. Sarrazin, M. Azzopardi and J. Besson, *Oxidation of Metals* 10 (1976) 113.
- [25] N. Serpone and A. Salinaro, *Pure Appl. Chem.* 71 (1999) 303.