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# The influence of the morphology of 1D TiO<sub>2</sub> nanostructures on photogeneration of reactive oxygen species and enhanced photocatalytic activity

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### Abstract

The influence of morphology in one-dimensional (1D) TiO<sub>2</sub> nanostructures—specifically nanotubes (TNT), nanofibers (TNF), nanorods (TNR), and nanowires (TNW)-on the photogeneration of reactive oxygen species (ROS) and the resulting effect on photocatalytic activity were investigated. 1D TiO<sub>2</sub> nanostructures were obtained by hydrothermal route, by employing changes in the crystalline phase of TiO<sub>2</sub> precursor and reaction temperature as the morphology-controlling factors. Morphological, structural, textural, and optical properties were studied using scanning and transmission electron microscopy, X-ray diffraction, BET surface area analysis, diffuse reflectance and photoluminescence spectroscopy. The photochemical behaviour of these 1D TiO<sub>2</sub> nanostructures was evaluated through ROS quantification including <sup>1</sup>O<sub>2</sub> and <sup>•</sup>OH, and it was found that TNF exhibits the highest amount of generated ROS, the following tendency was observed: TNF > TNT > TNR > TNW. In addition, the photocatalytic activity for degrading methyl orange (MO) under visible light was studied, and a similar tendency was found. The results showed a more intense photoluminescence emission spectra signal for TNF, suggesting a higher concentration of superficial defects associated with oxygen vacancies (Ov), the same trend on the resulting Ov amount was established. Finally, a correlation between 1D morphology, ROS photogeneration as well as photocatalytic properties was determined. The results suggest the amount of Ov on each material act as active sites that improve the production of ROS as well as the photocatalytic activity. These results unveiled that generation of ROS is mainly dependent on the morphology type of 1D TiO<sub>2</sub> nanostructures, significantly affecting the photocatalytic activity of nanomaterial.

**Keywords:** Morphology, One-dimensional (1D)  $TiO_2$  nanostructures, reactive oxygen species (ROS), photocatalytic activity, oxygen vacancies (Ov).

### 1. Introduction

Photocatalytic destruction of various organic compounds has been proposed as a viable process to detoxify drinking water based on semiconductor photochemistry. These photocatalytic reactions are strongly dependent on the capacity to generate reactive oxygen species (ROS), including  $O_2$ ,  $^1O_2$ ,  $H_2O_2$  and OH by the semiconductor under irradiation [1, 2]. Over the past decades, several studies have demonstrated the most effective semiconductor for this purpose is titanium dioxide (TiO<sub>2</sub>) due to its high chemical stability, low cost, nontoxicity, high oxidizing power, and especially their electronic and optical properties [3-5]. However, it is well known that there are many factors that can significantly influence its photocatalytic performance, such as particle size, specific surface area, porous structure, crystalline phase, and exposed surface facets [6, 7]. In addition, a large number of studies show that the morphology also greatly influences the photocatalytic activity of TiO<sub>2</sub> [8, 9]. Thus, recently research on TiO<sub>2</sub> photocatalysts has focused on improving its photocatalytic properties by adjusting this last parameter.

One-dimensional (1D) TiO<sub>2</sub> nanostructures (e.g., nanofibers, nanotubes, nanorods, nanowires) possess unique properties and advantages for photocatalytic reactions due to their 1D geometry [7, 9]. For example, these structures possess a larger surface area compared with TiO<sub>2</sub> bulk, which could significantly increase the surface reaction sites and reduce the electron/hole recombination rate. Moreover, their one geometry allows a high interfacial charge carrier transfer rate due to the shorter distance for diffusion of these carriers [8, 10-13]. Thus, these effects are favourable for photocatalytic reactions.

Several techniques for synthesizing 1D  $\text{TiO}_2$  nanomaterials have been reported, including chemical vapor deposition (CVD), template based, anodic oxidation, solvothermal and hydrothermal synthesis [3, 11, 14-16]. Among these methods, the hydrothermal route is a low-cost and simple method for the control of the shape and size with different morphology [16]. The method developed by Kasuga et al. [11] has been most widely used over the last few decades to

synthetize 1D TiO<sub>2</sub> nanomaterials. Their morphologies can be tuned by changing the synthesis conditions, including such variables as reaction temperature and time, alkaline concentration, TiO<sub>2</sub>/NaOH ratio, post-reaction wash [7, 13, 17-19], and even the crystalline phase of TiO<sub>2</sub> raw material. However, previous works have demonstrated that the crystalline phase of TiO<sub>2</sub> precursor does not influence the formation of nanotubes [11, 20]. Thus, a precise control of the synthesis conditions is essential in order to obtain the appropriated 1D morphology.

TiO<sub>2</sub> nanostructures with different 1D morphologies have showed clear differences in their ability to photodegrade organic contaminants, the results have demonstrated the shape of 1D TiO<sub>2</sub> nanostructures plays a significant role in determining their photocatalytic activity [9, 21, 22]. Camposeco et al. [23] studied the morphology effect of various 1D TiO<sub>2</sub> nanomaterials (e.g., nanotubes, nanofibers, nanowires) on photodegradation of dyes. In this work, nanotubular morphology showed the maximum photocatalytic efficiency, attributed to its tubular geometry and high hydroxylation degree, which provides a greater amount of active sites through the generation of oxygen vacancies (Ov). Recently, it was reported that changes in the density of surface defects of TiO<sub>2</sub>-based nanomaterials as Ov, affect the photoactivity of these materials. These Ov have a significant effect on electronic and physico-chemical properties (e.g., electronic band structures, optical absorption), which are beneficial for the effective separation and mobility of the photo-generated charge carriers, improving its photocatalytic behaviour [24, 25]. 1D TiO<sub>2</sub> nanostructures such as nanotubes, nanowires, and nanoribbons have exhibited these surface defects; for example, Conceicão and his coworkers [24], demonstrated that Ov improve charge separation and extend the lifetime of the excited charge carriers.

On the other hand, it is well established that ROS play a central role in the photocatalytic activity of  $TiO_2$ -based nanomaterials. In a recent work, we have shown that there is a synergistic effect between the photogeneration of ROS and photocatalytic activity in  $TiO_2$  materials [26]. However, some studies have shown that the photogeneration of these species in photocatalytic systems could be significantly influenced by different properties of  $TiO_2$  nanostructures [1, 27, 28]. For

example, Jie Zhang and Yoshio Nosaka [29], reported that •OH radical generation depends on crystalline phase of TiO<sub>2</sub>. While, Uchino et al. [30] studied the influence of crystal size on •OH generation. Recently, it has been suggested that the presence of surface defects, mainly oxygen vacancies on TiO<sub>2</sub> surface could promote the ROS generation, since these defects can react with dissolved O<sub>2</sub> and lead to formation of ROS [31]. Moreover, Molina-Reyes and colleagues [32], have synthesized different TiO<sub>2</sub> nanostructures (such as nanoparticles, nanotubes and ultra-thin films) and investigated a possible correlation between the morphology of these nanomaterials and photogeneration of ROS. The results showed a similar photocatalytic activity towards hydroxyl radical generation for both titania nanoparticles and nanotubes, however, nanotubes exhibited higher antibacterial activity due to 1D morphology, which may allow a greater contact of the bacteria on the solid surface. Despite of several studies have reported the influence the ROS on the photocatalytic activity, to our knowledge there are not reports that have studied a correlation between the morphology of 1D TiO<sub>2</sub> nanostructures and ROS photogeneration.

Whereas, the most of these works are inclined to highlight that photocatalytic activity depends on the concentration of oxidizing species that can be generated on the nanostructured material itself, there are still lack results on the effect of 1D morphologies on the photoproduction of ROS, and its influence on photodegradation of contaminants as dyes. To clarify the effect of different 1D morphologies on ROS generation, and their photocatalytic activity, we measured the amount of 'OH radical and <sup>1</sup>O<sub>2</sub> photogenerated after visible irradiation of a series of 1D TiO<sub>2</sub> nanostructures (e.g., nanotubes, nanofibers, nanorods, nanowires) prepared via a hydrothermal route, and correlated the 1D morphology of TiO<sub>2</sub>-based nanostructures with photogenerated ROS and photoactivity for the degradation of methyl orange (MO) under visible light.

### 2. Materials and methods

### 2.1. Materials

Two precursors were employed to synthesize TiO<sub>2</sub> nanotubes (TNT), TiO<sub>2</sub> nanofibers (TNF), and

TiO<sub>2</sub> nanorods using the alkali hydrothermal method: commercial anatase-TiO<sub>2</sub> powder (Merck, purity  $\geq$  98.5 %) and commercial rutile-TiO<sub>2</sub> powder (Sigma-Aldrich, purity  $\geq$  98.5 %). For the synthesis of 1D TiO<sub>2</sub> nanostructures, sodium hydroxide from Merck (purity  $\geq$  98.5 %) and hydrochloric acid (Merck, p.a.) were used as the mineralizer and neutralizer, respectively. Methyl orange (purity  $\geq$  97.0 %) and BaSO<sub>4</sub> (purity > 99.99 %) were purchased from Sigma-Aldrich and used without further purification. All solutions used in the experiments were prepared with deionized water.

### 2.2. Synthesis of 1D TiO<sub>2</sub> nanostructures

Two synthesis parameters were modified: TiO<sub>2</sub> precursor and reaction temperature. Commercial anatase-TiO<sub>2</sub> powder and rutile-TiO<sub>2</sub> powder were employed as precursors for the preparation of TNT and TNF, respectively. Conversely, TNR and TNW were obtained using commercial rutile-TiO<sub>2</sub> powder as the precursor with a modification in reaction temperature. The hydrothermal treatment was similar to that given in previous reports of nanotube preparation [11]. Briefly, 1.0 g of TiO<sub>2</sub> was dispersed in 60 mL of aqueous NaOH solution (10 mol L<sup>-1</sup>) and ultrasonically treated for 15 min. After treatment in the ultrasonic bath, the specimen was magnetically stirred for 15 min, and then the mixture was treated in a Teflon-lined autoclave at 130 °C for 72 h for TNT and TNF and at 110 °C and 180 °C for TNR and TNW, respectively. After hydrothermal treatment, the suspension was separated by centrifugation and washed with deionized water, then HCl (0.1 mol L<sup>-1</sup>), and finally with deionized water again until the pH of the rinsing solution reached 7. The final product was obtained through centrifugation and dried at 80 °C for approximately 12 h. The solids were subjected to calcination at 550 °C for 4 h.

### 2.3. Characterization

The morphology of the TiO<sub>2</sub> precursors was investigated by scanning electron microscopy (SEM, FEI Quanta 250) operated at 20 kV, and the morphologies of the obtained powders were investigated by high-resolution transmission electron microscopy (HRTEM, Tecnai F20 FEG-S/TEM) operated at 200 kV. The structural phases and crystallinity of the samples (the starting

material and the hydrothermally treated products) were determined using a Bruker D8 Advance X-ray diffractometer with  $CuK_{\alpha 1}$  radiation at room temperature. The XRD instrument was operated at 40 kV and 30 mA. The data was processed using the Diffrac-Plus-Eva software. The textural properties of the materials were characterized by N<sub>2</sub> adsorption porosimetry (Micromeritics, ASAP 2010). Surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method. All samples were characterized by diffuse reflectance spectroscopy (DRS). UV-Vis DR spectra were recorded at room temperature by employing a Lambda 35 UV-Vis spectrophotometer (Perkin Elmer) equipped with two photodiode detectors and an integrating sphere accessory. BaSO<sub>4</sub> was used as the reflectance reference sample. Measurements were carried out using two radiation sources, a deuterium and a halogen lamp, for exciting the samples within the working wavelength range of 200-700 nm. The absorption spectra were obtained by analyzing the reflectance measurement with the Kubelka-Munk (KM) remission function:  $F(R\infty)$ . The optical energy band gap (Eg) can be determined from the plot of E=1240/ $\lambda_{Abs}$  and  $[F(R\infty)hv]^{1/2}$ , where E is the photonic energy in eV, and hv is the energy of an incident photon. Photoluminescence (PL) measurements were performed at room temperature using a Perkin-Elmer spectrofluorometer (LS-55) equipped with a Xenon lamp.

### 2.4. Photochemical characterization

### 2.4.1. Detection of hydroxyl radicals by fluorescence in the heterogeneous phase

The hydroxyl radicals produced after illumination of the nanomaterials were detected and quantified by fluorescence spectroscopy through the hydroxylation reaction of terephthalic acid (TA) in the heterogeneous phase. The hydroxylated product of this reaction is 2-hydroxyterephthalic acid (2-HTA) (Scheme 1), which is stable and highly fluorescent, whereas TA is practically non-fluorescent [33, 34].

### **Inset Scheme 1**

TA was dissolved in dilute NaOH solution ( $2 \times 10^{-3}$  mol L<sup>-1</sup>), and then 50 mg of photocatalyst

was dispersed in 50 mL of TA solution ( $5 \times 10^{-4}$  mol L<sup>-1</sup>). The mixed solution was stirred in the dark for 24 h and subsequently irradiated for 60 min under visible light. At different irradiation times, an aliquot was removed, and the mixture was centrifuged for 10 min at 4000 rpm, respectively. The supernatant was collected and analyzed by fluorescence. Fluorescence spectra of 2-HTA at an emission wavelength of 425 nm were measured on a Perkin Elmer LS45 fluorescence spectrophotometer. A calibration curve using the hydroxylated product as a standard was constructed to quantify the relationship between the fluorescence signal and the produced hydroxyl radicals.

### 2.4.2. Determination of singlet oxygen in the heterogeneous phase

Generation of singlet oxygen was also detected chemically, employing a histidine test in heterogeneous phase, as described in our previous report [26]. In a quartz reactor, 16 mL of an aqueous solution of L-histidine  $(2 \times 10^{-4} \text{ mol L}^{-1})$  was added to 4 mL of N,N-p-nitrosodimethylaniline solution  $(2 \times 10^{-4} \text{ mol L}^{-1})$  and 20 mg of photocatalyst. The suspension was stirred in the dark for 24 h. Then, the material was irradiated with visible light in a LuzChem LZC-4V photoreactor for 60 min. At regular time intervals during irradiation, aliquots of the mixture were centrifuged, the supernatant was collected, and the generation of singlet oxygen was monitored spectrophotometrically by recording the decrease in the characteristic band of N,N-p-nitrosodimethylaniline at 440 nm using a Perkin Elmer Lambda 35 UV-Vis spectrophotometer.

The reaction between histidine and  ${}^{1}O_{2}$  results in the formation of a trans-annular peroxide, as can be seen in Scheme 2. The presence of the latter compound may be detected by bleaching the p-nitrosodimethylaniline at 440 nm. Singlet oxygen alone cannot cause bleaching of the latter compound; no bleaching occurs in the mixture of histidine and p-nitrosodimethylaniline without singlet oxygen.

### **Inset Scheme 2**

### 2.5. Photocatalytic activity for the degradation of methyl orange (MO)

Photocatalytic activity experiments were conducted in a slurry batch reactor using a LuzChem LZC-4V photoreactor equipped with 14 lamps emitting in the visible range (400-700 nm). The radiation was 52 W m<sup>-2</sup>, as measured with a UVX digital radiometer after 1 h of continuous illumination. A constant distance of 10 cm was maintained between the lamp surface and the solution, and the time of exposure was varied at 25 °C under continuous shaking. In a typical experiment, 100 mg of photocatalyst was dispersed in 100 mL of MO aqueous solution at a concentration of 10 mg L<sup>-1</sup>. The suspension was stirred in the dark for 1 h to ensure that the adsorption equilibrium was reached before irradiation. At regular time intervals during irradiation, aliquots of the mixture were collected and centrifuged, and the MO concentration in solution was measured using a Perkin Elmer Lambda 35 UV-Vis spectrophotometer at 466 nm, which is the maximum absorption wavelength of MO. The results were corrected for the decomposition of the dye in the absence of a photocatalyst. A calibration plot based on the Beer-Lambert law was established by relating the absorbance with the concentration. Photoactivity tests were done in duplicate in all samples, and all results were reproducible.

# 3. Results and discussion

### 3.1 Structural and morphological analysis

The corresponding SEM images of the  $TiO_2$  precursors are shown in Figure 1A and 1B. The starting material shows sphere-like  $TiO_2$  microparticles in both anatase and rutile  $TiO_2$  precursors, respectively.

# **Inset Figure 1**

The morphologies of the synthesized nanostructures were confirmed using TEM analysis. Figure 2 (A-H) shows typical TEM micrographs of 1D  $TiO_2$  nanomaterials and demonstrates that the hydrothermal reaction is efficient in the formation of one-dimensional structures.

The synthetized samples exhibited different morphologies. Changes in the precursor of TiO2 at

the same temperature produced change in the obtained morphology (Fig. 2A-D). Fig. 2 (A and B) show an entangled set of nanotubes (TNT) that was obtained with the anatase TiO<sub>2</sub> precursor. The sample shows a uniform nanotubular morphology with multilayered walls and inner diameters between 3 and 4 nm, external diameters of approximately 8 nm, and opened ends. TNT also presented a characteristic geometry—that is, long cylinders with a hollow cavity lying through the longitudinal axis of the tube. The TiO<sub>2</sub> nanomaterials obtained with the rutile TiO<sub>2</sub> precursor (Fig. 2C-D) consisted of a uniform fiber-like morphology (TNF). These nanofibers showed a tendency to form curled fibers with diameters between approximately 10 and 120 nm.

Changes in the reaction temperature using the same precursor allowed us to examine other evolutions in morphology (Fig. 2E-H). With temperature increases or decreases in solids, nonhollow nanostructures were observed. When the synthesis temperature was 110 °C using the  $TiO_2$  rutile precursor, rod-like morphology nanorods (TNR) were observed (Fig. 2E-F) with diameters between 15 and 50 nm and lengths between 50 and 200 nm. Finally, at a synthesis temperature of 180 °C, wire-type nonhollow structure named nanowires (TNW) were obtained (Fig. 2G-H). These structures showed a broad size distribution both in length and in diameter, ranging between 50 and 250 nm. In summary, TNF, TNR, and TNW nanostructures are dense and are longer and thicker than TNT, while all 1D  $TiO_2$  nanomaterials are randomly orientated. **Inset Figure 2** 

# Several reports have revealed that alkali hydrothermal treatment is a kinetically controlled process where morphological control can be strongly affected by the temperature [7, 13, 17-19]. These previous works have indicated that temperature changes cause morphology modifications; these findings agree with the present study with respect to TNF, TNR, and TNW samples. However, from our results, it can be observed that changes in morphology occurred not only by reaction temperature changes, but morphological changes can also be caused by variation in the crystalline phase of the starting material employed, affecting the product of the hydrothermal reaction between $TiO_2$ and NaOH. It has been reported that the formation of nanofibers occurs at

greater temperatures, while nanotubes are formed at 130 °C [15], independent of the employed precursor. Nevertheless, Dawson et al. [32] indicated that at this temperature (130 °C), the rutile phase does not react but only renders nanoplates and nanobelts at the higher temperature (170 °C) [35]. Notably, we have shown that it is possible to obtain morphological changes (e.g., nanofibers, nanotubes) with a constant reaction temperature (130 °C) by changing the crystalline phase of the precursor employed—in our case, rutile or anatase. This morphological change can be attributed to the different unit cell parameters. Because of those crystalline characteristics, anatase TiO<sub>2</sub> powder rather than rutile preferably forms nanotubes through continuous growth in a specific direction during the hydrothermal reaction [36].

In order to examine the structural changes in the synthesized solids after the hydrothermal process and subsequent calcination, the XRD patterns were measured and are shown in Fig. 3. It can be observed that TNT, TNF, and TNR samples possess high crystallinity and show preferably anatase TiO<sub>2</sub> phase. The peaks at  $2\theta = 25.2$ , 37.7, 48.1, 53.8, 55.1, 62.6, 68.7, 70.3, and 75.1° are indexed to the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0), and (2 1 5) crystal phases of anatase in concordance with previous reports [19, 37]. These XRD patterns indicate that crystal phase transitions occurred during thermal treatment at 550 °C.

On the other hand, TNW is composed mainly of trititanate. It has four main diffraction peaks at  $2\theta \approx 24.4^{\circ}$ , 28.4°, 44°, and 48°, corresponding well to the (1 1 0), (3 1 0), (2 0 4), and (0 2 0) lattice planes, respectively, of hydrogen trititanate (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>), according to standard XRD data (JCPDS 47-0561) [35]. This indicates that thermal treatment at 550 °C was insufficient to induce crystal phase transitions, and a higher calcination temperature is necessary for crystal phase transitions.

**Inset Figure 3** 

# 3.2. Surface and optical properties of 1D TiO<sub>2</sub> nanostructures

Table 1 shows the specific surface area and the total pore volume of all samples after

hydrothermal synthesis as well as their precursors. The surface areas for the synthesized materials follow the order TNF > TNT > TNR > TNW. In Table 1, it can be observed that the synthesized materials present higher specific area and pore volume than their precursors. This increase in the Brunauer-Emmett-Teller (BET) surface areas of these nanomaterials could be attributed to the significant morphological change from spherical precursors to 1D nanostructures due to the hydrothermal synthesis. Nevertheless, a major increase in the specific surface area of TNF was observed compared with that of TNT, TNR, and TNW, which can be attributed to a greater specific pore volume on the surface of this nanostructure (Table 1).

Sample	Surface Area BET (m <sup>2</sup> .g <sup>-1</sup> )	Pore Volume (cm <sup>3</sup> .g <sup>-1</sup> )
Anatase-type TiO <sub>2</sub>	8.98	0.02
Rutile-type TiO <sub>2</sub>	12.17	0.03
TNT	173.06	0.53
TNF	227.69	1.11
TNR	119.22	0.45
TNW	17.52	0.06

**Table 1.** Summary of BET specific surface area and total pore volume at single point  $P/P_0 = 0.99$  of TiO<sub>2</sub> precursors and TiO<sub>2</sub> nanomaterials hydrothermally treated.

 $N_2$  adsorption-desorption isotherms of the synthesized 1D TiO<sub>2</sub> nanomaterials revealed the presence of mesopores, as reported in Figure 4. All nanostructures show characteristic hysteresis loops; therefore, they can be classified as type IV isotherms [38]. The pore size distribution for the TNT and TNF samples is shown in the inset of Figure 4. In the TNT sample, the smaller pores (< 10 nm) could correspond to the pores inside of the nanotube, considering that the sizes of the pores are approximately equal to the inner diameter of this nanostructure, as was seen in TEM images. Alternatively, the TNF sample exhibits a trimodal pore size distribution. Very 12

small pores (3-10 nm) and larger pores (~ 20-30 nm) are apparent, which can be attributed to the voids in the aggregation of the nanofibers [24]. Changes in average pore diameter can be caused by variations in aggregations that can be formed between the nanostructures.

### **Inset Figure 4**

Figure 5 shows the optical band gap energy (Eg) and UV-Vis diffuse reflectance spectra (UV-Vis DRS) of  $TiO_2$  precursors and the synthesized 1D  $TiO_2$  nanostructures. UV-Vis DRS (Figure inset) was used to determine the band structure of the materials. The spectral lines of all solids exhibit only one characteristic absorption band, which is assigned to the intrinsic transition from the valence band (VB) to the conduction band (CB). As can be observed in the spectra, the UV-Vis absorption of 1D nanostructured  $TiO_2$  appears at shorter wavelengths than that of the starting materials.

### **Inset Figure 5**

The Eg of the synthetized nanomaterials was calculated by the Kubelka-Munk function F(R), which is related to the diffuse reflectance (R) of the sample according to the following equation [39]:

$$F(R) = \frac{(1-R)^2}{2R}$$
 Eq. (1)

Eg values of the nanostructured solids were calculated from their diffuse reflectance spectra by plotting  $[F(R)hv]^{1/2}$  vs. energy (hv) in electron volts (i.e., the so-called Tauc plot), where h is Planck's constant, and v is the frequency of the photon. The linear region of the curve was extrapolated to  $[F(R)hv]^{1/2} = 0$  to determine the indirect Eg, as shown in Figure 5. The absorption band edge in TNF sample is shifted to lower energy compared to the other nanomaterials. In addition, TNF spectrum shows the appearance of a tail in the visible region, which could favor a

Sample	Eg (eV)	Absorption edge (nm)
Anatase-type TiO <sub>2</sub>	3.02	412
Rutile-type TiO <sub>2</sub>	2.87	434
TNT	3.04	409
TNF	2.92	426
TNR	3.02	412
TNW	3.25	382

higher absorption in this region compared with the other samples. The Eg and calculated absorption maxima of all samples are given in Table 2.

**Table 2.** Optical band gaps (Eg) and adsorption edge wavelengths of  $TiO_2$  precursors and 1D  $TiO_2$  nanostructures synthesized.

According to the table, the absorption edge of the nanostructures is in the visible light region (~ 426 nm for TNF, ~ 409 nm for TNT, and ~ 412 nm for TNR), corresponding to band gap energies of approximately 2.92, 3.04, and 3.02 eV, respectively. However, TNW presented an absorption edge in the ultraviolet light region (~ 382 nm), corresponding to a band gap energy of 3.25 eV. The Eg was increased (blue-shifted) for all nanomaterials compared with that of both TiO<sub>2</sub> precursors. This fact can be attributed to their different morphologies and the decrease at the nanometer scale. Some reports have demonstrated that the Eg increases in nanostructured materials due to the effect of quantum confinement, which is generally observed in the optical properties of TiO<sub>2</sub> nanostructures, and shifts all optical transitions to higher energies as the dimensions of the nanostructures decrease [37, 40].

Figure 6A exhibits the photoluminescence (PL) emission spectra of 1D  $TiO_2$  nanostructures under the 254-nm excitation. The emission peak of each of the samples were deconvoluted using

a Gaussian fitting method ( $r^2 = 0.9945$ ) (Fig. 6B). It is known that visible emissions from TiO<sub>2</sub> structures are mainly due to self-trapped excitons (STE) located at the TiO<sub>6</sub> octahedra, Ov, and surface states [41-43]. Among them, the existence of oxygen vacancies is the most accepted source of emission for TiO<sub>2</sub>.

The deconvoluted spectra in Fig. 6B show that all of the samples had similar luminescence centers, one band in the range of 2.97 to about 2.91 eV (Peak 1), and others around 2.55 (Peak 2) and 2.33 eV (Peak 3). According to the literature, the blue emission bands formed in the spectral range of 2.97 to 2.91 eV (418 to 426 nm) originate from STE for all samples, while the green emission at 2.55 eV (486 nm) and 2.33 eV (531 nm) are assigned to surface Ov that are located below the conduction band [41-43]. These Ov are intrinsic defects of the TiO<sub>2</sub> lattice that form intermediate energy levels within the TiO<sub>2</sub> band gap. The surface Ov act as electron traps, affecting the electric and optical properties of the materials and preventing e<sup>-/h+</sup> recombination, which improve the photocatalytic behaviour of TiO<sub>2</sub> [25]. In addition, it was well known that the PL intensity is closely related to the surface defects of the materials [44]. Thus, larger Ov values imply a stronger emission PL signal. The figure inset in Fig. 6A shows that the photoluminescence intensity strongly depends on the morphology of the 1D TiO<sub>2</sub> nanostructures. The Ov amounts vary as follows: TNF > TNT > TNR> TNW. Thus, TNF presents the higher PL intensity of all materials, indicating higher Ov concentration with respect to the others nanomaterials, while in TNW, the PL intensity sharply decreased.

### **Inset Figure 6**

### 3.3. ROS measurement on 1D TiO<sub>2</sub> nanostructures

### 3.3.1. Hydroxyl radical photogeneration on 1D TiO<sub>2</sub> nanostructures

The effect of morphology of 1D  $TiO_2$  nanostructures with respect to the photogeneration of 'OH radicals was examined converting TA to 2-HTA under visible irradiation (Scheme 1). A major

advantage of this heterogeneous method to quantify the amount of photogenerated 'OH radicals is that the symmetry of the TA molecule leads to only one hydroxylated product, which is highly stable [33, 34]. Figure 7 shows the concentration of hydroxyl radicals generated by each material. Increases in the amount of photogenerated 'OH radicals during irradiation time were observed in all of cases. It is proposed that Ov states can take part in the photoexcitation process to enhance the photoproduction of 'OH radicals. As can be seen in Fig. 7, photogenerated 'OH concentrations have the same trend compared with the amount of Ov presented by the 1D TiO<sub>2</sub> nanostructures (Fig. 6A, TNF > TNT > TNR> TNW); therefore, a correlation can be noted between the production of 'OH radicals and the amount of Ov on the nanostructures according to the morphology of material. In order to explain the effect of Ov on the production of 'OH, Schaub et al. [45] used a combined experimental and theoretical approach to show that Ov act as active sites for water dissociation on the TiO<sub>2</sub> surface, improving the formation of hydroxyl groups. Then, these surface hydroxyl groups can react with photoproduced holes to generate a higher number of 'OH radicals. Our results are in good agreement with literature data, indicating that an increase in the Ov also results in a increased generation of 'OH radicals, which could enhance photocatalytic performance. This demonstrates that the Ov play a crucial role in photocatalytic reactions for different morphologies.

### **Inset Figure 7**

### 3.3.2. Singlet oxygen photogeneration on 1D TiO<sub>2</sub> nanostructures

Singlet oxygen  $({}^{1}O_{2})$  is also an active oxygen species that is considered a strong oxidation reagent and plays an important role in the photooxidation of organic compounds [14, 46]. Figure 8 shows the formation of  ${}^{1}O_{2}$  as a function of irradiation time for all photocatalysts. Photocatalysts with higher Ov (as seen in Fig. 6A) also exhibit an increase in the formation of  ${}^{1}O_{2}$ , and there is a similar tendency for both parameters. This suggests that the existence of Ov on 1D TiO<sub>2</sub> nanomaterials can aid the formation of reactive species such as  ${}^{1}O_{2}$  and  $O_{2}^{-}$  through adsorption and reaction of oxygen species at these defect sites, as it has recently been proposed

[31]. A better explanation for *t*his effect could be through the excitation process on semiconductors, which is proposed in Scheme 3. When the photocatalyst is excitated with an energy greater than its band gap, an electron-hole pair is created in which an electron is excited from the valence band (VB) to the conduction band (CB), leaving a hole in the VB. Both charge carriers migrate to the surface to generate ROS, where the electrons react with molecular oxygen producing  $O_2^{--}$  and the holes with water or surface-absorbed groups generating 'OH [5, 14]. Therefore, the Ov on the solid surface can facilitate  $O_2$  adsorption, and the free electrons located on the Ov states can reduce the absorbed  $O_2$  and simultaneously produce  $O_2^{--}$  [4, 31, 41]. In addition, the produced  $O_2^{--}$  can be oxidized by photogenerated holes to form  ${}^{1}O_2$  through of an electron-transfer mechanism [14, 46, 47]. According to the above description, the largest concentration of ROS including  ${}^{1}O_2$  and 'OH radicals can be associated with the Ov defects, showing similar tendencies in all of cases (TNF > TNT > TNR> TNW). Therefore, the photogeneration of ROS is greatly dependent on the Ov amount on the surface of the nanomaterials, which in turn is influenced by the morphology of the 1D TiO<sub>2</sub> nanostructures.

### **Inset Figure 8**

### **Inset Scheme 3**

### 3.4. Photocatalytic Activity for the Degradation of Methyl Orange

The photocatalytic properties of 1D TiO<sub>2</sub> nanostructures with respect to degradation of MO under visible irradiation after 300 min of reaction were investigated (Figure 9 (A-B)). After equilibration in the dark for 1 h, MO concentration did not decrease due to the lack of physical MO adsorption on the surface of TiO<sub>2</sub> nanostructures. The MO concentration decreased slightly after 300 min of irradiation for the TNF, TNT, TNR, and TNW photocatalysts, showing percentages of MO degradation near 49%, 40%, 13%, and 9%, respectively. TNW presented lowest photocatalytic activity due to the presence of only titanates in the crystal phase, which is known to have low photoactivity for degradation of organic species in aqueous solution [46].

### **Inset Figure 9**

# **Inset Figure 10**

The kinetic curves of the MO photodegradation were fit using pseudo-first-order kinetics (Figure 10) via the reaction dynamic equation:

$$\ln\left(\frac{Co}{Ct}\right) = -kt$$
 Eq. (2)

where Co is the initial concentration of the MO solution, Ct is the instant concentration of the MO solution at the irradiation time t, and k is the apparent rate constant.

Sample	k <sub>app</sub> x 10 <sup>-3</sup> (min <sup>-1</sup> )	$\mathbf{R}^2$	
TNT	5.5	0.9127	
TNF	6.8	0.8921	
TNR	1.0	0.9792	
TNW	0.8	0.9694	

**Table 3.** Apparent pseudo-first-order reaction rate constant and the linear regression coefficients  $(R^2)$  for MO photodegradation by 1D TiO<sub>2</sub> nanostructures synthesized.

The apparent pseudo-first-order reaction rate constant (kapp) and the linear regression coefficients are presented in Table 3. Significant differences in the rate of MO degradation between the photocatalysts evaluated were observed, demonstrating the influence of morphology on their photoactivity. It has been reported that the photocatalytic activity of metal oxides is strongly dependent on their morphological properties [12]. As was previously demonstrated, changes in the morphology imply significant differences in the Ov amount and the concentration of ROS photogenerated for each 1D TiO<sub>2</sub> nanostructure studied, which could affect their photocatalytic behavior. For example, better photocatalytic performance was observed for the

TNF nanostructure, which showed higher Ov concentration and a higher amount of ROS photogeneration. A clear correlation between photogenerated ROS and photocatalytic activity was observed, keeping the same tendency for each parameter (TNF > TNT > TNR > TNW), as shown in Figure 11. Therefore, we conclude that structural defects such as Ov play a vital role in the photocatalytic behavior of 1D TiO<sub>2</sub> nanostructures through ROS generation, which in turn are related to the different morphologies presented by TiO<sub>2</sub>-based nanostructures.

### **Inset Figure 11**

### 4. Conclusions

Four types of 1D TiO<sub>2</sub> morphologies (i.e., nanotubes, nanofibers, nanorods and nanowires) were successfully achieved using a hydrothermal method and varying two parameters: the crystalline phase of TiO<sub>2</sub> precursor and reaction temperature. Both parameters play an important role in controlling the morphology of 1D TiO<sub>2</sub> nanostructures, However, changes in the crystalline phase of TiO<sub>2</sub> precursors (rutile or anatase), produce morphological differences during hydrothermal synthesis at identical reaction temperature (130 °C). Optical characterization via photoluminescence spectra confirmed that the nanostructures present differences in the Ov amount according to their morphology, which influenced the photocatalytic properties of the nanomaterial through of the variations in the ROS production. Significant changes in the rate of MO photodegradation between the morphologies studied were observed, the results demonstrate their morphology-dependent photocatalytic activity. Based on the findings obtained in this study, a clear correlation between 1D morphology, ROS photogeneration, and photocatalytic activity was observed, maintaining the same tendency for both parameters (TNF > TNT > TNR > TNW). We suggest that MO degradation is governed by the amount of photogenerated ROS, which in turn is mainly depended of the morphology type of 1D TiO<sub>2</sub> nanostructures and the presence of structural defects type Ov. Therefore, we propose that the morphology of the material plays a key role in both greater Ov amount as well as photogeneration of ROS and thus consequently the photocatalytic enhancement of the nanomaterial.

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# **Figure Captions**

Scheme 1. Hydroxylation reaction of terephthalic acid.

Scheme 2. Mechanism of histidine test.

Figure 1. SEM images, TiO<sub>2</sub> precursors: (A) Anatase TiO<sub>2</sub>, (B) Rutile TiO<sub>2</sub>.

Figure 2. High resolution TEM images of 1D TiO<sub>2</sub> nanostructures hydrothermally synthesized: (A,B) TNT, (C,D) TNF, (E,F) TNR and (G,H) TNW.

Figure 3. XRD patterns of synthesized 1D TiO<sub>2</sub> nanostructures.

Figure 4. Nitrogen adsorption-desorption isotherms of the obtained 1D TiO<sub>2</sub> nanostructures. The inset shows pore size distribution curves of TNT and TNF samples.

Figure 5. Optical band gap energy and UV-Vis diffuse reflectance spectra in R (insert) of TiO<sub>2</sub> precursors and 1D TiO<sub>2</sub> nanostructures synthesized.

Figure 6. (A) Photoluminescence emission spectra of the samples synthesized excited at 254 nm. (B) Deconvolution of photoluminescence emission spectra using a Gaussian fitting.

Figure 7. Quantification of hydroxyl radical generated by photocatalysts.

Scheme 3. Mechanism of ROS photogeneration.

Figure 8. Quantification of singlet oxygen produced by photocatalysts.

Figure 9. (A) MO photodegradation by photocatalysts, (B) Comparison of the photoactivities in MO degradation under visible light irradiation after 300 min of reaction.

Figure 10. The pseudo-first order kinetic model for MO degradation by photocatalysts.

Figure 11. Correlation between photocatalytic activity and photogenerated ROS by 1D  $TiO_2$  nanostructures after 60 min of irradiation.

# HIGHLIGHTS

- Crystalline phase of TiO<sub>2</sub> precursor influences on 1D nanostructures morphology.
- ROS photogeneration dependents on the morphology type of 1D TiO<sub>2</sub> nanostructures.
- Oxygen vacancies act as active sites improving the ROS production.
- Correlation between 1D morphology, photogenerated ROS concentration, and photocatalytic properties is established.
- The nanofibrous morphology exhibits better photocatalytic performance under visible light illumination.







Figure 3



Figure 4













Figure 10



Figure 11