



HAL
open science

N-doped TiO₂ nanotubes synthesized by atomic layer deposition for acetaminophen degradation

Syreina Sayegh, Mahmoud Abid, Fida Tanos, Geoffroy Lesage, François Zaviska, Eddy Petit, Igor Iatsunskyi, Roman Viter, Emerson Coy, Victoria Fedorenko, et al.

► **To cite this version:**

Syreina Sayegh, Mahmoud Abid, Fida Tanos, Geoffroy Lesage, François Zaviska, et al.. N-doped TiO₂ nanotubes synthesized by atomic layer deposition for acetaminophen degradation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2022, 670, pp.131543. 10.1016/j.colsurfa.2022.130213 . hal-04102383

HAL Id: hal-04102383

<https://hal.umontpellier.fr/hal-04102383v1>

Submitted on 5 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

N-doped TiO₂ nanotubes synthesized by atomic layer deposition for acetaminophen degradation

Syreina Sayegh^{1,2}, Mahmoud Abid¹, Fida Tanos^{1,2}, Marc Cretin¹, Geoffroy Lesage¹, François Zaviska¹, Eddy Petit¹, Bruno Navarra¹, Igor Iatsunskiy³, Emerson Coy³, Roman Viter^{4,5}, Victoriia Fedorenko⁴, Arunas Ramanavicius⁶, Antonio Razzouk², Juliette Stephan² and Mikhael Bechelany^{1*}

1 Institut Européen des Membranes, IEM UMR 5635, Univ Montpellier, CNRS, ENSCM
Place Eugène Bataillon, 34095 Montpellier cedex 5, France.

2 Laboratoire d'Analyses Chimiques, LAC – Lebanese University, Faculty of Sciences,
Jdeidet 90656, Lebanon

3 NanoBioMedical Centre, Adam Mickiewicz University, Wszechnicy Piastowskiej 3, 61-
614 Poznan, Poland

4 Institut of Atomic Physics and Spectroscopy, University of Latvia, Rainis Blvd., LV-1586,
Riga, Latvia

5 Center for Collective Use of Scientific Equipment, Sumy State University, 31,
Sanatornaya st., 40018 Sumy, Ukraine

6 Department of Physical Chemistry, Faculty of Chemistry and Geosciences, Institute of
Chemistry, Vilnius University, Vilnius, Lithuania

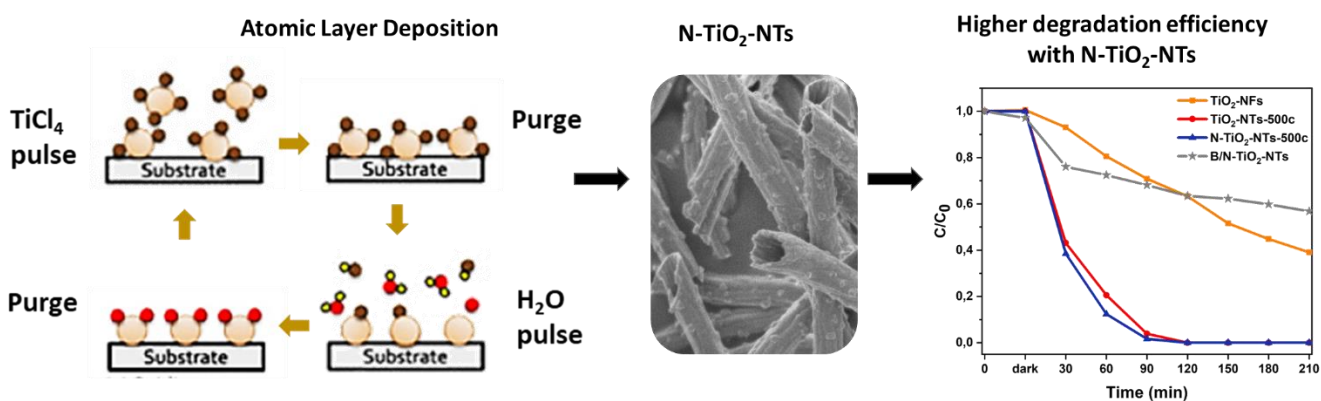
*Corresponding author: mikhael.bechelany@umontpellier.fr

ABSTRACT

Titanium dioxide (TiO₂) is widely used in photocatalysis applications for wastewater treatment. Investigations demonstrated that titanium dioxide structure strongly contributes to increase micropollutant degradation efficiency. Indeed, pollutant degradation rates are enhanced when using photocatalysts with highly ordered structures and high specific surface area, such as TiO₂ nanotubes (NTs) synthesized by atomic layer deposition (ALD). Here, TiO₂ NTs, fabricated by ALD followed by nitrogen doping via thermal treatment, were compared with TiO₂ nanofibers (NFs), prepared by electrospinning. Their morphology and structure were investigated by scanning and transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. Photoluminescence measurements showed that TiO₂ NT photoluminescence intensity was lower than that of TiO₂ NFs, due to lower electron-hole pair recombination, and consequently their degradation efficiency was higher. As the surface to volume ratio was higher in TiO₂ NTs than NFs, the rate of non-radiative surface recombination also was higher in TiO₂ NTs. Comparison of their performance for photocatalytic degradation of acetaminophen showed higher degradation activity with TiO₂ NTs than TiO₂ NFs. TiO₂ NT doping with nitrogen (N-TiO₂ NTs) further enhanced their photocatalytic activity that was 5 times higher than that of TiO₂ NFs (degradation rates: 0.05 and 0.01 mg.L⁻¹.min⁻¹, respectively). The N-TiO₂ NT photocatalyst was stable after four cycles of acetaminophen degradation. Acute toxicity assays confirmed the release of harmful by-products during the first hours of acetaminophen degradation, but toxicity strongly decreased after 5 hours.

Keywords: TiO₂ nanotubes; N-doped TiO₂; atomic layer deposition; photocatalysis; acetaminophen

Graphical abstract



Highlights

- TiO₂ nanotubes (NTs) were fabricated by atomic layer deposition on polyacrylonitrile nanofibers
- The as-prepared samples efficiently degraded acetaminophen upon visible light exposure
- The photocatalytic efficiency of TiO₂ NTs was 3 times higher than that of TiO₂ nanofibers after 90 minutes of visible light irradiation
- Nitrogen doping further improved TiO₂ NT degradation efficiency by increasing the separation time of the photogenerated charge carriers
- N-TiO₂ NTs displayed the lowest charge transfer resistance and the largest electroactive surface area

1. Introduction

The pressing increase in clean water demand has led researchers to focus on developing new technologies for water treatment because the conventional systems cannot efficiently degrade micropollutants (e.g. drugs, pesticides, personal care products, dyes) and eliminate microorganisms^{1,2} that can resist to the conventional methods and then contaminate drinking water^{3,4}. Although these contaminants are usually present at very low concentrations, they can harm human health and other living organisms^{5,6}. For instance, acetaminophen (ACT) is a pharmaceutical product used as painkiller that have been detected in the range of ppm to ppt and has significant negative impacts to the aquatic and ecological systems⁷.

The main challenge is the development of new removal techniques that are cheap and require less energy consumption. Advanced oxidation processes (AOP), particularly photocatalysis, are good candidates at the place or in combination with conventional techniques⁸⁻¹⁰. Photocatalysis is a green technology in which, pollutants under visible light irradiation are degraded to CO₂, H₂O, and in some cases small non-toxic molecules, as final degradation products.^{11,12} In this system, upon irradiation, the semiconductor is activated by photon energy that is equal to or higher than its bandgap energy. This leads to the formation of electron-hole pairs between the conduction and valence bands that will then generate radicals implicated in the pollutant mineralization^{13,14}.

Titanium dioxide (TiO₂) is among the most used semiconductors. TiO₂ is not expensive and displays good chemical and thermal stability and low toxicity¹⁵⁻¹⁸, but its wide bandgap and fast electron-hole pair recombination limit its use under visible light¹⁹⁻²¹. Previous studies on the development of materials and technologies with higher degradation efficiency for water treatment indicate that the catalyst structure and morphology strongly contribute to its catalytic activity under visible light.²²⁻²⁴ In agreement, TiO₂ photocatalytic activity is influenced by its morphology, crystallinity, surface, and textural properties. Many groups have tried to tailor TiO₂ morphology to increase its photocatalytic performance²⁵⁻²⁸. For instance, 0D, 1D, 2D and 3D TiO₂-based materials have been fabricated using various techniques²⁹⁻³³. One-dimensional (1D) materials, such as 1D TiO₂ nanofibers (NFs), nanorods, nanotubes (NTs),

nanowhiskers and nanowires^{34–36}, are particularly interesting due to their higher light absorption and slower recombination rates, leading to better photocatalytic activity^{37–39}. Among these structures, tubular nanostructured TiO₂ is a versatile material for photocatalysis and photoelectrolysis^{40–42}. Many preparation techniques have been tested for fabricating such 1D nanostructures (e.g. hydrothermal synthesis, template synthesis, anodization, electrospinning and atomic layer deposition, ALD)^{43–46}. ALD is a thin film deposition technique based on gas-phase precursors for the deposition of thin-film layers with thickness control at the Ångstrom level^{47–49}. ALD has been often combined with electrospinning for the deposition of the desired materials on polymeric fibers that are used as substrate^{50–53}. Upon removal of the polymeric core by thermal treatment after the ALD cycles, a tubular structure is formed⁵⁴. McClure *et al.* described TiO₂ deposition on polymeric nanofibers by ALD, and then compared the precursor effect on the film coating. They found that the precursor choice influenced the final structure of TiO₂ NTs⁵⁵. Su *et al.* reported the fabrication of TiO₂ NTs by ALD using titanium chloride and H₂O as precursors and assessed the doping effect on NT photocatalytic and photoelectrochemical performance⁵⁶. In addition, the number of ALD cycles and the deposition temperature may affect the material crystalline structure⁴⁵.

As TiO₂ catalysts are often not stable and not much active under visible light irradiation, improving TiO₂ morphology might positively influence the photocatalytic behavior compared with unmodified TiO₂ (commercial Degussa p25)⁵⁷. Several methods have been described to extend the semiconductor photo-response to the visible light region, such as doping TiO₂ with metals and non-metals and coupling with other semiconductors^{58–60}. Doping with non-metals (e.g. carbon, sulfur, phosphorus, nitrogen^{61–65}) reduces the recombination of photogenerated electron-hole pairs in TiO₂. Several non-metal dopants were mentioned in the literature such as carbon (C), sulfur (S), phosphorus (P) and nitrogen (N)^{61–65}. N-doping is the most studied⁶⁶ and allows shifting the TiO₂ band into the visible light range⁶⁷. Asahi *et al.* found that N-doping extends TiO₂ optical absorbance towards the visible light region⁶⁸. Moreover, the presence of non-metals in TiO₂ generally increases the specific surface area and the anatase phase percentage, while limiting the crystallite size growth⁶⁹. Huang *et al.* fabricated N-doped TiO₂ (N-TiO₂) by hydrothermal synthesis and calcination under NH₃ atmosphere. They found that N-doping promoted the generation of hydroxyl and superoxide radicals that enhanced the photocatalytic activity⁷⁰. Another study showed that N-doping promotes the formation of

oxygen vacancies that contribute to visible light absorption⁵⁹. These two effects were also observed in hierarchical structures grown by ALD in which N-doping of TiO₂ was obtained by incorporating N atoms on the substrate⁷¹. Hence, co-doping TiO₂ with nitrogen and boron can enhance both the visible light absorption of TiO₂ and implement an efficient charge recombination regarding the synthesis technique⁷².

On the other hand, it was widely reported that the morphologies of 1D structures can influence TiO₂ photocatalytic properties. Interestingly, the photocatalytic activity can be tuned by several parameters such as particle size, specific surface area, porous structure, crystalline phase etc.¹⁹. Rosales *et al.* compared the photocatalytic activity of different 1D morphologies (NTs, NFs, NWs) on the degradation of methyl orange. The author found that the shape of TiO₂ has a major role in determining their photocatalytic activity³⁴, herein the importance of comparing different 1D morphologies such as TiO₂ nanofibers and nanotubes for the degradation of organic micropollutant.

Here, we fabricated 1D TiO₂ NTs by ALD for photocatalysis. To the best of our knowledge no previous reports have been published on elaboration of TiO₂ nanotubes by Atomic Layer Deposition for catalytic activity. Hence 1D TiO₂ NTs have shown a great interest for the degradation of micropollutants when compared to NFs and NWs because of their higher efficiency to absorb light. Variation of the number of ALD cycles confirmed that the photocatalytic efficiency was directly influenced by the NT wall thickness. Moreover, TiO₂ doping with non-metals (nitrogen) further improved the photocatalytic activity by modifying the NT charge transportation, surface area, reflection and absorption. By comparing the catalytic activity of these TiO₂ NTs and of TiO₂ NFs prepared by electrospinning we found that ALD allows the formation of a well-structured nanotubular catalyst with higher degradation efficiency than NFs. More than 98% of acetaminophen was degraded in the presence of N-TiO₂ NTs after 180 min of visible light irradiation. N-TiO₂ NTs recyclability and toxicity tests showed the potential of this catalyst for real applications. We also performed quenching tests to determine the active species responsible for acetaminophen degradation.

2. Experimental

2.1. Materials and chemicals

Titanium(IV) isopropoxide (TTIP, 97%, CAS: 546-68-9), titanium (IV) chloride (TiCl_4 , 99.9%, CAS: 7550-45-0), polyacrylonitrile (PAN, $M_w=150000$, CAS: 25014-41-9), polyvinyl pyrrolidone (PVP, $M_w=1300000$, CAS: 9003-39-8), acetaminophen ($\geq 99\%$, CAS: 103-90-2), formalin solution (HCHO , CAS: 50-00-0), boron tribromide (BBr_3 , 99.9%, CAS: 10294-33-4), Nafion™ perfluorinated resin solution (CAS: 31175-20-9), potassium chloride (KCl , $\geq 99\%$, CAS:), sodium sulfate (Na_2SO_4 , $\geq 99\%$, CAS: 7757-82-6), sodium chloride (NaCl , $\geq 99\%$, CAS: 7647-14-5), potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$, $\geq 99\%$, CAS: 13746-66-2), 2-propanol (99.9%, CAS: 67-63-0), p-benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$, $\geq 99.5\%$, CAS: 106-51-4), and ethylenediaminetetraacetic acid (EDTA, 99.995%, CAS: 60-00-4) were purchased from Sigma-Aldrich. Tetrahydrofuran (99.9%, CAS: 109-99-9) was bought from Honeywell. Acetic acid ($\geq 96\%$ CAS: 64-19-7) and ethanol ($\geq 99.8\%$ CAS: 64-17-5) were purchased from VWR Chemicals and used as solvents. All chemicals were used without any additional purification. Indium tin oxide (ITO) deposited on quartz was purchased from Präzisions Glas & Optik. Deionized water (>18.2 M Ω), prepared with the Millipore (Milli-Q® Academic) water purification system, was used for all dilutions and reagent preparation. Argon gas, ammonia and nitrogen were from Linde and were used as received.

2.2. Support and catalyst preparation

2.2.1. Synthesis of TiO_2 nanofibers and PAN nanofibers by electrospinning

For TiO_2 NF fabrication, a mix of TTIP, PVP, acetic acid and ethanol was stirred for 2h before electrospinning. The solution was loaded into a 22 mL syringe, and the needle was connected to high voltage. The electrospinning conditions were: needle-collector distance of 10cm, tension of 25kV, and solution flow of $1\text{mL}\cdot\text{h}^{-1}$. For the preparation of PAN NFs, 18mL of tetrahydrofuran was mixed with 2 mg of PAN at 60°C for 24 h and then electrospun using a previously described home-built electrospinning system^{50,51,73}. The collected TiO_2 NFs underwent calcination at 750°C for 4h before utilization. PAN NFs were stabilized at 250°C for 2h (heating rate of $1^\circ\text{C}\cdot\text{min}^{-1}$) before ALD.

2.2.2. Deposition of TiO_2 nanotubes by atomic layer deposition

Stabilized PAN NFs were used as substrates for TiO₂ deposition at 100°C, using TiCl₄ and H₂O as precursors in a home-built ALD device. After ALD deposition, we removed the PAN upon annealing under air at high temperatures allowing to transform into nanotubes structures.

The typical ALD cycle consisted of 0.2 s TiCl₄ pulse, followed by 10 s exposure and 60 s purge. Then, the H₂O valve was opened for 2 s, followed by 10 s exposure and 60 s purge with argon gas. The line connected to the reactor was heated at 100°C to avoid condensation. The number of ALD cycles varied between 500 and 1000 to vary TiO₂ shell thickness. After TiO₂ deposition, PAN-TiO₂ NTs were heated at 750°C for 4h with a heating rate of 1 °C/min under air before use.

2.3. Nitrogen-doped and boron/nitrogen-co-doped TiO₂ NTs

After 500 ALD cycles, PAN-TiO₂ NTs were exposed to nitrogen at 750°C for 15 min and the samples were denoted (N-TiO₂ NTs) hereafter. For boron/nitrogen co-doped TiO₂ NTs (B/N-TiO₂ NTs), BN was deposited following a previously described method and five ALD cycles were used in this case⁷³.

2.4. Characterization of the synthesized nanocomposites

The NT and NF morphology was analyzed by scanning electron microscopy (SEM Hitachi S4800, JAPAN). Samples were placed on aluminum stubs and were sputter-coated with platinum/palladium using a Polaron SC7620 Mini Sputter Coater. X-ray diffraction (XRD) analyses were carried out using a PanAlytical X'pert system with Cu K α radiation ($\lambda = 0.15406$ nm). The diffraction patterns were measured between 10 and 80° with a step size of 0.0167°. The tubular morphology NTs was confirmed by transmission electron microscopy (TEM) using the JEOL 2200FS (200 kV) and JEOL ARM-200F (200kV) microscopes. For TEM analysis, samples were dispersed in ethanol, and a drop of the suspension was dried on a carbon support film that covered a standard copper grid. The samples' chemical composition and bandgap were determined by X-ray photoelectron spectroscopy (XPS) measurements, with an Escalab 250 apparatus, and by UV–Visible spectrophotometry (Jasco model V570; equipped with a diffuse reflectance attachment (Shimadzu IRS-2200)), respectively. Optical absorbance was measured by recording the photoluminescence spectra with an optical fiber spectrometer (Ocean Optics

usb2000), equipped with excitation wavelength of 266 nm and a nitrogen Nd:YAG laser of 9mW.

2.5. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) and electrochemical active surface (EAS) characterization carried out by cyclic voltammetry (CV) were performed in a three-electrode cell system connected to a Solartron SI 1287 galvanostatic-potentiostat. A halogen lamp (150 w), placed at a distance of 10 cm from the electrode surface, was used as the light source. Platinum wire and Ag/AgCl were the counter and reference electrode, respectively. The working electrode (2x2.5cm) was a suspension of 5 mg photocatalyst, 1 mL isopropanol, and 40 μ L Nafion[®] aqueous solution. After 30 min in an ultrasonic cleaner, this suspension was dropped on the ITO glass, to obtain the working electrode after isopropanol evaporation. For EIS measurements, the three electrodes were immersed in a Na₂SO₄ solution (0.1 mol.L⁻¹) considered as the electrolyte. For EAS analysis, 10 mM K₃[Fe(CN)₆] and 1.0 M KCl were used as electrolytes. The samples' electroactive surface area was estimated by CV performed in a voltage range of -0.4 to 0.8 V vs reference at scan rate of 20 mV.s⁻¹. The EAS was calculated using the Randles–Sevcik equation:

$$I_p = 2.69 \times 10^5 \times A D^{1/2} \times n^{3/2} \times C v^{1/2} \quad (1)$$

where I_p is the maximum current (A), n is the number of transferred electrons ($n = 1$), A is the electrode area (cm²), D is the diffusion coefficient of [Fe(CN)₆]³⁻ (7.60×10^{-6} cm².s⁻¹), C is the concentration of [Fe(CN)₆]³⁻ (1×10^{-5} mol.cm⁻³), and v is the scan rate (0.01 V.s⁻¹).

2.6. Acetaminophen degradation

The TiO₂ samples' photocatalytic activity under visible light (linear halogen lamp; 400W, Avidé) was tested by quantifying acetaminophen degradation in an aqueous solution. The solution was maintained at 10 cm from the lamp for all experiments. First, TiO₂ NT samples with different wall thicknesses (different ALD cycle number) were compared. Then, the catalytic performances of TiO₂ NTs (500 ALD cycles), TiO₂ NFs, and doped TiO₂ NTs were evaluated.

The photocatalytic degradation experiments were performed in the following conditions: the photocatalyst with an initial concentration of 0.5 g.L⁻¹ was added to 250 mL of acetaminophen aqueous solution (5 mg.L⁻¹) in a 600 mL glass reactor put in a water bath at 30°C to minimize the temperature increase in the solution under light irradiation. After stirring in the dark for 30 min to ensure equilibrium adsorption, the solution was exposed to visible light and at different intervals, 2 mL aliquots were collected and filtered with 0.22 µm filters. Acetaminophen degradation was quantified by high-performance liquid chromatography coupled to a Quattro-Micro mass spectrometer with an Electrospray ionization probe (Waters Micromass, Wythenshawe, Manchester, UK) as detector (HPLC-MS). The separation was carried out using a C-18 column (RP18 Column, Nucleoshell). The mobile phase was composed of Buffer A (0.1% formic acid in HPLC-grade water) and Buffer B (0.1% formic acid in HPLC-grade acetonitrile) with a 97:3 (A:B) ratio. The flow rate was set at 0.25 mL min⁻¹ and the run time was 3 min.

The recyclability of the catalyst with the highest degradation efficiency was further investigated for 5 cycles of acetaminophen degradation in the same conditions.

The degradation efficiency (D(%)), was calculated according to equation (2):

$$D(\%) = [(C_0 - C)/C_0] \times 100 \quad (2)$$

where C₀ and C are the initial and final acetaminophen concentrations after the test, respectively.

2.7. Photocatalytic kinetic model

TiO₂ degradation kinetics is usually described using the Langmuir–Hinshelwood model^{74,75}. When the pollutant concentration is low, a pseudo-first-order kinetics is applied⁷⁶, as described in Equation (3):

$$\ln(C_0/C) = kt \quad (3)$$

where C₀ (mg/L) is the initial pollutant concentration, C is the pollutant concentration at time t (min), and k (min⁻¹) is the pseudo-first-order rate constant.

2.8. Eco-toxicity assays

During acetaminophen degradation many by-products may be formed⁷⁷. To assess their toxicity, inhibition of *Vibrio fischeri* bioluminescence was monitored using a Microtox® Model 500 Analyzer (Modern Water Inc.; United Kingdom) as previously described⁶⁹.

2.9. Quenching tests

Scavenger tests were performed to determine the main active species responsible for acetaminophen degradation. Benzoquinone, isopropanol and EDTA were added to the solution at a concentration of 10 mM before exposure to visible light (same conditions as for the degradation experiments). Aliquot were collected at different intervals, and acetaminophen concentration was measured by HPLC-MS as described in 5.6.

3. Results and Discussion

3.1. Morphological characterization

The morphology of all prepared materials (calcinated TiO₂ NFs after electrospinning and TiO₂ deposited on PAN NFs by ALD) was verified by scanning electron microscopy (SEM). Before the analysis, TiO₂ was deposited on PAN nanofibers substrate by ALD and TiO₂ nanofibers elaborated by electrospinning were subject to thermal treatment at 750°C under air for 4h. A well nanotubular structure was observed after ALD deposition with a TiO₂ pulse time of 0.2 s, but not with shorter pulse times (Erreur ! Source du renvoi introuvable.). In addition, it was reported elsewhere that more than 200 ALD cycles are necessary to obtain well-structured NTs⁷⁸. Moreover, **Figure 1a** shows TiO₂ nanotubular morphology of several microns in length after removal of the PAN substrate. This indicates that PAN NFs were an efficient 'template' for TiO₂ NT synthesis. TiO₂ NTs with an inner diameter of approximately 400 nm and high surface roughness were obtained after 500 ALD cycles (**Figure 1b**). SEM confirmed the nanofibrous structure of TiO₂ NFs (**Figure 1(c)**). The surface roughness is attributed to the crystalline structure of the nanofibers at 750°C. No clear difference was observed after NT doping (**Figure 1 (d-e)**), confirming the previous findings that N- and B-doping do not change TiO₂ shape⁷⁰ and that doping with non-metals could occur in the NT bulk⁷⁹.

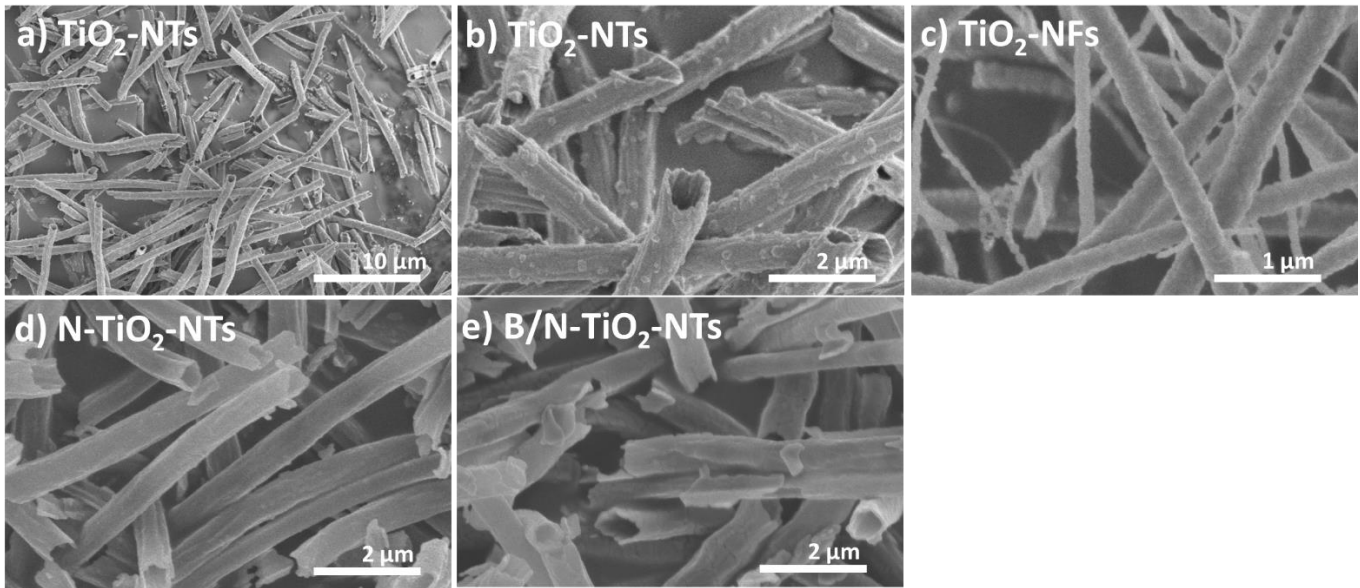


Figure 1. SEM images of (a-b) TiO₂NTs, (c) TiO₂ NFs, (d) N-TiO₂ NTs, and (e) B/N-TiO₂ NTs.

TEM images (**Figure 2**) confirmed TiO₂ NT nanotubular structure with a nanotube wall thickness of ~60 nm in doped and non-doped samples. After N-doping, TiO₂ nanotubular morphology and crystal lattice values (selected area electron diffraction images (SAED)) were not changed. Moreover, elemental mapping (**Figure 2b**) indicated the presence of N, T and O.

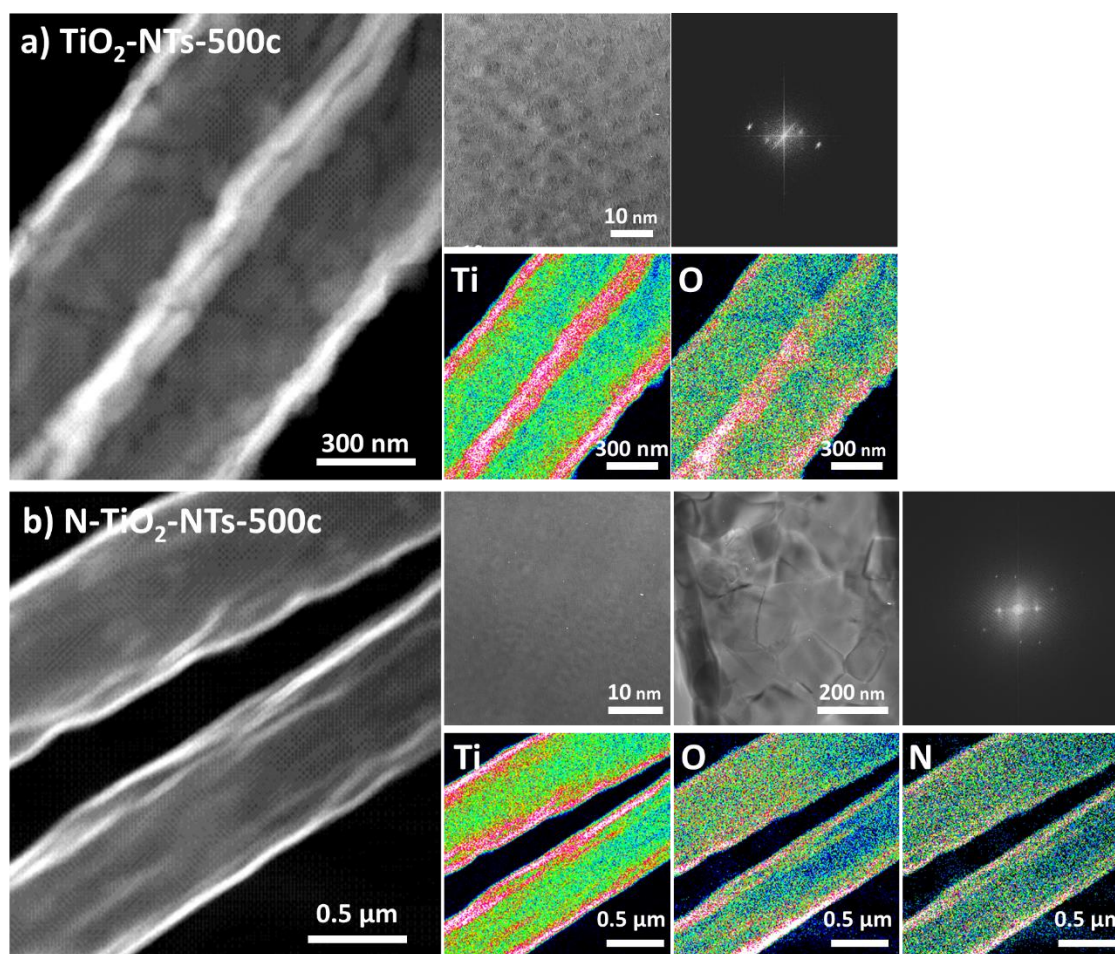


Figure 2. High resolution TEM, elemental mapping, and selected area electron diffraction images SAED of (a) TiO_2 NTs and (b) N-TiO_2 NTs (500 ALD cycles in both cases).

The crystalline structure was characterized by X-Ray Diffraction (XRD). TiO_2 NT samples with different thickness were composed of an anatase phase at 750°C , as previously described⁸⁰ (**Figure 3 and S2**). TiO_2 NTs and N-TiO_2 NTs displayed the anatase crystalline structure peaks at $2\theta = 25.3, 36.9, 37.7, 38.5, 48.0, 53.8, 55.0, 62.6, 68.7, 70.2, 74.9$ and 75.9° ⁸¹ that corresponded to the anatase phase planes (101), (004), (200), (105), (211), (204), (116) and (107) (JCPDS-00-071-1167), respectively⁸². The anatase phase was more active than the rutile phase due to the presence of an indirect bandgap in the anatase crystal that increased the electron-hole pair separation⁸³. In N-TiO_2 NTs, the anatase peaks were slightly shifted compared with TiO_2 NTs, possibly due to N incorporation in TiO_2 bulk or crystal lattice, as confirmed by XPS⁸⁴. Unlike B/N co-doping, N-doping inhibits the rutile phase formation. Co-doping with B and N (B/N-TiO_2 NTs) led to the appearance of additional peaks^{85,86}. The peak at $2\theta = 28.0^\circ$ was associated with the rutile phase of the (110) plane⁸⁷. It was reported

elsewhere that the rutile phase formation is linked to the percentage of B incorporation into TiO₂⁸⁸. Lastly, in TiO₂ NFs, both anatase and rutile phases were observed with the rutile phase diffraction peaks (1 1 0), (1 0 1), (1 1 1), (2 1 0), (2 1 1), (2 2 0), (3 1 0) and (1 1 2) (rutile TiO₂, JCPDS 21-1276)⁸⁹. TiO₂ NFs did not show the same crystallinity as TiO₂ NTs, since the crystalline nature of TiO₂ varies with synthesizing techniques and parameters⁹⁰.

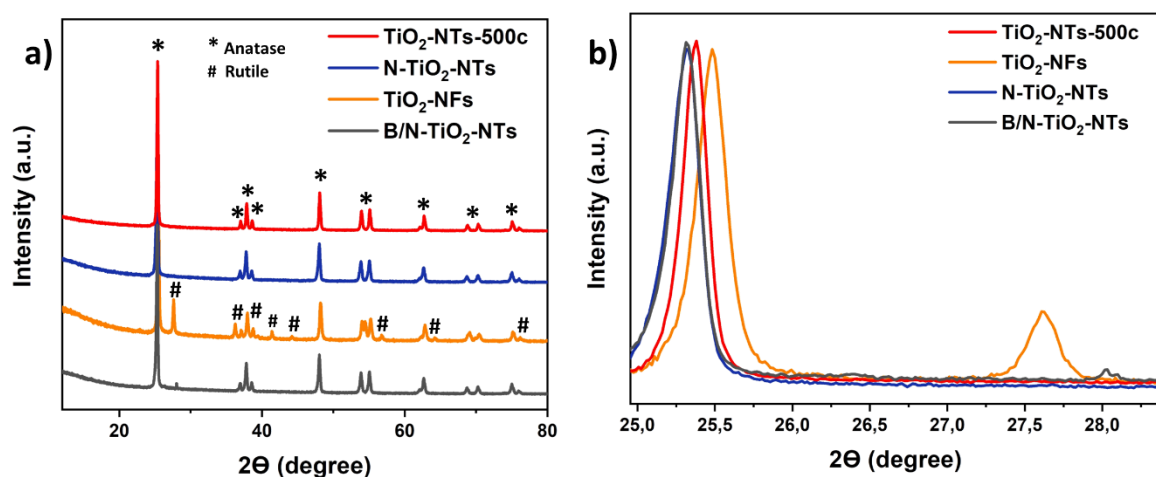


Figure 3. XRD analysis of doped and non-doped TiO₂ NTs (500 ALD cycles) and of TiO₂ NFs (a) from 15 to 80° and (b) zoom on the peaks from 24 to 29°.

To understand the effect of the different morphologies and modifications on TiO₂ structure, the percentage of anatase/rutile phase and the crystallite sizes were calculated using the Spurr (4) and Scherrer (5) equations^{91,92}:

$$\%R = \frac{1}{1 + 0.8 \left[\frac{I_A(101)}{I_R(110)} \right]} \quad (4)$$

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (5)$$

where I_A and I_R are the integrated intensities of the anatase (101) and rutile (110) diffraction peaks, D is the mean crystallite size, K is a shape factor = 0.89, λ is the X-ray wavelength, β is the full width at half maximum of the diffraction peak, and θ is the Bragg angle.

Comparison of the percentage of anatase/rutile phases and their particle sizes in all samples (**Table 1**) showed that in TiO₂ NT samples, doping decreased the crystallite size due to B and N inhibitory effect on the grain growth of TiO₂ particles. The anatase particle size of

non-doped TiO₂ NTs and N-TiO₂ NTs were 37.2 nm and 29.9 nm, respectively. This is probably due to the crystal lattice deformation and oxygen vacancies left by the substitution of O atoms by N atoms. The particle size decrease allows the photo-generated electrons to move faster to the TiO₂ surface and consequently it improves the catalyst degradation efficiency^{67,93}. In TiO₂ NFs, the crystallite sizes of the anatase and rutile phases were 30.9 and 34.3 nm, respectively. Previous works showed that the rutile phase displays lower photocatalytic activity than the anatase phase⁹⁴.

Then, TEM and XPS were used to better describe the morphology of non-doped TiO₂ NTs and N-doped TiO₂ NTs compared with TiO₂-NFs.

Table 1: Percentage of anatase and rutile phases and crystallite sizes of the indicated samples.

Sample	Anatase (A) phase (%)	Rutile (R) phase (%)	Crystallite size (A) (nm)*	Crystallite size (R) (nm)*
TiO ₂ NTs (500 AD cycles)	100.0	-	37.2	-
TiO ₂ NTs (1000 ALD cycles)	100.0	-	42.1	-
TiO ₂ NFs	24.5	75.5	30.9	34.3
B/N-TiO ₂ NTs	91.0	9.0	32.1	46.5
N-TiO ₂ NTs	100.0	-	29.9	-

*The error on the crystallite size is lower than $\pm 0.01\%$

The XPS survey of N-TiO₂ NTs confirmed the presence of Ti, O, C and N (**Figure 4a**). Carbon detection could be due to the presence of residues after calcination and PAN NF removal. The high-resolution XPS spectra of Ti 2p and of O 1s included two peaks (at 458.4 for Ti 2p_{3/2} and at 464.1 eV for Ti 2p_{1/2}) and three peaks (at 529.5, 530.6 and 532.3 eV), respectively. The binding energies of Ti 2p and O 1s for TiO₂ NTs (Erreur ! Source du renvoi introuvable.) were lower than those of doped TiO₂ NTs, unlike previous literature data showing that N-doping decreases the binding energy values^{95,96}. These reports demonstrated the presence of oxygen vacancies due to O substitution by N. Conversely, in our samples, the N peak (**Figure 4d**) at 399.9 eV was assigned to the presence of interstitial N atoms in the O–Ti–N environment, and not to substitutional doping of TiO₂ lattice by N. The N-O interaction in TiO₂ NT lattice increases the binding energy of the N 1s level, in agreement with our results⁹⁷. Moreover, the existence of Ti-N bonds could be excluded because N1s would be located at lower binding energies

(<397 eV)^{71,98}. This result might be interesting for photocatalytic applications because N-doping in TiO₂ NTs without Ti–N bonding causes visible-light sensitization. The total N amount in N-TiO₂ NTs was ~0.7%. Conversely, in B/N-TiO₂-NTs, B and N amounts were estimated at 6.6 and 1.3%, respectively. The higher N amount in the co-doped samples could be explained by the different doping method used. Only one peak at 192.3 eV was attributed to B 1s (**Figure 4e**), suggesting the presence of B-O-Ti groups⁹⁹. The absence of B-N linkages indicates that B/N-TiO₂-NTs were not doped by BN, but co-doped by B and N. The N 1s peak at 398.2 eV (N 1s A) was explained by the substitutional N atom that replaced one O atom in the TiO₂ lattice. The peak at 401.5 (N 1s B) eV corresponded to NH₄⁺ ions at the TiO₂ surface¹⁰⁰. The N atom location in the TiO₂ lattice depended on the synthetic route of N-doped TiO₂.

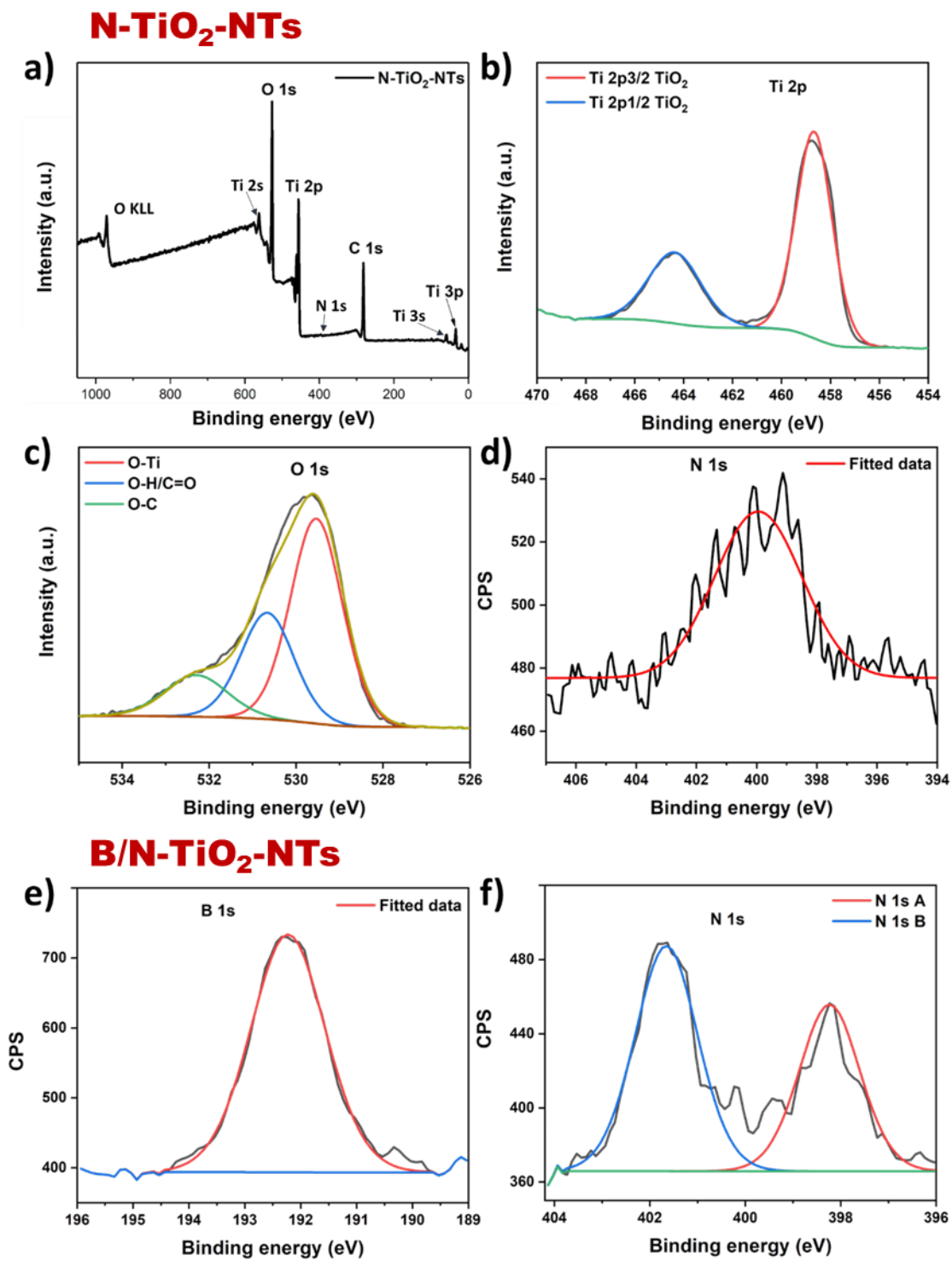


Figure 4. XPS spectra of N-TiO₂ NTs: (a) Survey spectra, (b) Ti 2p, (c) O 1s, (d) N 1s; and of B/N-TiO₂-NTs: (e) B1s and (f) N1s.

3.2. Electrochemical measurements

The fabrication of catalysts with low electron-hole pair recombination rate and high electron-charge transport is crucial for enhancing their degradation efficiency under visible light. Photoluminescence (Erreur ! Source du renvoi introuvable.), EIS and EAS measurements were carried out to investigate the interfacial charge transport process. The Nyquist plots of TiO₂ NTs, TiO₂ NFs, N-TiO₂ NTs and B/N-TiO₂ NTs are shown in **Figure 5 (a)**. The Nyquist plot of TiO₂ is described by its semicircle frequency region related to the electron transfer from the TiO₂ conduction band to the electrolyte¹⁰¹. The radius arc resistance is directly correlated to the catalyst charge transportability and is determined based on the electrical model given in **Figure 5 (a)** in which R₁ is the electrolyte resistance and R₂ the charge transfer resistance. N-TiO₂ NTs displayed the lowest radius arc (i.e. R₂ value) among all samples, indicating higher charge transport and very low recombination rate. Calculation of the charge transfer resistance values (R₂) (**Table 2**) confirmed that N-TiO₂ NTs had the lowest R₂ (15.22 kΩ vs 19.11 kΩ for non-doped TiO₂ NTs and 16.52 kΩ for TiO₂ NFs). This suggests that N-doping decreases TiO₂ surface resistance and delays charge recombination at the TiO₂-electrolyte interface. Concerning TiO₂ morphology (NTs vs NFs), TiO₂ NFs showed better electron-hole pair separation resistance (i.e. lower R₂ than non-doped TiO₂ NTs), possibly due to their higher crystallinity that favors the charge carrier separation and transport²⁵. Co-doping affected negatively the charging kinetics, indicating the occurrence of trap states and recombination centers¹⁰². CV with [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ were used to investigate the effect of morphology and doping on the electrochemical response (**Figure 5b** and **Table 2**). Concerning the morphology, the current density peak was higher in TiO₂ NFs than TiO₂ NTs, possibly because of their higher EAS (**Table 2**), despite their slightly higher ΔE_{peak}. N-doping led to the highest current density response towards [Fe(CN)₆]^{3/4} and lower ΔE_{peak}, suggesting higher electrode reaction rate.

Table 2: Electrochemical results for TiO₂ NTs, TiO₂ NFs, B/N-TiO₂ NTs, and N TiO₂ NTs.

Sample	R ₂ (kΩ)	I _p (A.cm ⁻²)	ΔE (mV)	EAS (cm ²)
--------	------------------------	---	------------	---------------------------

TiO ₂ NTs	19.11	1.86±0.02	0.38	1.78±0.01
TiO ₂ NFs	16.52	1.94±0.01	0.43	1.85±0.02
B/N-TiO ₂ NTs	51.35	2.01±0.01	0.40	1.90±0.01
N-TiO ₂ NTs	15.22	2.50±0.03	0.37	2.40±0.04

The $\Delta E = E_{\text{anode}} - E_{\text{cathode}}$ values showed that the mean peak-to-peak separation was shorter in N-TiO₂ NTs (0.3711 mV at V= 20 mV/s). When ΔE is shorter, electron transfer is faster in the redox reaction and the electrode surface is more conductive. The EAS values were 1.78 (TiO₂ NTs, 500 ALD cycles), 1.85 (TiO₂ NFs), 1.90 (B/N-TiO₂ NTs), and 2.40 cm² (N-TiO₂ NTs)¹⁰³. This confirmed that doping plays a major role in enhancing TiO₂ photocatalytic activity by improving the electron-hole pair separation, as confirmed by the photoluminescence results. According to the literature, a smaller grain size increases the number of active surface sites and also the surface charge carrier transfer rate in 1D structured photocatalysts, leading to higher photocatalytic activity¹⁰⁴. N-TiO₂ NTs had the smallest crystallite grain size compared with TiO₂ NFs, non-doped TiO₂ NTs and B/N co-doped TiO₂ NTs. It is worth noted that TiO₂ photocatalytic performance is influenced not only by one factor but different factors in the same time such as particle size, specific surface area, porous structure, crystalline phase, and exposed surface facets. All these parameters should be assessed to understand the catalytic performance of the material.

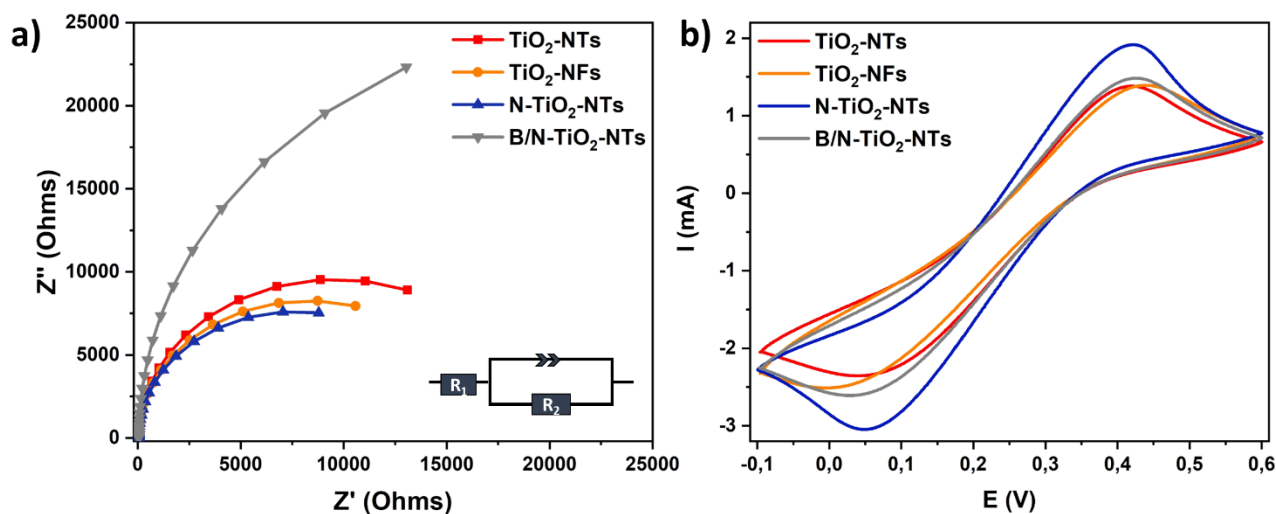


Figure 5. a) Nyquist plots and b) Cyclic voltammograms, obtained in potassium hexacyanoferrate solution with a scan rate of 20 mV/s, for TiO_2 NTs, TiO_2 NFs, N- TiO_2 NTs, and B/N- TiO_2 NTs (surface= 1 cm^2).

3.3. Photocatalytic experiments

3.3.1. Photocatalytic degradation

Visible light photodegradation of acetaminophen (**Figure 6**) was compared using different TiO_2 -based catalysts. This showed that higher number of ALD cycles increased the wall thickness (not presented in this paper) that strongly affected acetaminophen degradation efficiency (**Figure 6a**), in agreement with the literature⁸⁰. The highest degradation efficiency was obtained with TiO_2 NTs prepared using 500 ALD cycles compared with 800 and 1000 ALD cycles: 95.7% after 90 minutes of visible light irradiation versus 76.6% and 56.0%, respectively. On the basis of these results, TiO_2 NTs fabricated using 500 ALD cycles were used for all the other experiments. As the catalyst morphology plays a major role in the degradation of pharmaceutical pollutants, it was important to understand the effects of the surface area, crystallinity, electron-hole pair recombination, and bandgap on the photocatalytic properties⁹⁵. The visible light catalytic properties of TiO_2 NFs (fabricated by electrospinning followed by calcination at 750°C for 4h) were compared with those of TiO_2 NTs (**Figure 6**). As

N-TiO₂ NTs have lower recombination rate and higher surface area than TiO₂ NFs (see EIS and EAS data), their photocatalytic activity was higher. It was previously reported that anatase TiO₂ displays higher degradation efficiency than a catalyst with both crystalline phases^{80,93}. Wang *et al.* observed better photocatalytic degradation of methylene blue by TiO₂ nanosheets than TiO₂ nanoparticles, highlighting the importance of the catalyst structure. Moreover, they reported that higher surface area further improves degradation under visible light¹⁰⁵.

Then, different TiO₂ NT samples were prepared by varying the dopant nature to explore how to limit the recombination of photogenerated electron-hole pairs for feasible charge separation and transfer, and how to expand the absorption edge to the visible light range. After 90 minutes of visible light exposure, 98.3%, 95.7% and 31.9% of acetaminophen were degraded in the presence of N-TiO₂ NTs, TiO₂ NTs, and B/N-TiO₂ NTs, respectively (Erreur ! Source du renvoi introuvable.). This indicates the N-doping better increase the degradation efficiency compared with B and D co-doping. This modification step might be affected by many factors, including the type and level of N-doping and the concentration of O₂ vacancies, and this will greatly influence the photocatalytic activity^{106,107}.

The positive effect of N-doping on TiO₂ catalyst properties has been widely reported. Indeed, N-doping creates O₂ vacancies that participate in trapping the photoinduced electrons and act as a reactive center for the photocatalytic process. As the number of articles on TiO₂ modification by N-doping is too high, comparing their results is complicated due to the many different experimental conditions (e.g. catalyst structure, concentrations, matrix, lamp source)^{69,93,108–110}.

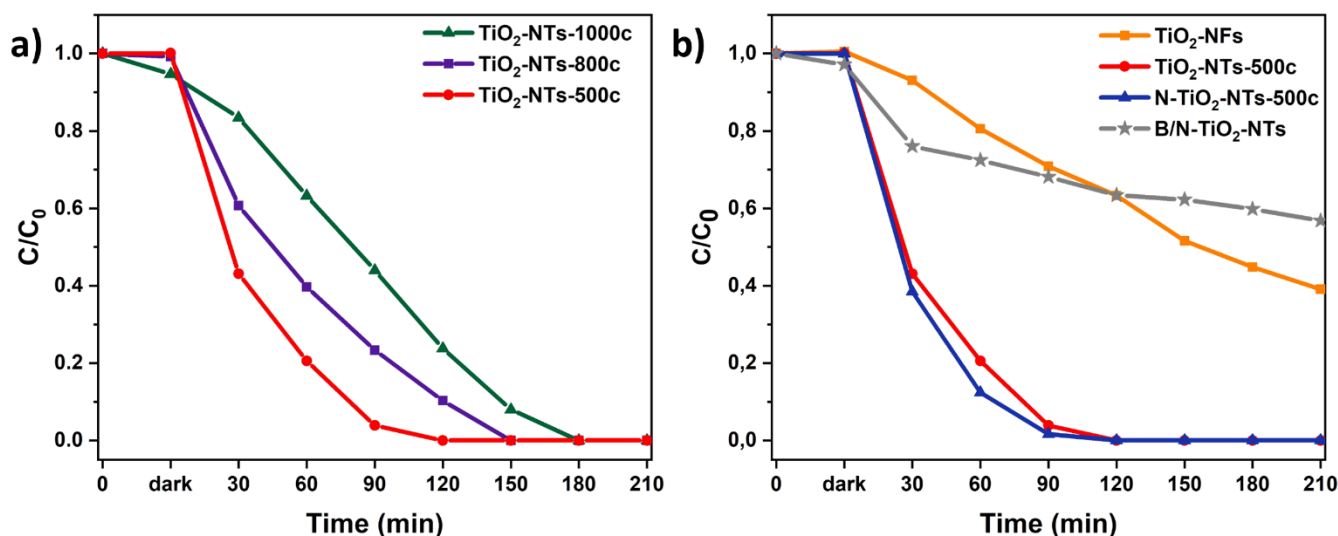


Figure 6. Acetaminophen degradation under visible light in function of a) TiO₂ wall thickness (number of ALD cycles), b) TiO₂ structure, morphology, and doping.

3.3.2. Photocatalytic kinetic model

The photocatalytic degradation of acetaminophen under visible light followed a pseudo-first-order kinetics. Indeed, the closely linear relationship between $\ln(C_0/C)$ and irradiation time (t) fits well with the first-order reaction rate of acetaminophen degradation (**Figure 7a**). The degradation rate in the presence of N-TiO₂ NTs was 0.045 min^{-1} , which is 4 times higher than with TiO₂ NFs. This result was in agreement with the lower electron-hole pair recombination rate (photoluminescence and EIS measurements). Moreover, the high percentage of rutile phase in TiO₂ NFs decreased their degradation efficiency. In conclusion, ALD is a promising technique for fabricating catalysts with well-organized structure and good degradation performance under visible light.

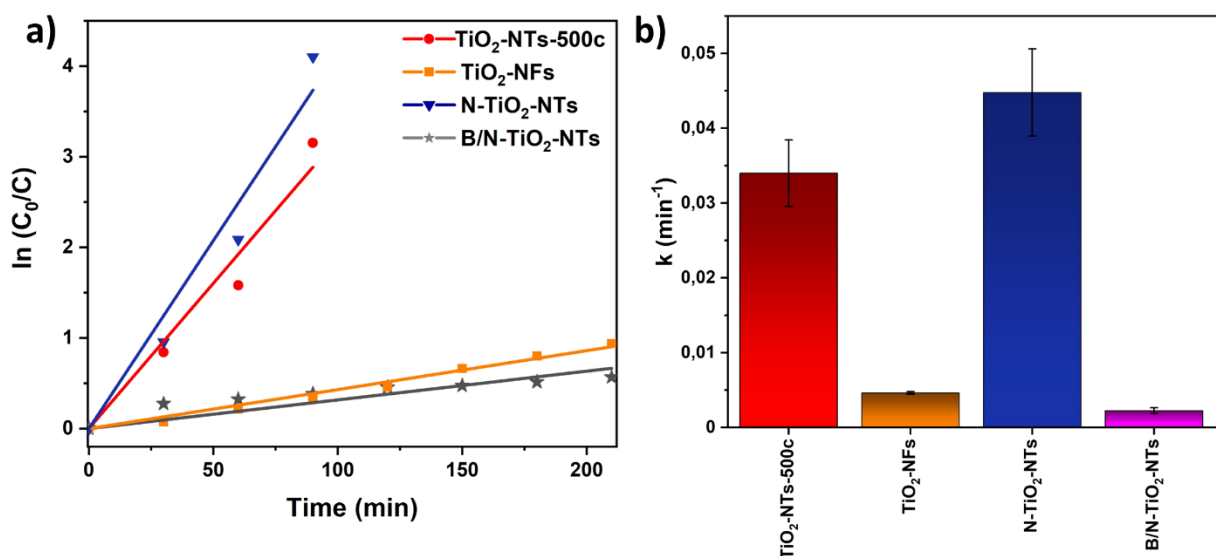


Figure 7. Photocatalytic degradation of acetaminophen by the indicated TiO_2 catalysts. a) Plot of $\ln(C_0/C)$ in function of time (fitted to first order rate law), and b) Values the first order rate constant.

3.3.3. Stability, quenching, and toxicity tests

N-TiO_2 NTs (500 ALD cycles) recyclability and stability were tested for five consecutive cycles (**Figure 8a**). After each cycle, the catalyst was rinsed several times with distilled water and dried at 70°C before the next cycle. Acetaminophen degradation rates, after 90 min of visible light irradiation, were 98.3% (first cycle), 97.5% (second cycle), 96.0% (third cycle), 93.9% (fourth cycle), and 82.6% (fifth cycle). This indicates a slight loss of degradation efficiency over time, although acetaminophen removal was still $>82\%$ after five runs. This activity decrease might be related to N loss in the catalyst after consecutive cycles, or to the accumulation of by-products that are formed during the catalyst surface degradation, thus decreasing the available active sites¹¹¹. Despite this loss of activity ($<20\%$) after five cycles, N-TiO_2 NTs can be considered a promising stable catalyst material for water treatment.

Organic pollutant degradation by advanced oxidation processes can lead to the production of by-products^{112,113} with cyclic and aromatic structure that are highly toxic, sometimes more than the initial pollutant. To evaluate the acute toxicity of intermediates generated during acetaminophen photodegradation, *V. fischeri* luminescence intensity variations were quantified after 15-min incubation with aqueous solution aliquots collected during acetaminophen degradation (**Figure 8b**). Acetaminophen toxicity was very low at the used

concentration, as we previously reported¹¹⁴. Toxicity strongly increased and luminescence was inhibited by ~90% after 1h of visible light irradiation. This result is consistent with previous studies showing the formation of toxic aromatic by-products (e.g. 1,4-benzoquinone, hydroquinone, benzoic acid, and benzaldehyde) during acetaminophen degradation^{115–117}. Then, toxicity progressively decreased and luminescence intensity inhibition was <20% after 3h of irradiation. During this period, further oxidation of the formed molecules would result in the breakdown of their aromatic structures. After 6h of irradiation, when short-chain carboxylic acids are converted into CO₂ and H₂O, the luminescence inhibition rate was <5%.

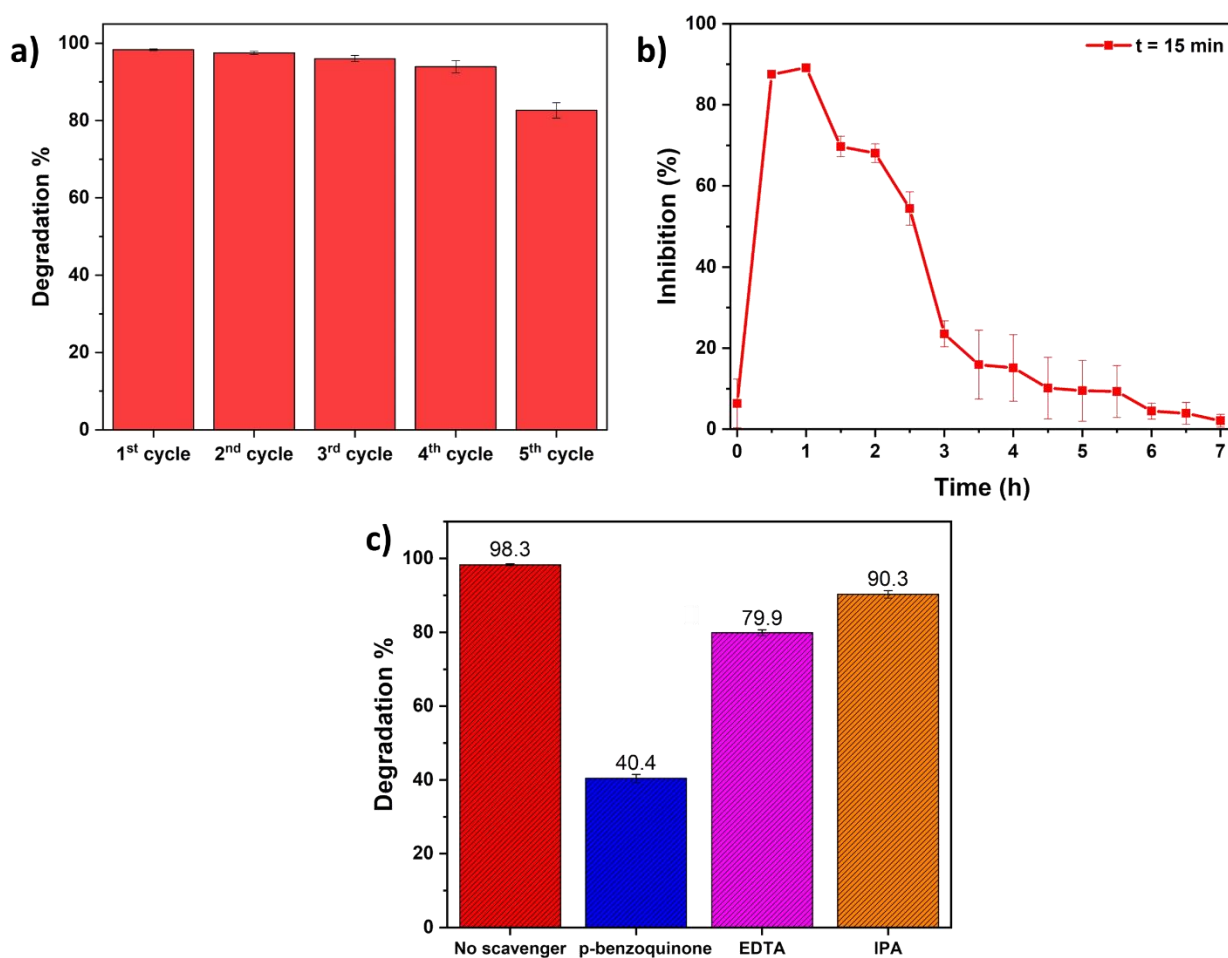


Figure 8. a) Reusability of N-TiO₂-NTs for photocatalytic activity. b) Inhibition of *V. fischeri* luminescence emission during acetaminophen photodegradation. c) Effect of radical scavengers on acetaminophen degradation.

During photodegradation, OH° radicals, h^+ and O_2^- radicals are generally considered as active species. To determine their contribution to acetaminophen degradation, scavenger tests were performed using EDTA (h^+ scavenger), isopropanol (OH radicals), and p-benzoquinone (O_2^- radicals) and N-TiO₂ NTs as catalyst. The results (**Figure 8c**) suggested that all three active radical species are implicated in acetaminophen degradation because all scavengers decreased its photodegradation, particularly p-benzoquinone (O_2^- radical scavenger) that reduced acetaminophen degradation rate from 98.3% to 40.4%.

4. Conclusion

In this work, we first compared the photocatalytic properties of two different 1D TiO₂ structures fabricated using two different approaches. TiO₂ NTs, synthesized by ALD, displayed 3 times higher acetaminophen degradation rates (after 90 min of visible light irradiation) than TiO₂ NFs, produced by electrospinning. Then, we investigated whether non-metal doping increased TiO₂ NT degradation efficiency. N-doping enhanced the catalytic properties, as indicated by the degradation rate of 0.045 min⁻¹ of N-TiO₂ NTs. This result could be explained by the lower recombination rate of the photogenerated charges and higher electroactive surface area (2.40 cm² in N-TiO₂ NTs versus 1.78 cm² in TiO₂ NTs). The recyclability results suggest that ALD is an interesting technique for preparing photocatalysts on immobilized supports with good degradation efficiency and high stability. Quenching tests indicated that superoxide radicals played a major role in acetaminophen degradation. In this work, we confirmed the higher degradation activity of highly structured 1D materials under visible light. Now, these catalysts should be tested using a real wastewater matrix with different organic pollutant to test the selectivity of the photocatalyst and the ability to degrade different types of pollutants.

Acknowledgements

This work was funded by the H2020-MSCA-RISE-2017 project, 'Novel 1D photonic metal oxide nanostructures for early stage cancer detection' (Project number: 778157). This study

was supported also by the Research Council of Lithuania (LMTLT), GILIBERT 2021 program agreement No S-LZ- 21–4, and was co-funded by Campus France grant No. 46593RA (PHC GILIBERT 2021). I.I. acknowledges partial financial support from the SONATA BIS project 2020/38/E/ST5/00176.

References

1. Takeuchi N, Yasuoka K. Review of plasma-based water treatment technologies for the decomposition of persistent organic compounds. *Jpn J Appl Phys.* 2020;60(SA):SA0801. doi:10.35848/1347-4065/abb75d
2. Gehrke I, Geiser A, Somborn-Schulz A. Innovations in nanotechnology for water treatment. *Nanotechnol Sci Appl.* 2015;8:1-17. doi:10.2147/NSA.S43773
3. World Health Organization. Pharmaceuticals in drinking-water. Published online 2012.
4. Houtman CJ. Emerging contaminants in surface waters and their relevance for the production of drinking water in Europe. *J Integr Environ Sci.* 2010;7(4):271-295.
5. Tran NH, Reinhard M, Gin KYH. Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review. *Water Res.* 2018;133:182-207.
6. Nam SW, Jo BI, Yoon Y, Zoh KD. Occurrence and removal of selected micropollutants in a water treatment plant. *Chemosphere.* 2014;95:156-165. doi:10.1016/j.chemosphere.2013.08.055
7. Phong Vo HN, Le GK, Hong Nguyen TM, et al. Acetaminophen micropollutant: Historical and current occurrences, toxicity, removal strategies and transformation pathways in different environments. *Chemosphere.* 2019;236:124391. doi:10.1016/j.chemosphere.2019.124391

8. Stasinakis A. Use of selected advanced oxidation processes (AOPs) for wastewater treatment—a mini review. *Glob NEST J.* 2008;10(3):376-385.
9. Rodriguez-Narvaez OM, Peralta-Hernandez JM, Goonetilleke A, Bandala ER. Treatment technologies for emerging contaminants in water: A review. *Chem Eng J.* 2017;323:361-380.
10. Teodosiu C, Gilca AF, Barjoveanu G, Fiore S. Emerging pollutants removal through advanced drinking water treatment: A review on processes and environmental performances assessment. *J Clean Prod.* 2018;197:1210-1221. doi:10.1016/j.jclepro.2018.06.247
11. Friedmann D, Mendive C, Bahnemann D. TiO₂ for water treatment: parameters affecting the kinetics and mechanisms of photocatalysis. *Appl Catal B Environ.* 2010;99(3-4):398-406.
12. Chong MN, Jin B, Chow CWK, Saint C. Recent developments in photocatalytic water treatment technology: A review. *Water Res.* 2010;44(10):2997-3027. doi:10.1016/j.watres.2010.02.039
13. Ameta R, Solanki MS, Benjamin S, Ameta SC. Chapter 6 - Photocatalysis. In: Ameta SC, Ameta R, eds. *Advanced Oxidation Processes for Waste Water Treatment*. Academic Press; 2018:135-175. doi:10.1016/B978-0-12-810499-6.00006-1
14. Serpone N. Photocatalysis. In: *Kirk-Othmer Encyclopedia of Chemical Technology*. American Cancer Society; 2000. doi:https://doi.org/10.1002/0471238961.1608152019051816.a01
15. Gaya UI, Abdullah AH. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *J Photochem Photobiol C Photochem Rev.* 2008;9(1):1-12.
16. Hong SP, Park J, SM Bhat S, et al. Comprehensive study on the morphology control of TiO₂ nanorods on foreign substrates by the hydrothermal method. *Cryst Growth Des.* 2018;18(11):6504-6512.
17. Ramanavicius S, Ramanavicius A. Insights in the application of stoichiometric and non-stoichiometric titanium oxides for the design of sensors for the determination of gases and VOCs (TiO_{2-x} and Ti_nO_{2n-1} vs. TiO₂). *Sensors.* 2020;20(23):6833.
18. Ramanavicius S, Tereshchenko A, Karpicz R, et al. TiO_{2-x}/TiO₂-structure based 'self-heated' sensor for the determination of some reducing gases. *Sensors.* 2020;20(1):74.
19. Nakata K, Fujishima A. TiO₂ photocatalysis: Design and applications. *J Photochem Photobiol C Photochem Rev.* 2012;13(3):169-189. doi:10.1016/j.jphotochemrev.2012.06.001

20. Nasr M, Eid C, Habchi R, Miele P, Bechelany M. Recent Progress on Titanium Dioxide Nanomaterials for Photocatalytic Applications. *ChemSusChem*. 2018;11(18):3023-3047. doi:10.1002/cssc.201800874
21. Nasr O, Mohamed O, Al-Shirbini AS, Abdel-Wahab AM. Photocatalytic degradation of acetaminophen over Ag, Au and Pt loaded TiO₂ using solar light. *J Photochem Photobiol Chem*. 2019;374:185-193. doi:10.1016/j.jphotochem.2019.01.032
22. Bui XT, Chiemchaisri C, Fujioka T, Varjani S. Introduction to Recent Advances in Water and Wastewater Treatment Technologies. In: Bui XT, Chiemchaisri C, Fujioka T, Varjani S, eds. *Water and Wastewater Treatment Technologies*. Springer Singapore; 2019:3-12. doi:10.1007/978-981-13-3259-3_1
23. Xiang Q, Ma X, Zhang D, et al. Interfacial modification of titanium dioxide to enhance photocatalytic efficiency towards H₂ production. *J Colloid Interface Sci*. 2019;556:376-385. doi:10.1016/j.jcis.2019.08.033
24. Bethi B, Sonawane SH, Bhanvase BA, Gumfekar SP. Nanomaterials-based advanced oxidation processes for wastewater treatment: A review. *Chem Eng Process - Process Intensif*. 2016;109:178-189. doi:10.1016/j.cep.2016.08.016
25. Akple M, Low J, Qin Z, et al. Nitrogen-doped TiO₂ microsheets with enhanced visible light photocatalytic activity for CO₂ reduction. *Chin J Catal*. 2015;36:2127-2134.
26. Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ Int*. 2009;35(2):402-417.
27. Katal R, Masudy-Panah S, Tanhaei M, Farahani MHDA, Jiangyong H. A review on the synthesis of the various types of anatase TiO₂ facets and their applications for photocatalysis. *Chem Eng J*. 2020;384:123384. doi:10.1016/j.cej.2019.123384
28. Ghorri MZ, Veziroglu S, Henkel B, et al. A comparative study of photocatalysis on highly active columnar TiO₂ nanostructures in-air and in-solution. *Sol Energy Mater Sol Cells*. 2018;178:170-178. doi:10.1016/j.solmat.2018.01.019
29. Yang HG, Liu G, Qiao SZ, et al. Solvothermal Synthesis and Photoreactivity of Anatase TiO₂ Nanosheets with Dominant {001} Facets. *J Am Chem Soc*. 2009;131(11):4078-4083. doi:10.1021/ja808790p
30. Ramakrishnan VM, Natarajan M, Santhanam A, Asokan V, Velauthapillai D. Size controlled synthesis of TiO₂ nanoparticles by modified solvothermal method towards effective photo catalytic and photovoltaic applications. *Mater Res Bull*. 2018;97:351-360. doi:10.1016/j.materresbull.2017.09.017
31. Mamaghani AH, Haghghat F, Lee CS. Role of titanium dioxide (TiO₂) structural design/morphology in photocatalytic air purification. *Appl Catal B Environ*. 2020;269:118735. doi:10.1016/j.apcatb.2020.118735

32. El-Maghrabi HH, Barhoum A, Nada AA, et al. Synthesis of mesoporous core-shell CdS@TiO₂ (0D and 1D) photocatalysts for solar-driven hydrogen fuel production. *J Photochem Photobiol Chem*. 2018;351:261-270. doi:10.1016/j.jphotochem.2017.10.048
33. Ramanavicius S, Ramanavicius A. Progress and Insights in the Application of MXenes as New 2D Nano-Materials Suitable for Biosensors and Biofuel Cell Design. *Int J Mol Sci*. 2020;21(23). doi:10.3390/ijms21239224
34. Rosales M, Zoltan T, Yadarola C, Mosquera E, Gracia F, García A. The influence of the morphology of 1D TiO₂ nanostructures on photogeneration of reactive oxygen species and enhanced photocatalytic activity. *J Mol Liq*. 2019;281:59-69. doi:10.1016/j.molliq.2019.02.070
35. Guo MY, Fung MK, Fang F, et al. ZnO and TiO₂ 1D nanostructures for photocatalytic applications. *J Alloys Compd*. 2011;509(4):1328-1332. doi:10.1016/j.jallcom.2010.10.028
36. Erdogan N, Park J, Choi W, Kim SY, Ozturk A. Alkaline hydrothermal synthesis, characterization, and photocatalytic activity of TiO₂ nanostructures: the effect of initial TiO₂ phase. *J Nanosci Nanotechnol*. 2019;19(3):1511-1519.
37. Ge M, Li Q, Cao C, et al. One-dimensional TiO₂ Nanotube Photocatalysts for Solar Water Splitting. *Adv Sci*. 2017;4(1):1600152. doi:10.1002/advs.201600152
38. Feng T, Feng GS, Yan L, Pan JH. One-dimensional nanostructured TiO₂ for photocatalytic degradation of organic pollutants in wastewater. *Int J Photoenergy*. 2014;2014.
39. Shahrezaei M, Babaluo AA, Habibzadeh S, Haghghi M. Photocatalytic properties of 1D TiO₂ nanostructures prepared from polyacrylamide gel-TiO₂ nanopowders by hydrothermal synthesis. *Eur J Inorg Chem*. 2017;2017(3):694-703.
40. Chatzitakis A, Grandcolas M, Xu K, et al. Assessing the photoelectrochemical properties of C, N, F codoped TiO₂ nanotubes of different lengths. *Sel Contrib 9th Eur Meet Sol Chem Photocatal Environ Appl SPEA-9*. 2017;287:161-168. doi:10.1016/j.cattod.2016.11.040
41. Roy P, Berger S, Schmuki P. TiO₂ nanotubes: synthesis and applications. *Angew Chem Int Ed*. 2011;50(13):2904-2939.
42. Paramasivam I, Jha H, Liu N, Schmuki P. A review of photocatalysis using self-organized TiO₂ nanotubes and other ordered oxide nanostructures. *small*. 2012;8(20):3073-3103.
43. Zhu S, Nie L. Progress in fabrication of one-dimensional catalytic materials by electrospinning technology. *J Ind Eng Chem*. 2021;93:28-56. doi:10.1016/j.jiec.2020.09.016
44. Kowalski D, Kim D, Schmuki P. TiO₂ nanotubes, nanochannels and mesosponge: Self-organized formation and applications. *Nano Today*. 2013;8(3):235-264. doi:10.1016/j.nantod.2013.04.010

45. Meng X, Banis MN, Geng D, et al. Controllable atomic layer deposition of one-dimensional nanotubular TiO₂. *Appl Surf Sci.* 2013;266:132-140. doi:10.1016/j.apsusc.2012.11.116
46. Liang HC, Li XZ, Nowotny J. Photocatalytical properties of TiO₂ nanotubes. In: Vol 162. Trans Tech Publ; 2010:295-328.
47. Weber M, Julbe A, Kim SS, Bechelany M. Atomic layer deposition (ALD) on inorganic or polymeric membranes. *J Appl Phys.* 2019;126(4):041101. doi:10.1063/1.5103212
48. George SM. Atomic Layer Deposition: An Overview. *Chem Rev.* 2010;110(1):111-131. doi:10.1021/cr900056b
49. Elias J, Utke I, Yoon S, et al. Electrochemical growth of ZnO nanowires on atomic layer deposition coated polystyrene sphere templates. *Electrochem Adv Mater Technol Instrum.* 2013;110:387-392. doi:10.1016/j.electacta.2013.04.168
50. Abi Younes P, Sayegh S, Nada AA, et al. Elaboration of porous alumina nanofibers by electrospinning and molecular layer deposition for organic pollutant removal. *Colloids Surf Physicochem Eng Asp.* 2021;628:127274. doi:10.1016/j.colsurfa.2021.127274
51. Najem M, Nada AA, Weber M, et al. Palladium/Carbon Nanofibers by Combining Atomic Layer Deposition and Electrospinning for Organic Pollutant Degradation. *Materials.* 2020;13(8). doi:10.3390/ma13081947
52. Kim WS, Lee BS, Kim DH, Kim HC, Yu WR, Hong SH. SnO₂ nanotubes fabricated using electrospinning and atomic layer deposition and their gas sensing performance. *Nanotechnology.* 2010;21(24):245605.
53. Kim GM, Lee SM, Michler G, Roggendorf H, Gosele U, Knez M. Nanostructured pure anatase titania tubes replicated from electrospun polymer fiber templates by atomic layer deposition. *Chem Mater.* 2008;20(9):3085-3091.
54. Szilágyi IM, Nagy D. Review on one-dimensional nanostructures prepared by electrospinning and atomic layer deposition. *J Phys Conf Ser.* 2014;559:012010. doi:10.1088/1742-6596/559/1/012010
55. McClure CD, Oldham CJ, Walls HJ, Parsons GN. Large effect of titanium precursor on surface reactivity and mechanical strength of electrospun nanofibers coated with TiO₂ by atomic layer deposition. *J Vac Sci Technol Vac Surf Films.* 2013;31(6):061506.
56. Su CY, Wang LC, Liu WS, Wang CC, Perng TP. Photocatalysis and Hydrogen Evolution of Al- and Zn-Doped TiO₂ Nanotubes Fabricated by Atomic Layer Deposition. *ACS Appl Mater Interfaces.* 2018;10(39):33287-33295. doi:10.1021/acsami.8b12299
57. Lee SY, Park SJ. TiO₂ photocatalyst for water treatment applications. *J Ind Eng Chem.* 2013;19(6):1761-1769.
58. Fang W, Xing M, Zhang J. Modifications on reduced titanium dioxide photocatalysts: A review. *J Photochem Photobiol C Photochem Rev.* 2017;32:21-39.

59. Fujishima A, Zhang X, Tryk DA. TiO₂ photocatalysis and related surface phenomena. *Surf Sci Rep.* 2008;63(12):515-582. doi:10.1016/j.surfrep.2008.10.001
60. Khaki MRD, Shafeeyan MS, Raman AAA, Daud WMAW. Application of doped photocatalysts for organic pollutant degradation - A review. *J Environ Manage.* 2017;198:78-94. doi:10.1016/j.jenvman.2017.04.099
61. Mrowetz M, Balcerski W, Colussi A, Hoffmann MR. Oxidative power of nitrogen-doped TiO₂ photocatalysts under visible illumination. *J Phys Chem B.* 2004;108(45):17269-17273.
62. Park JH, Kim S, Bard AJ. Novel carbon-doped TiO₂ nanotube arrays with high aspect ratios for efficient solar water splitting. *Nano Lett.* 2006;6(1):24-28.
63. Tachikawa T, Tojo S, Kawai K, et al. Photocatalytic Oxidation Reactivity of Holes in the Sulfur- and Carbon-Doped TiO₂ Powders Studied by Time-Resolved Diffuse Reflectance Spectroscopy. *J Phys Chem B.* 2004;108(50):19299-19306. doi:10.1021/jp0470593
64. Takeshita K, Yamakata A, Ishibashi T aki, Onishi H, Nishijima K, Ohno T. Transient IR absorption study of charge carriers photogenerated in sulfur-doped TiO₂. *J Photochem Photobiol Chem.* 2006;177(2-3):269-275.
65. Ohno T, Akiyoshi M, Umebayashi T, Asai K, Mitsui T, Matsumura M. Preparation of S-doped TiO₂ photocatalysts and their photocatalytic activities under visible light. *Appl Catal Gen.* 2004;265(1):115-121.
66. Liu R, Yang F, Xie Y, Yu Y. Visible-light responsive boron and nitrogen codoped anatase TiO₂ with exposed {0 0 1} facet: Calculation and experiment. *Appl Surf Sci.* 2019;466:568-577.
67. Wang SQ, Liu WB, Fu P, Cheng WL. Enhanced photoactivity of N-doped TiO₂ for Cr(VI) removal: Influencing factors and mechanism. *Korean J Chem Eng.* 2017;34(5):1584-1590. doi:10.1007/s11814-017-0003-7
68. Dong F, Wang H, Wu Z, Qiu J. Marked enhancement of photocatalytic activity and photochemical stability of N-doped TiO₂ nanocrystals by Fe³⁺/Fe²⁺ surface modification. *J Colloid Interface Sci.* 2010;343(1):200-208. doi:10.1016/j.jcis.2009.11.012
69. Zhang Z, Wang X, Long J, Gu Q, Ding Z, Fu X. Nitrogen-doped titanium dioxide visible light photocatalyst: Spectroscopic identification of photoactive centers. *J Catal.* 2010;276(2):201-214. doi:10.1016/j.jcat.2010.07.033
70. Huang J, Dou L, Li J, Zhong J, Li M, Wang T. Excellent visible light responsive photocatalytic behavior of N-doped TiO₂ toward decontamination of organic pollutants. *J Hazard Mater.* 2021;403:123857. doi:10.1016/j.jhazmat.2020.123857
71. Kertmen A, Barbé E, Szkoda M, et al. Photoelectrochemically Active N-Adsorbing Ultrathin TiO₂ Layers for Water-Splitting Applications Prepared by Pyrolysis of Oleic Acid

- on Iron Oxide Nanoparticle Surfaces under Nitrogen Environment. *Adv Mater Interfaces*. 2019;6(3):1801286. doi:10.1002/admi.201801286
72. Chen C, Ma W, Zhao J. Photocatalytic degradation of organic pollutants by co-doped TiO₂ under visible light irradiation. *Curr Org Chem*. 2010;14(7):630-644.
 73. Sayegh S, Tanos F, Nada A, et al. Tunable TiO₂-BN-Pd nanofibers by combining electrospinning and atomic layer deposition to enhance photodegradation of acetaminophen. *Dalton Trans*. 2022;51(7):2674-2695.
 74. Lin L, Lin L, Jiang W, Bechelany M, Nasr M, Jarvis J. Adsorption and photocatalytic oxidation of ibuprofen using nanocomposites of TiO₂ nanofibers combined with BN nanosheets: Degradation products and mechanisms. *Chemosphere Adsorption and photocatalytic oxidation of ibuprofen using nanocomposites of TiO₂ n*. *Chemosphere*. 2019;220(December 2018):921-929. doi:10.1016/j.chemosphere.2018.12.184
 75. Konstantinou IK, Albanis TA. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review. *Appl Catal B Environ*. 2004;49(1):1-14. doi:10.1016/j.apcatb.2003.11.010
 76. Konstantinou IK, Albanis TA. Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways. *Appl Catal B Environ*. 2003;42(4):319-335. doi:10.1016/S0926-3373(02)00266-7
 77. Xuan T, Le H, Nguyen T Van, et al. Chemosphere Correlation between degradation pathway and toxicity of acetaminophen and its by-products by using the electro-Fenton process in aqueous media. 2017;172:1-9. doi:10.1016/j.chemosphere.2016.12.060
 78. Borbón-Nuñez HA, Dominguez D, Muñoz-Muñoz F, et al. Fabrication of hollow TiO₂ nanotubes through atomic layer deposition and MWCNT templates. *Powder Technol*. 2017;308:249-257. doi:10.1016/j.powtec.2016.12.001
 79. Lazar MA, Varghese S, Nair SS. Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates. *Catalysts*. 2012;2(4). doi:10.3390/catal2040572
 80. Wang CC, Kei CC, Perng TP. Fabrication of TiO₂ nanotubes by atomic layer deposition and their photocatalytic and photoelectrochemical applications. *Nanotechnology*. 2011;22(36):365702.
 81. López de Dicastillo C, Patiño C, Galotto MJ, Palma JL, Alburquenque D, Escrig J. Novel Antimicrobial Titanium Dioxide Nanotubes Obtained through a Combination of Atomic Layer Deposition and Electrospinning Technologies. *Nanomaterials*. 2018;8(2). doi:10.3390/nano8020128
 82. Thamaphat K, Limsuwan P, Ngotawornchai B. Phase characterization of TiO₂ powder by XRD and TEM. *Agric Nat Resour*. 2008;42(5):357-361.

83. Soo JZ, Lee KM, Ang BC, Ong BH. Optimal electrospun TiO₂ nanofiber photocatalytic performance via synergistic morphology and particle crystallinity with anatase/rutile phase tuning. *Phys Status Solidi A*. 2019;216(16):1900066.
84. Sinha I, De AK. Chapter 1 - An overview of synthesis techniques for preparing doped photocatalysts. In: Singh P, Borthakur A, Mishra PK, Tiwary D, eds. *Nano-Materials as Photocatalysts for Degradation of Environmental Pollutants*. Elsevier; 2020:1-13. doi:10.1016/B978-0-12-818598-8.00001-8
85. Lu N, Quan X, Li J, Chen S, Yu H, Chen G. Fabrication of Boron-Doped TiO₂ Nanotube Array Electrode and Investigation of Its Photoelectrochemical Capability. *J Phys Chem C*. 2007;111(32):11836-11842. doi:10.1021/jp071359d
86. Szkoda M, Lisowska-Oleksiak A, Siuzdak K. Optimization of boron-doping process of titania nanotubes via electrochemical method toward enhanced photoactivity. *J Solid State Electrochem*. 2016;20(6):1765-1774. doi:10.1007/s10008-016-3185-8
87. Natarajan TS, Natarajan K, Bajaj HC, Tayade RJ. Enhanced photocatalytic activity of bismuth-doped TiO₂ nanotubes under direct sunlight irradiation for degradation of Rhodamine B dye. *J Nanoparticle Res*. 2013;15(5):1-18.
88. Gombac V, De Rogatis L, Gasparotto A, et al. TiO₂ nanopowders doped with boron and nitrogen for photocatalytic applications. *Doping Funct Photoactive Semicond Met Oxides*. 2007;339(1):111-123. doi:10.1016/j.chemphys.2007.05.024
89. Doh SJ, Kim C, Lee SG, Lee SJ, Kim H. Development of photocatalytic TiO₂ nanofibers by electrospinning and its application to degradation of dye pollutants. *J Hazard Mater*. 2008;154(1):118-127. doi:10.1016/j.jhazmat.2007.09.118
90. Yu J, Yu H, Cheng B, Trapalis C. Effects of calcination temperature on the microstructures and photocatalytic activity of titanate nanotubes. *J Mol Catal Chem*. 2006;249(1):135-142. doi:10.1016/j.molcata.2006.01.003
91. Yang Z, Shi Y, Wang B. Photocatalytic activity of magnetically anatase TiO₂ with high crystallinity and stability for dyes degradation: Insights into the dual roles of SiO₂ interlayer between TiO₂ and CoFe₂O₄. *Appl Surf Sci*. 2017;399:192-199. doi:10.1016/j.apsusc.2016.12.078
92. Jin X, Yuan K, Xu C, et al. Water steam modified crystallization and microstructure of mesoporous TiO₂ nanofibers. *Ceram Int*. 2018;44(2):2158-2164. doi:10.1016/j.ceramint.2017.10.168
93. Vaiano V, Sannino D, Sacco O. Heterogeneous photocatalysis: how doping with nitrogen can improve the performance of semiconductor nanoparticles under visible light irradiation. In: *Nanomaterials for the Detection and Removal of Wastewater Pollutants*. Elsevier; 2020:285-301.

94. Lai Y, Sun L, Chen Y, Zhuang H, Lin C, Chin JW. Effects of the Structure of TiO₂ Nanotube Array on Ti Substrate on Its Photocatalytic Activity. *J Electrochem Soc.* 2006;153(7):D123. doi:10.1149/1.2203112
95. Sauthier G, György E, Figueras A, Sánchez RS, Hernando J. Laser Synthesis and Characterization of Nitrogen-Doped TiO₂ Vertically Aligned Columnar Array Photocatalysts. *J Phys Chem C.* 2012;116(27):14534-14540. doi:10.1021/jp304324e
96. Calisir MD, Gungor M, Demir A, Kilic A, Khan MM. Nitrogen-doped TiO₂ fibers for visible-light-induced photocatalytic activities. *Ceram Int.* 2020;46(10):16743-16753.
97. Sathishkumar P, Pugazhenthiran N, Mangalaraja RV, Guesh K, Contreras D, Anandan S. Contemporary Achievements of Visible Light-Driven Nanocatalysts for the Environmental Applications. In: *Photocatalytic Functional Materials for Environmental Remediation.* John Wiley & Sons, Ltd; 2019:69-129. doi:https://doi.org/10.1002/9781119529941.ch3
98. Di Valentin C, Finazzi E, Pacchioni G, et al. N-doped TiO₂: Theory and experiment. *Doping Funct Photoactive Semicond Met Oxides.* 2007;339(1):44-56. doi:10.1016/j.chemphys.2007.07.020
99. Liu D, Zhang M, Xie W, Sun L, Chen Y, Lei W. Porous BN/TiO₂ hybrid nanosheets as highly efficient visible-light-driven photocatalysts. *Appl Catal B Environ.* 2017;207:72-78. doi:10.1016/j.apcatb.2017.02.011
100. Tran VA, Truong TT, Phan TAP, et al. Application of nitrogen-doped TiO₂ nano-tubes in dye-sensitized solar cells. *Appl Surf Sci.* 2017;399:515-522. doi:10.1016/j.apsusc.2016.12.125
101. Shu T, Xiang P, Zhou ZM, et al. Mesoscopic nitrogen-doped TiO₂ spheres for quantum dot-sensitized solar cells. *Electrochimica Acta.* 2012;68:166-171. doi:10.1016/j.electacta.2012.02.068
102. Garlisi C, Lai CY, George L, Chiesa M, Palmisano G. Relating Photoelectrochemistry and Wettability of Sputtered Cu- and N-Doped TiO₂ Thin Films via an Integrated Approach. *J Phys Chem C.* 2018;122(23):12369-12376. doi:10.1021/acs.jpcc.8b03650
103. Le TXH, Charmette C, Bechelany M, Cretin M. Facile preparation of porous carbon cathode to eliminate paracetamol in aqueous medium using electro-Fenton system. *Electrochimica Acta.* 2016;188:378-384.
104. Li H, Zhang W, Pan W. Enhanced Photocatalytic Activity of Electrospun TiO₂ Nanofibers with Optimal Anatase/Rutile Ratio. *J Am Ceram Soc.* 2011;94(10):3184-3187. doi:10.1111/j.1551-2916.2011.04748.x
105. Wang B, Leung MKH, Lu XY, Chen SY. Synthesis and photocatalytic activity of boron and fluorine codoped TiO₂ nanosheets with reactive facets. *Appl Energy.* 2013;112:1190-1197. doi:10.1016/j.apenergy.2013.03.084

106. Film N, Haiying Wang, Hu Y. The Photocatalytic Property of Nitrogen-Doped TiO₂. In: ; 2015.
107. Wang H, Hu Y. The Photocatalytic Property of Nitrogen-Doped TiO₂ Nanoball Film. *Int J Photoenergy*. 2013;2013:1-6.
108. Li X, Liu P, Mao Y, Xing M, Zhang J. Preparation of homogeneous nitrogen-doped mesoporous TiO₂ spheres with enhanced visible-light photocatalysis. *Appl Catal B Environ*. 2015;164:352-359. doi:10.1016/j.apcatb.2014.09.053
109. Bakar SA, Ribeiro C. Nitrogen-doped titanium dioxide: An overview of material design and dimensionality effect over modern applications. *J Photochem Photobiol C Photochem Rev*. 2016;27:1-29. doi:10.1016/j.jphotochemrev.2016.05.001
110. Choi WH, Lee CH, Kim H eun, Lee SU, Bang JH. Designing a high-performance nitrogen-doped titanium dioxide anode material for lithium-ion batteries by unravelling the nitrogen doping effect. *Nano Energy*. 2020;74:104829. doi:10.1016/j.nanoen.2020.104829
111. Noorisepehr M, Kakavandi B, Isari AA, et al. Sulfate radical-based oxidative degradation of acetaminophen over an efficient hybrid system: Peroxydisulfate decomposed by ferrous iron oxide nanocatalyst anchored on activated carbon and UV light. *Sep Purif Technol*. 2020;250:116950. doi:10.1016/j.seppur.2020.116950
112. Dirany A, Sirés I, Oturan N, Özcan A, Oturan MA. Electrochemical treatment of the antibiotic sulfachloropyridazine: kinetics, reaction pathways, and toxicity evolution. *Environ Sci Technol*. 2012;46(7):4074-4082.
113. Le TXH, Nguyen TV, Yacouba ZA, et al. Correlation between degradation pathway and toxicity of acetaminophen and its by-products by using the electro-Fenton process in aqueous media. *Chemosphere*. 2017;172:1-9. doi:https://doi.org/10.1016/j.chemosphere.2016.12.060
114. Zhang J, Sun B, Xiong X, et al. Removal of emerging pollutants by Ru/TiO₂-catalyzed permanganate oxidation. *Water Res*. 2014;63:262-270. doi:10.1016/j.watres.2014.06.028
115. Zhao B, Yu H, Liu Y, et al. Enhanced photoelectrocatalytic degradation of acetaminophen using a bifacial electrode of praseodymium-polyethylene glycol-PbO₂//Ti//TiO₂-nanotubes. *Chem Eng J*. 2021;410:128337. doi:10.1016/j.cej.2020.128337
116. Yang L, Yu LE, Ray MB. Photocatalytic Oxidation of Paracetamol: Dominant Reactants, Intermediates, and Reaction Mechanisms. *Environ Sci Technol*. 2009;43(2):460-465. doi:10.1021/es8020099
117. Le TXH, Nguyen TV, Yacouba ZA, et al. Toxicity removal assessments related to degradation pathways of azo dyes: Toward an optimization of Electro-Fenton treatment. *Chemosphere*. 2016;161:308-318. doi:10.1016/j.chemosphere.2016.06.108

