

Optimization of Ta-, V-, or Nb-doped TiO₂ for photocatalytic and electrophotocatalytic degradation of p-nitrophenol under UV–visible light

Antoine Farcy^a, Stéphanie D. Lambert^a, Maxine Mathy^a, Louise Lejeune^b, Pierre Eloy^b , Sophie Hermans^b , Julien G. Mahy^{a,*}

^a Department of Chemical Engineering – Nanomaterials, Catalysis & Electrochemistry, University of Liège, Liège, Belgium

^b Institute of Condensed Matter and Nanosciences - Molecular Chemistry, Materials and Catalysis (IMCN/MOST), Université catholique de Louvain, Place Louis Pasteur 1, Box L4.01.03, 1348 Louvain-La-Neuve, Belgium

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ABSTRACT

The objective of this study is to investigate the enhancement of TiO₂ photocatalytic activity under UV/visible and visible light by doping with tantalum (Ta), vanadium (V) or niobium (Nb) precursors. Thus, TiO₂-based photocatalysts are prepared at room temperature via aqueous sol–gel synthesis. These photocatalysts are doped with different molar ratios of dopants. The physicochemical properties of the obtained photocatalysts are characterized using various complementary techniques. X-ray diffraction (XRD) is used to determine the distribution of different crystalline phases of TiO₂ and the proportion of amorphous TiO₂ in the samples. BET measurements give textural properties with specific surface area reaching up to 292 m²/g and TEM images illustrating their spherical morphology. Inductively coupled plasma atomic emission spectroscopy (ICP-AES), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS) analyses confirmed the presence of Ti, O and Ta, V or Nb elements in the samples. Additionally, XPS spectra highlights the incorporation of nitrogen in the undoped synthesized TiO₂. Additionally, band gap widths measured by UV–vis diffuse reflectance spectroscopy (DRUS) are done to see the impact of the dopants on the bandgap, with V-doping reducing its value from 2.95 to 1.88 eV. A screening of the photocatalytic activity of undoped and doped photocatalysts is carried out by evaluating the degradation of p-nitrophenol under UV–visible light (300 < λ < 800 nm) and visible light only (395 < λ < 800 nm). This study suggests that photocatalytic activity is significantly influenced by the nature and dopant content. Photocatalytic tests show an improvement in the activity of the photocatalyst when doped with tantalum and niobium (from 22 % with undoped TiO₂ under visible light to 37 % and 55 % with the best Ta and Nb-doped samples respectively), while a notable decrease in activity is observed with vanadium doping (dropping to 3–12 % with the V-doped series). Finally, a preliminary electrophotocatalysis experimental setup is implemented and appears to show an improvement in the mineralization of the PNP solution when the anode is coated with layers of the best doped-TiO₂ material (Nd doping), compared to an uncoated anode (the mineralization rate increases from 72 % to 94 %).

1. Introduction

During the 20th century, industrial development intensified worldwide, affecting various sectors such as the chemical, pharmaceutical, cosmetics and oil industries [1]. This expansion led to the emergence of refractory organic compounds (ROCs), including dyes, aromatics, pesticides, solvents, endocrine disruptors (EDCs) and pharmaceutical and personal care products (PPCPs) such as analgesics, disinfectants, antibiotics, perfumes, sunscreens, etc. [2]. Despite the efforts made, only a

limited proportion of these micropollutants, between 20 and 50 %, are currently eliminated in conventional wastewater treatment plants [3]. These substances, which have been present for years in wastewater, surface water, groundwater, soil and aquatic organisms, are now attracting increasing attention due to recent advances in analytical techniques that enable the detection of minute quantities of substances, sometimes as low as picograms per liter (pg/L) [4].

A revision of the European Wastewater Treatment Directive (91/271) was done, with the aim of tightening quality standards for treated

* Corresponding author at: Allée du Six Août 11, 4000 Liège, Belgium.

E-mail address: julien.mahy@uliege.be (J.G. Mahy).

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wastewater by imposing an additional, so-called 'quaternary' treatment designed to perfect the purification process [5]. In other words, quaternary treatment aims to eliminate, on the one hand, the widest possible range of micropollutants and, on the other, pathogenic germs upstream of bathing areas, for example.

With the increasing complexity of contaminants in wastewater, it is essential to explore unconventional approaches, advanced control techniques, that surpass traditional methods. These approaches include membrane filtration, sorption and advanced oxidation processes (AOPs). The latter processes have gained popularity over the last few decades. They are now seen not only as one of the most promising complementary treatment options, but also as a competitive alternative to conventional methods. AOPs are used both to improve the biodegradability of wastewater and to inactivate pathogenic micro-organisms [6].

One of these advanced oxidation methods is photocatalysis. There are two types of photocatalysis: homogeneous and heterogeneous [7]. In homogeneous photocatalysis, the catalyst acts in the same phase as the reactants, making separation and recycling difficult. Heterogeneous photocatalysis, on the other hand, is distinguished by using compound that is in a different phase to the reactants. Heterogeneous photocatalysts are generally nanostructured solids, offering numerous active sites and a large surface area for increased photocatalytic activity [8]. Another way to enhance the efficiency of photocatalysis is to combine it synergistically with another process, especially to degrade recalcitrant pollutants. For instance, electrophotocatalysis processes are emerging in literature, combining electrooxidation and photocatalysis to degrade organic pollutants [9].

Titanium dioxide (TiO_2) stands out as the most recognized and widely used semiconducting photocatalyst. However, this material has two main drawbacks: a fast charge recombination [10] and a wide band gap (3.2 eV for its anatase phase) requiring UV illumination for its activation [11]. Consequently, under solar irradiation, where the proportion of UV light is of the order of 3 %–5 %, the photocatalytic activity of TiO_2 decreases significantly. But to take full advantage of TiO_2 under solar irradiation, it is crucial to extend its photocatalytic activity to longer wavelengths. Likewise, improving its activity in the UV region is of paramount importance, especially for water treatment using artificial irradiation sources. To prevent these two limitations, dopings/modifications of TiO_2 have been performed [12–14]. Most studies consisted in doping/modifying TiO_2 with metallic or non-metallic ions, with photosensitive molecules or with other semiconductors [12–14]. Depending on the type of modification, the photoactivity of TiO_2 is changed following different mechanisms. With the introduction of non-metallic ions as N, P or S, usually the band gap of TiO_2 is reduced, resulting in visible absorption and activity under less energetic light [15]. With metallic ions doping, it can produce intermediate levels in the band gap resulting in an improvement of the photoactivity under UV light thanks to better charge separation but also in some studies an extension of absorption in visible region [13]. The main metallic ions used are Fe, Cu, and Ag [13,14,16]. The introduction of photosensitive molecules like porphyrins [17–19] produces an electron transfer between the visible light excited molecules and the TiO_2 , resulting in activity under visible light. The main drawback of this modification is that the photosensitive molecules are progressively degraded by TiO_2 resulting in a loss of activity with time. The coupling of TiO_2 with other semiconductors such as ZnO, ZrO_2 , SnO_2 , Ce_2O_3 [2,12,20] can be useful to produce defects, modification of the bandgap by the creation of oxygen vacancies [21] and/or heterojunctions allowing better charge separation thanks to electron or hole traps. In this study, Ta, V and Nb transition metal dopants will be explored to increase TiO_2 activity and extend its absorption in visible range. These transition metals are particularly interesting for photocatalytic applications because they can increase the ionic and electric conductivity of TiO_2 [22,23], create intermediate level in the band gap to trap photo-generated species [22–24], modify the absorption spectrum to visible range [22,25]

produce heterojunction between TiO_2 and their respective metallic oxide [26]. Currently, only few studies have focused on Ta, V and Nb doping TiO_2 for pollutant degradation with mainly degradation on dye molecules like methylene blue or methyl orange [27–29] and under energetic lights (UVC, 305 nm UV or solar light).

In addition, the introduction of these dopants could allow better activity of TiO_2 when it is used in an electrophotocatalysis process due to the electrical conductivity the dopants can bring and the stability of these dopants under current [30,31]. Indeed, Nb and Ta are n-type dopants that can increase the density of charge carriers and so a better transfer of electrons to the electrode [31–33]. The introduction of V can reduce the charge recombination by creating defects to trap the photo-generated species [30,34].

In each study about TiO_2 doping, it is necessary to mention that the ratio of dopant is always different from one study to another and one dopant to another, so an evaluation of the optimized amount of dopant must always be conducted by producing different doped TiO_2 catalysts and characterized them [12–14]. Also, in most studies about TiO_2 and doped TiO_2 , the materials require a calcination step to obtain crystalline materials (anatase phase) and the best reference TiO_2 material is the Evonik P25, an anatase and rutile phase in 80/20 proportion TiO_2 produced by an aerosol process which involves high temperature treatments (1000–1300 °C) [35].

The aim of this study is therefore to increase TiO_2 photoactivity with three different dopants poorly reference in the literature: tantalum, vanadium and niobium in different molar percentages to find the optimized amount for each dopant and evaluate their potential in photocatalytic and electrophotocatalytic degradation of organic pollutants. A low-temperature sol–gel method is developed to synthesize the doped photocatalysts with special focus on using low amounts of organic reagents. The benefit of this synthesis is to produce crystalline TiO_2 without any calcination step that is very costly. X-ray diffraction is used to identify the TiO_2 crystalline phases obtained and eventually give information about the dopants. Nitrogen sorption isotherms highlight the specific surface modifications brought about by doping. Determination of the amount of incorporated dopant is made by Inductively Coupled Plasma (ICP) and Energy Dispersive X-ray Spectroscopy (EDX). X-Ray photoelectron spectroscopy (XPS) provides information on the binding energy and oxidation states of the dopants added to the crystalline structure, and finally, Diffuse Reflectance UV–vis Spectroscopy (DRUS) provides information on the bandgap values and the modifications brought about by doping. In order to estimate the efficiency of the photocatalysts synthesized in this way, a model pollutant (p-nitrophenol) is degraded under UV–visible light for 8 h and under visible light for 24 h. This chemical is used in industry to produce pesticides, herbicides and insecticides, which can cause methemoglobinemia, and eye and skin irritation upon contact [35,36]. To determine which species is the most important in the degradation process of p-nitrophenol, scavenger experiments are conducted with the best photocatalysts for each dopant. Recycling photocatalytic experiments are also performed to assess the durability of the photoactivities of the best samples.

Moreover, the evaluation of the best photocatalysts in an electrophotocatalytic set-up is also performed, again with p-nitrophenol as model pollutant. A comparison with previous studies on Ta, V and Nb doping and with the commercial Evonik P25 photocatalyst tested in the same condition is presented at the end of the study.

2. Materials and methods

2.1. Synthesis of undoped TiO_2

The undoped TiO_2 synthesis is described in [11]. Briefly, in 250 mL of milliQ water, nitric acid (HNO_3 , 65 %, AnalaR NORMAPUR) is added to reach a pH = 1. The addition of 35 mL of Titanium tetraisopropoxide (TTiP , ≥ 97 %, Sigma-Aldrich) dissolved in 15 mL of isopropanol (ISOP, 99.5 %, Acros) is done directly under stirring. After 5 h at 80 °C under

reflux, the medium is put in the oven under air at 120 °C overnight to evaporate the solvent and a powder is obtained. This powder is washed with water then dried again 4 h at 120 °C.

2.2. Synthesis of Ta, V and Nb doped-TiO₂

The same procedure as above is followed for doping, but metal precursors are added in the TTiP-ISOP solution in different molar proportions i.e. for Tantalum between 0.1 and 5 mol.% (Tantalum(V) ethoxide, 99.8 %, Sigma-Aldrich), for vanadium from 0.1 to 16 mol.% (Vanadium(V) oxytriethoxide, 95 %, Sigma-Aldrich) and finally, for niobium from 0.1 to 10 mol.% (Niobium(V) ethoxide, 99.95 %, Sigma-Aldrich).

Seven-doping ratios are studied for Ta and V doping while 6 doped samples are made with Nb. These dopant ratios were chosen to cover a large range of doping in order to find the optimized amount for each dopant from 0.1 mol% to the highest amount introduced for each dopant resulting in stable TiO₂ colloids. This range of ratios corresponds to doping concentrations usually found for doped- TiO₂ in the literature [2,27,29,37].

Samples are denoted as TiO₂/XY where X corresponds to the dopant (either Ta, V or Nb) and Y corresponds to the real dopant amount in mol. %. The full list of synthesized samples can be found in Table 1 below with their names, their theoretical and actual dopant ratios.

2.3. Materials characterization

The actual amount of Ta, V and Nb in the doped TiO₂ samples is determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), equipped with an ICAP 6500 THERMO Scientific device, and the measurement is made in triplicate. The dosing method is described in [35].

The crystallographic properties are observed through the X-ray diffraction (XRD) patterns, recorded with a Bruker D8 Twin-Twin powder diffractometer using Cu-K α radiation. The Scherrer formula (Eq. (1)) is used to determine the size of the TiO₂ crystallites, d_{XRD} :

$$d_{XRD} = 0.9 \frac{\lambda}{B \cos(\theta)} \quad (1)$$

where d_{XRD} is the crystallite size (nm), B the peak full-width at half

Table 1
Theoretical and actual dopant ratios.

Sample	Theoretical dopant content (mol %)	Actual dopant content* (mol %)
Undoped TiO ₂	–	–
TiO ₂ /Ta _{0.08}	0.1	0.08
TiO ₂ /Ta _{0.32}	0.3	0.32
TiO ₂ /Ta _{0.64}	0.5	0.64
TiO ₂ /Ta _{0.97}	1.0	0.97
TiO ₂ /Ta _{1.6}	1.5	1.60
TiO ₂ /Ta _{3.16}	3.0	3.16
TiO ₂ /Ta _{5.25}	5.0	5.25
TiO ₂ /V _{0.12}	0.1	0.12
TiO ₂ /V _{0.24}	0.3	0.24
TiO ₂ /V _{0.47}	0.5	0.47
TiO ₂ /V _{0.94}	1.0	0.94
TiO ₂ /V _{1.41}	1.5	1.41
TiO ₂ /V _{3.23}	3.0	3.23
TiO ₂ /V ₁₆	16	16.0
TiO ₂ /Nb _{0.13}	0.1	0.13
TiO ₂ /Nb _{0.73}	1.0	0.73
TiO ₂ /Nb _{1.33}	1.5	1.33
TiO ₂ /Nb _{2.61}	3.0	2.61
TiO ₂ /Nb _{6.12}	5.0	6.12
TiO ₂ /Nb _{10.24}	10.0	10.24

* = Actual dopant amount measured by ICP-AES.

maximum after correction of the instrumental broadening (rad), λ the wavelength (nm), and θ the Bragg angle (rad).

The repartition of the crystallographic phases is estimated with the Rietveld method using Profex software [2]. The proportion of amorphous-crystalline phase is estimated with CaF₂ (calcium fluoride, Sigma-Aldrich, anhydrous powder, 99.99 % trace metal basis) internal standard methods and then processing the data with Profex software [2]. The lattice parameters are also obtained with the Rietveld refinement with Profex.

The nanoparticle sizes are observed with transmission electron microscopy (FEI TECNAI G2-20 TWIN microscope under an accelerating voltage of 160 kV). The powder sample is dispersed in ethanol using ultrasound, the suspension is then deposited as droplets on a copper grid (Formvar/Carbon 200 Mesh Cu from Agar Scientific) and dried before imaging.

The sample textural properties are characterized by nitrogen adsorption-desorption isotherms in an ASAP 2420 multi-sampler adsorption-desorption volumetric device from Micromeritics. From these isotherms, the microporous volume is calculated using the Dubinin-Radushkevich theory (V_{μ}). The surface area is evaluated using the Brunauer, Emmett, and Teller theory (S_{BET}).

Optical properties of TiO₂-based materials in the range of 250–750 nm region are obtained on a UV 3600 Plus UV-VIS-NIR spectrophotometer from Shimadzu Kyoto Japan. Measurements are performed in diffuse reflectance mode. The baseline is realized using Spectralon as a reference. The spectra are transformed using the Kubelka-Munk function to produce a signal, normalized for comparison between samples, enabling the band gaps to be calculated. The details of this treatment method are described elsewhere [11]. These measurements will provide information about the potential influence of the dopants on the light absorption spectrum.

X-ray photoelectron spectra are obtained with a SSI-X-probe (SSX-100/206) spectrometer equipped with a monochromatized micro-focused Al X-ray source (1486.6 eV), operating at 10 kV and 20 mA. Samples are placed in the analysis chamber where the residual pressure is about 10⁻⁶ Pa. The charging effect is adjusted using flood gun energy at 8 eV and a fine-meshed nickel grid placed 3 mm above the sample surface. The pass energy is 150 eV and the spot size is 1.4 mm². The angle between the normal to the sample surface and the direction of electron collection is 55°. Under these conditions, the mid-height width (FWHM) of the Au 4f7/2 peak photo-peak measured on a standard sample of cleaned gold is about 1.6 eV. The following sequence of spectra is recorded: survey spectrum, C 1s, O 1s, N 1s, Ta 4f, V 2p or Nb 3d and Ti 2p and again C 1s to check the stability of charge compensation with time and absence of degradation of the samples.

The C-(C, H) component of the carbon C 1s peak is fixed at 284.8 eV to calibrate the scale in binding energy. Three other components of the carbon peak (C-(O, N), C=O or O-C-O and O-C=O) have been resolved, notably to determine the amount of oxygen involved in the carbon contamination. Data processing is carried out with the CasaXPS program (Casa Software Ltd, UK). Some spectra are decomposed using the Gaussian and Lorentzian function product model (least squares fitting) after subtraction of a nonlinear Shirley baseline. The molar fractions are calculated using the normalized peak areas based on acquisition parameters and sensitivity factors supplied by the manufacturer. These measurements will provide information on the dopant species and their chemical environment in the doped samples.

2.4. Photocatalytic experiments

The photocatalytic properties of the materials are estimated through the degradation of a model pollutant, p-nitrophenol (PNP). For each test, the degradation percentage of PNP is calculated from triplicate experiments.

The experimental set-up is described in a previous study [35]. The PNP degradation is evaluated after 8 h under UV/visible light, thanks to

illumination by a halogen lamp with a continuous spectrum from 300 to 800 nm (300 W, 220 V) measured with a Mini-Spectrometer TM-UV/vis C10082MD from Hamamatsu. The PNP degradation under visible light is evaluated after 24 h with the same halogen lamp covered by an UV filter that removes wavelengths shorter than 395 nm. The residual concentration of PNP is measured by UV/Vis spectroscopy (GENESYS 10S UV-Vis from Thermo Scientific) at 318 nm and the mineralization is measured using a total organic carbon analyzer (TOC-L CPN from Shimadzu, Kyoto, Japan). For each tested catalyst, three flasks containing the catalytic powder are exposed to light to calculate the PNP degradation, and one is kept in the dark to evaluate PNP adsorption on the sample. One additional flask is exposed to light without catalyst to evaluate PNP natural decomposition under UV/visible or visible light only. In each flask, the initial concentrations of catalyst (if present) and PNP are equal to 1 g/L and 10^{-4} M respectively. The volume of each flask is 10 mL, and the flasks are agitated by a magnetic stirrer. These tubes are placed in a cylindrical glass reactor with the halogen lamp in the center. The reactor is maintained at constant temperature (20 °C) by a cooling system with recirculating water. The lamp is also cooled by a similar system. Aluminum foil covers the outer wall of the reactor to prevent any interaction with the room lighting. Each catalyst is tested both under UV/visible light and under visible light.

A kinetic study is performed for undoped TiO_2 , $\text{TiO}_2/\text{Ta}_{0.32}$, $\text{TiO}_2/\text{V}_{16}$ and $\text{TiO}_2/\text{Nb}_{0.73}$ samples. The kinetic equations are fully described in [38], PNP degradation can be described by the following equation:

$$C = C_0 e^{(-k \frac{m}{V_0} t)} \quad (2)$$

where C is the concentration of the pollutant, C_0 is the initial concentration of the pollutant, k is the kinetic constant, m is the mass of the catalyst, V_0 is the initial solution volume, and t is the time.

By plotting $-\ln(C/C_0)$ as a function of time t , the constant reaction rate k , can be determined [38].

2.5. Scavenger experiments

Ammonium oxalate (AO, 5 mM), isopropanol (ISOP, 5 mM), and p-benzoquinone (PB, 0.5 mM) are used as, respectively, hole, hydroxyl radical and superoxide scavenger in p-nitrophenol aqueous solution filled with undoped TiO_2 , $\text{TiO}_2/\text{Ta}_{0.32}$, $\text{TiO}_2/\text{V}_{16}$ and $\text{TiO}_2/\text{Nb}_{0.73}$ samples to reach a 1 g/L concentration, inspired by [38,39]. Measurements are performed after 8 h (under UV/visible light) or 24 h (under visible light) using a UV/visible spectrophotometer at a wavelength of 318 nm.

2.6. Recycling photocatalytic activity study

To assess the stability of the photoactivity of the TiO_2 samples, recycling experiments are done on undoped TiO_2 , $\text{TiO}_2/\text{Ta}_{0.32}$, $\text{TiO}_2/\text{V}_{16}$ and $\text{TiO}_2/\text{Nb}_{0.73}$ samples. These tests consist of doing successive photocatalytic experiments on the samples with centrifugation and washing steps in between, ultrasonic bath is used to resuspend the samples. After 24 h of the photocatalytic test described in section 2.4, the photocatalysts are recovered by centrifugation (15,000 rpm for 20 min). Then, the same test is executed again for another 24 h. This recycling is made 5 successive times, both under UV/visible light and under visible light, corresponding to 120 h of total irradiation.

The amount of metal ion released during photocatalytic experiments in aqueous medium was also measured for $\text{TiO}_2/\text{Ta}_{0.32}$, $\text{TiO}_2/\text{V}_{16}$ and $\text{TiO}_2/\text{Nb}_{0.73}$ samples during the recycling experiments. After 24 h of photocatalytic experiments under UV/visible light, the water medium is filtered with syringe filter (polypropylene, 13 mm diameter, 0.2 μm pore size, Whatman™, VWR) and the metal ion (Ti and dopant) content in the filtrate is measured by ICP-AES. This measurement was done after 1st, 2nd and 3rd photocatalytic experiments and the limit of detection is 0.01 mg/L.

2.7. Electrophotocatalytic experiments

An experimental electrophotocatalysis device was set up to complete this work. The system includes a carbon cathode, a titanium anode covered with platinum, a Plexiglas reactor with polluted water, UV light (365 nm) and a generator (see Fig. S1).

The experiment took place in two phases: first, the metal anode was used without coating; then, secondly, it was covered with different TiO_2 films. The objective of these experiments was to determine whether the TiO_2 coatings improved the degradation of p-nitrophenol compared to an uncoated anode. Fig. S1 shows the hardware used for this experimental device. The TiO_2 coatings were applied to the platinum electrode by dip-coating: three successive layers were deposited.

The solution used in the system was prepared from p-nitrophenol (to obtain a concentration of 10^{-4} M), milli-Q® water, and sodium sulfate (10^{-2} M to ensure the conductivity of the solution). For this, 13.911 mg of p-nitrophenol and 2 g of sodium sulfate were dissolved in a liter of water milli-Q®. Then the generator was set to a current of 0.1 A through the circuit, which corresponded to a voltage of approximately 7 V. Three distinct experimental conditions were set up, each for a duration of 8 h: (i) Operation under electrical current with an uncoated anode and without exposure to light; (ii) Operation under electrical current with an uncoated anode under UV illumination; (iii) Operation under electrical current with a coated anode under UV illumination. Three TiO_2 coatings were evaluated: the undoped TiO_2 and the best Ta- and Nb-doped samples selected from the photocatalytic batch experiments. A similar experiment was performed in the presence of isopropanol (ISOP, 5 mM, •OH scavenger), to assess the influence of •OH radical in the degradation process, it was done for undoped and $\text{TiO}_2/\text{Nb}_{0.73}$ samples.

3. Results and discussion

3.1. Crystallinity and texture

The crystal structure of the synthesized samples is examined by XRD. The results of the analyses, including diffractograms of the undoped sample and samples doped with tantalum ($\text{TiO}_2/\text{Ta}_{1.16}$ and $\text{TiO}_2/\text{Ta}_{5.25}$), vanadium ($\text{TiO}_2/\text{V}_{0.47}$ and $\text{TiO}_2/\text{V}_{16}$) and niobium ($\text{TiO}_2/\text{Nb}_{0.73}$ and $\text{TiO}_2/\text{Nb}_{10.24}$), are shown in Fig. 1. The overall diffraction pattern is similar for all samples, despite varying molar proportions of Ta, V or Nb to TiO_2 . This indicates that the dopant contents used do not have a significant impact on the obtained crystal structure. Comparing the positions of the peaks with reference spectra of the different crystalline phases of TiO_2 , it appears that most of the characteristic peaks correspond to the anatase phase (reference profile (A)). However, an additional peak around $2\theta = 31^\circ$ also suggests the presence of the brookite phase (reference profile (B)). No trace of rutile is observed in these samples, probably because the synthesis is carried out at a fairly low temperature. The synthesized samples are therefore biphasic.

Rietveld refinement is made with Profex software, the results are presented in Table 2. Based on the results in Table 2, it appears that the doped samples generally exhibit a higher amorphous proportion than the undoped TiO_2 sample. However, the amorphous proportion does not differ dramatically between the samples, remaining between 47 % and 60 %. Besides this, no particular trend emerges from the results. It can simply be noted that the most heavily doped samples appear to contain the highest proportion of amorphous phase. One reason for this could be the greater disruption of the TiO_2 crystal lattice at high doping levels, but to be certain, additional measurements at higher dopant concentrations should be performed.

Furthermore, impurity phases or characteristic peaks related to elemental tantalum or Ta_2O_5 is not detected in the tantalum-doped samples, suggesting that tantalum is either uniformly integrated into the TiO_2 crystal lattice as a replacement for Ti^{4+} cations or that the quantity of Ta_2O_5 is too small to be detected by XRD. The ionic radius of Ta^{5+} with octahedral coordination (0.64 Å) is slightly larger than that of

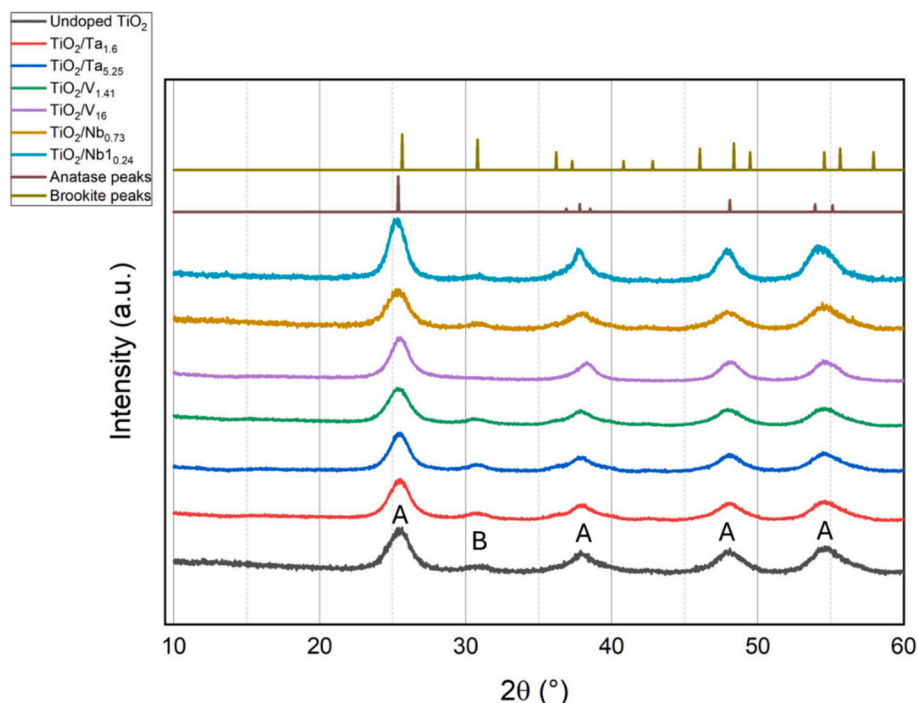


Fig. 1. Representative XRD patterns for two catalysts in each series of doped materials: undoped TiO_2 (in black), $\text{TiO}_2/\text{Ta}_{1.6}$ and $\text{TiO}_2/\text{Ta}_{5.25}$ (in red and blue), $\text{TiO}_2/\text{V}_{0.47}$ and $\text{TiO}_2/\text{V}_{16}$ (in green and purple), and $\text{TiO}_2/\text{Nb}_{0.73}$, $\text{TiO}_2/\text{Nb}_{10.24}$ (in yellow and blue), reference pattern of anatase (in brown) and reference pattern of brookite (in khaki). (A) Peaks of anatase, and (B) Peaks of brookite.

Table 2

Sample properties extracted from XRD analysis.

Sample	Phase distribution (%)	d_{XRD} (nm)	Lattice parameters anatase		Lattice parameters brookite		
			a = b (Å)	c (Å)	a (Å)	b (Å)	c (Å)
Undoped TiO_2	A[44 %] + B[9 %] + Am[47 %]	4.7	3.795	9.442	9.152	5.419	5.190
$\text{TiO}_2/\text{Ta}_{0.08}$	A[43 %] + B[8 %] + Am[49 %]	4.9	3.798	9.469	9.153	5.457	5.201
$\text{TiO}_2/\text{Ta}_{0.32}$	A[36 %] + B[7 %] + Am[57 %]	5.2	3.797	9.472	9.166	5.450	5.196
$\text{TiO}_2/\text{Ta}_{0.64}$	A[40 %] + B[7 %] + Am[53 %]	4.9	3.797	9.479	9.175	5.450	5.195
$\text{TiO}_2/\text{Ta}_{0.97}$	A[45 %] + B[7 %] + Am[48 %]	4.8	3.792	9.467	9.227	5.421	5.190
$\text{TiO}_2/\text{Ta}_{1.6}$	A[42 %] + B[8 %] + Am[50 %]	5	3.800	9.490	9.215	5.458	5.201
$\text{TiO}_2/\text{Ta}_{3.16}$	A[37 %] + B[9 %] + Am[54 %]	5.3	3.799	9.497	9.213	5.459	5.199
$\text{TiO}_2/\text{Ta}_{5.25}$	A[34 %] + B[7 %] + Am[59 %]	5.3	3.801	9.508	9.226	5.458	5.201
$\text{TiO}_2/\text{V}_{0.12}$	A[41 %] + B[7 %] + Am[52 %]	4.8	3.796	9.469	9.172	5.460	5.189
$\text{TiO}_2/\text{V}_{0.24}$	A[42 %] + B[6 %] + Am[52 %]	5	3.793	9.471	9.152	5.463	5.190
$\text{TiO}_2/\text{V}_{0.47}$	A[41 %] + B[7 %] + Am[52 %]	4.7	3.796	9.473	9.179	5.460	5.196
$\text{TiO}_2/\text{V}_{0.94}$	A[42 %] + B[6 %] + Am[52 %]	4.7	3.798	9.465	9.114	5.464	5.193
$\text{TiO}_2/\text{V}_{1.41}$	A[44 %] + B[5 %] + Am[51 %]	4.4	3.795	9.493	9.264	5.454	5.186
$\text{TiO}_2/\text{V}_{3.23}$	A[46 %] + B[3 %] + Am[51 %]	4.5	3.797	9.483	9.267	5.466	5.177
$\text{TiO}_2/\text{V}_{16}$	A[40 %] + B[0 %] + Am[60 %]	5.6	3.796	9.453	–	–	–
$\text{TiO}_2/\text{Nb}_{0.13}$	A[44 %] + B[9 %] + Am[47 %]	5.3	3.794	9.376	9.117	5.404	5.174
$\text{TiO}_2/\text{Nb}_{0.73}$	A[44 %] + B[8 %] + Am[48 %]	5.1	3.786	9.413	9.083	5.404	5.162
$\text{TiO}_2/\text{Nb}_{1.33}$	A[42 %] + B[8 %] + Am[50 %]	5.0	3.787	9.420	9.083	5.404	5.170
$\text{TiO}_2/\text{Nb}_{2.61}$	A[43 %] + B[8 %] + Am[49 %]	5.0	3.791	9.441	9.083	5.404	5.181
$\text{TiO}_2/\text{Nb}_{6.12}$	A[41 %] + B[7 %] + Am[52 %]	5.6	3.793	9.474	9.083	5.404	5.185
$\text{TiO}_2/\text{Nb}_{10.24}$	A[39 %] + B[7 %] + Am[54 %]	6.2	3.803	9.511	9.083	5.404	5.201

d_{XRD} = crystallite size estimated with the Scherrer formula, – = not present.

Ti^{4+} (0.61 Å) but is still compatible. At low concentrations, the partial replacement of Ti cations by Ta cations seems thermodynamically favorable, as reported by Ranjan *et al.* [40]. Similarly, there are no diffraction peaks associated with impurities or vanadium compounds in the vanadium-doped samples. This implies either that the V^{5+} ions are incorporated into the TiO_2 lattice, or that the V oxides crystals are very small and highly dispersed, so that they cannot be detected by the XRD technique, as suggested by Liu *et al.* [41]. Finally, the same conclusions can be drawn regarding niobium doping, with no new peak appearing following the addition of niobium, suggesting as well incorporation of Nb^{5+} in the crystal lattice or the presence of Nb_2O_5 in low quantity [42].

Moreover, the crystallite size is determined with Scherrer formula (Eq. (1)) and compiled in Table 2: all samples have similar size between 4 and 6 nm.

The lattice parameters were also estimated with the Rietveld refinement for the crystalline phase distribution, the results are depicted in Table 2. It is observed that the evolution of their values followed a trend that can be expected with their radius i.e. an increase of the lattice parameters with Ta and Nb and a decrease with V. Indeed, as mentioned before Ta and Nb have higher radius than Ti [23,29] while V as a smaller radius [25]. Therefore, the introduction of Ta or Nb to replace some Ti atoms could lead to an increase in the lattice parameters while it can be

the opposite with V. These modifications are very small and more pronounced when the doping ratio is high.

Fig. 1 shows the benefit of this synthesis that produces crystalline TiO₂ photocatalysts without calcination step usually conducted around 500 °C to obtain anatase. Calcination is a costly step in the production of TiO₂ material, developing a process which does not require it would be an advantage for industrialization.

The pore texture of the samples is determined using the BET method. The nitrogen adsorption and desorption isotherms for undoped TiO₂ sample, and those doped with tantalum, vanadium or niobium, are shown in Fig. 2. Overall, all the isotherms have a similar appearance. They appear to correspond to type IVa, characteristic of mesoporous materials (pores ∈ [2; 50] nm). Indeed, these isotherms exhibit hysteresis at p/p_0 values between 0.4 and 0.6, as well as a final saturation plateau. This observation is also made by Liu *et al.* [41]. In addition, the presence of a gentle bend, indicating a sharp increase in the volume of nitrogen adsorbed at low pressure followed by a more gradual growth to hysteresis, rules out the V-type classification for low values of p/p_0 . This relatively sharp bend suggests that the samples also have some microporosity (pores < 2 nm). This configuration of isotherm is characteristic of the results obtained with the synthesis method used, as can be seen in [35,43]. Concerning the adsorption/desorption isotherms of tantalum-doped samples, no clear trend emerges from the results (Table 3). Indeed, the variation in the values reached by the elbow and the saturation plateau seems random. In comparison, in the case of isotherms for vanadium-doped samples, the volume of nitrogen adsorbed at low p/p_0 values increases more rapidly for increasing vanadium doping rates. This trend is also reflected in the increasing values reached by the saturation plateau. Niobium-doped samples show an optimum reached for TiO₂/Nb_{1.33} with a specific surface area up to 234 m²/g, decreasing as the doping rate increases to 214 m²/g for the last sample, TiO₂/Nb_{10.24}.

TEM images of undoped TiO₂, TiO₂/Ta_{5.25}, TiO₂/V₁₆, and TiO₂/Nb_{10.24} samples at different scales are shown in Fig. 3 a, b, c, d. All the

Table 3

Physico-chemical properties of all the catalysts samples.

Sample	S_{BET} (m ² /g)	d_{TEM} (nm)	$E_{\text{g,indirect}}$ (eV)	$E_{\text{g,direct}}$ (eV)	% PNP degradation (UV/ vis 8 h – vis 24 h)
Undoped TiO ₂	186	5	2.95	3.28	26 – 22
TiO ₂ /Ta _{0.08}	224	5	3.01	3.33	32 – 18
TiO ₂ /Ta _{0.32}	191	6	3.04	3.36	39 – 32
TiO ₂ /Ta _{0.64}	211	6	3.02	3.34	25 – 37
TiO ₂ /Ta _{0.97}	219	5	2.95	3.32	28 – 30
TiO ₂ /Ta _{1.6}	232	5	3.00	3.30	29 – 37
TiO ₂ /Ta _{3.16}	196	5	2.99	3.31	33 – 18
TiO ₂ /Ta _{5.25}	211	4	2.95	3.32	34 – 36
TiO ₂ /V _{0.12}	187	6	2.61	3.22	8 – 10
TiO ₂ /V _{0.24}	200	7	2.53	3.21	5 – 5
TiO ₂ /V _{0.47}	244	5	2.45	3.20	4 – 4
TiO ₂ /V _{0.94}	249	5	2.30	3.13	4 – 3
TiO ₂ /V _{1.41}	261	5	2.16	3.05	4 – 5
TiO ₂ /V _{3.23}	274	5	1.88	3.02	7 – 3
TiO ₂ /V ₁₆	292	5	1.95	2.55	15—12
TiO ₂ /Nb _{0.13}	225	6	2.97	3.31	74 – 48
TiO ₂ /Nb _{0.73}	232	6	2.98	3.31	80 – 55
TiO ₂ /Nb _{1.33}	234	6	2.99	3.34	74 – 43
TiO ₂ /Nb _{2.61}	232	6	3.09	3.39	73 – 44
TiO ₂ /Nb _{6.12}	222	5	3.01	3.38	60 – 34
TiO ₂ /Nb _{10.24}	214	5	3.13	3.45	45–29

S_{BET} = specific surface area measured with BET method, d_{TEM} = nanoparticle size estimated by TEM; $E_{\text{g,indirect}}$ = indirect band gap calculated with the Kubelka-Monk data, $E_{\text{g,direct}}$ = direct band gap calculated with the Kubelka-Monk data.

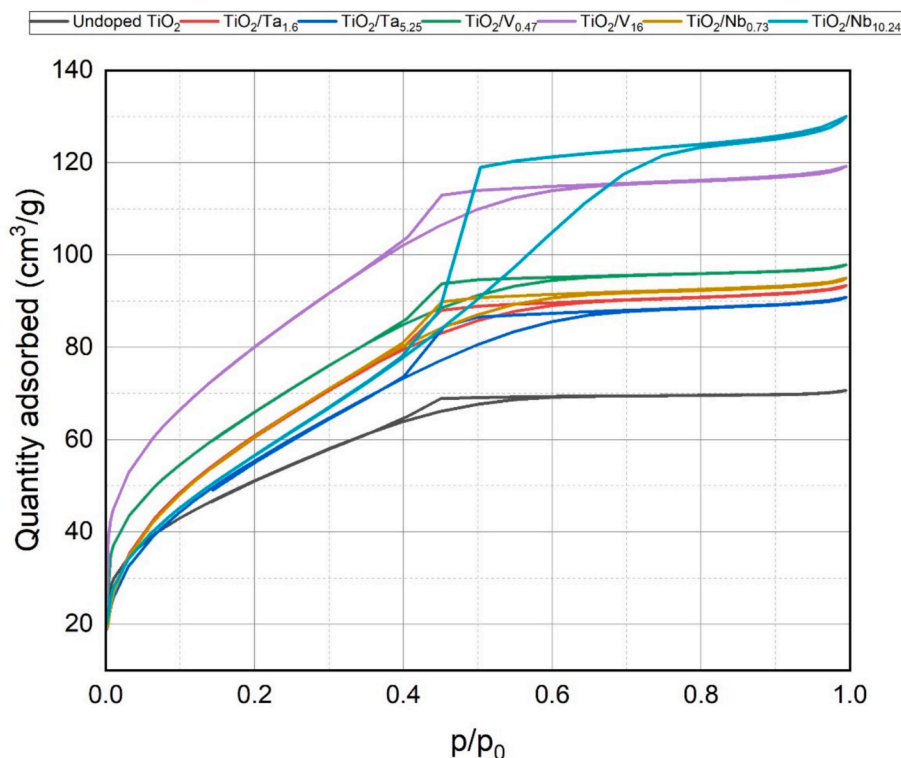


Fig. 2. Representative nitrogen adsorption-desorption isotherms: undoped TiO₂ (in black), TiO₂/Ta_{1.6} and TiO₂/Ta_{5.25} (in red and blue), TiO₂/V_{0.47} and TiO₂/V₁₆ (in green and purple) and TiO₂/Nb_{0.73} and TiO₂/Nb_{10.24} (in yellow and blue).

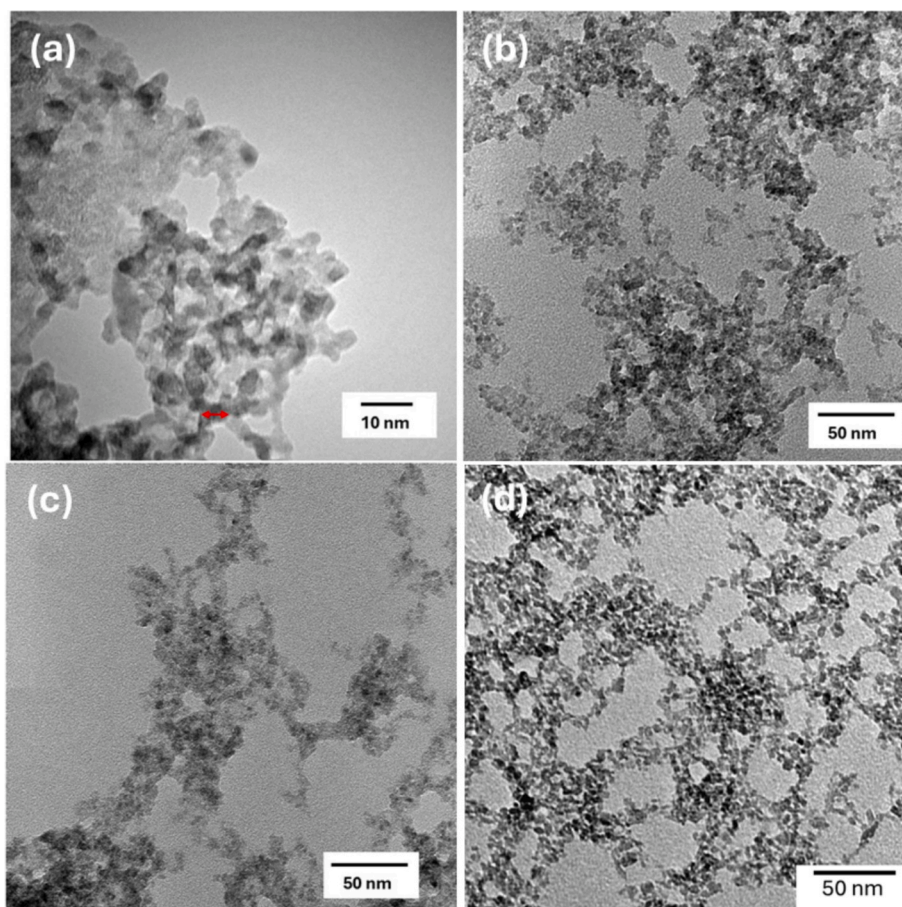


Fig. 3. TEM images of (a) undoped TiO_2 , (b) $\text{TiO}_2/\text{Ta}_{5.25}$, (c) $\text{TiO}_2/\text{V}_{16}$, and (d) $\text{TiO}_2/\text{Nb}_{10.24}$ samples.

samples show a comparable structure consisting of aggregates of TiO_2 nanoparticles that are not clearly defined in the bright-field TEM images, probably because of their low contrast. The similarity between the doped and undoped samples may reflect a good dispersion of the dopants in the TiO_2 matrix. Furthermore, although these particles are not perfectly separated, it is possible to discern shapes reminiscent of small spheres. In Fig. 3a, a double red arrow indicates the assumed diameter of a particle. By comparing this diameter with the 10 nm scale, it is estimated to be around 5 nm. The diameters of the particles making up the samples are determined in the same way and are given in Table 3. The average size of the TiO_2 particles estimated by TEM, d_{TEM} , is in the same range to that obtained by XRD for the crystallites. With this type of synthesis [2,11], it is expected to have nanoparticle size close to crystallite size.

3.2. Composition: XPS, ICP, EDX

ICP results are listed in Table 1 as indices of various dopants in the catalysts formulations. Indeed, the measured values are close to theoretical values calculated based on engaged reactants amounts.

EDX analysis confirmed the presence of the elements Ti and O as well as the elements Ta and V, represented respectively by small red and pink dots in Fig. 4 a and b, in the samples. In both figures, the dots corresponding to the dopants are evenly distributed over the surface of the samples. The samples highlighted in these figures are those containing the highest levels of tantalum and vanadium.

To obtain more data on the composition and chemical states of the elements on the surface of the photocatalysts, and to verify the effectiveness of Ta, V and Nb doping in the TiO_2 networks, an XPS analysis is carried out. The dopant composition of the samples is depicted in

Table 4 and the global quantification for all measured samples is provided in Table S1 in Supplementary Materials.

The C 1s contribution is divided into four distinct components (Fig. 5a, the deconvolution is presented in Fig. S2 for undoped TiO_2 sample). The C–(C, H) contribution at 284.8 eV is attributable to classical contamination of the aliphatic carbon (resulting from oil pollution) and is used to calibrate the measurements. The peak at 286.3 eV indicates the presence of carbon bound to oxygen or nitrogen (C–(O, N)) while the signal at around 287.8 eV is associated with the presence of carbon doubly bound to oxygen: C=O, O–C–O (some of this carbon may come from CO_2 present in the air, absorbed at the surface of the sample as mentioned by Wang T. *et al.* [44]). Finally, a peak at 288.7 eV suggests the presence of the O=C–O bond. All the samples show a similar decomposition of the C 1s envelope.

The O 1s contribution usually breaks down into three distinct peaks. The main one, at 530 eV, visible in part in Fig. 5 b, corresponds to the Ti–O bond in TiO_2 . This peak is also spotted in the XPS analyses of Cui *et al.* [45]. In each sample, the O 1s (530 eV)/Ti 2p ratio is greater than 2 (~3), indicating an amount of oxygen in excess of that required for the formation of stoichiometric TiO_2 . To explain this phenomenon, it is important to consider several factors. Firstly, excess oxygen is introduced when nitric acid is used. Secondly, it should be noted that no decomposition of the O 1s peak is performed in this study, which means that the measured value probably includes contamination. In other words, the extra proportion of oxygen present in the samples is potentially due in part to sample preparation under ambient atmospheric conditions and in the presence of nitric acid. The other two components with higher binding energies are, in general, more difficult to attribute, as they appear to be related to carbon oxygen (C–O, C=O, O–C=O) and/or nitrogen binding (N–O–Ti, N=O) due to contamination, according to

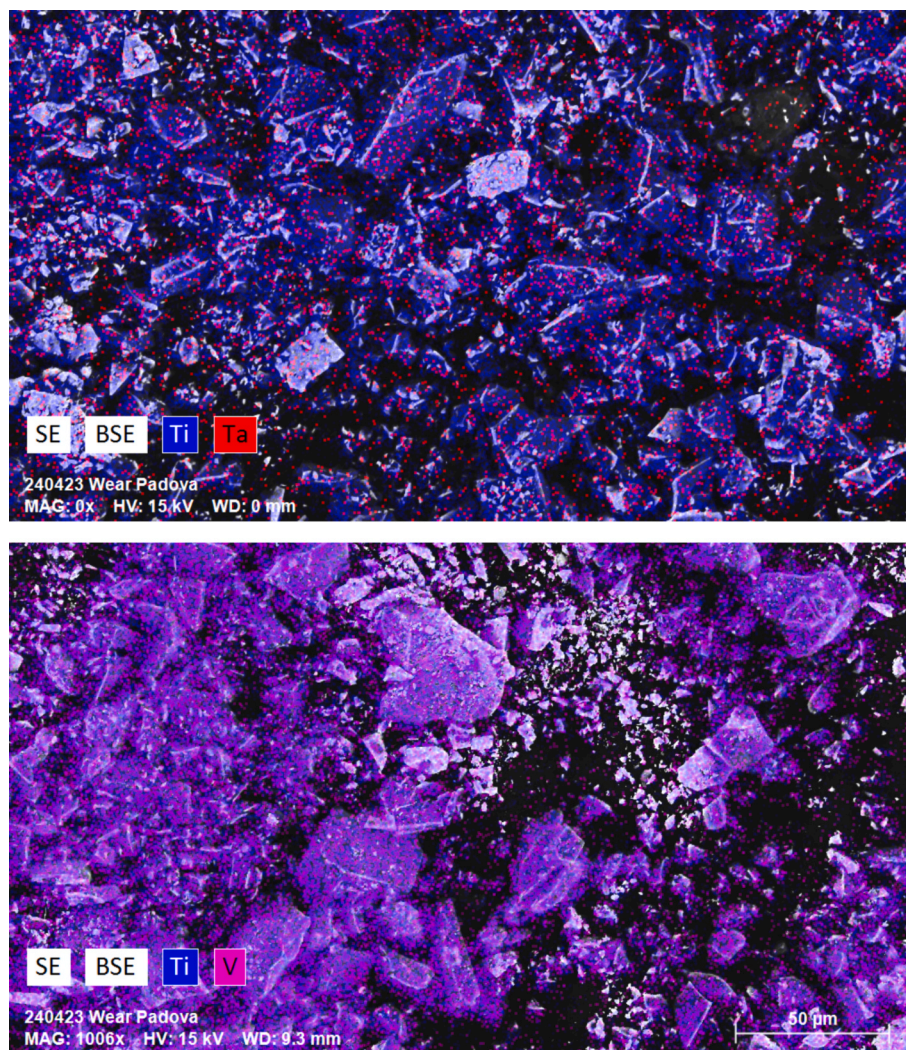


Fig. 4. EDX mapping of Ti (blue) and Ta (red) or V (pink) in $\text{TiO}_2/\text{Ta}_{5.25}$ (top) and $\text{TiO}_2/\text{V}_{16}$ (bottom) samples.

Table 4

Sample composition by ICP, XPS and EDX.

Sample	Dopant% by ICP	Dopant% by XPS	Dopant% by EDX	N% by XPS (peak at 400 eV)
Undoped TiO_2	— ^b	— ^b	— ^b	3.23
$\text{TiO}_2/\text{Ta}_{0.08}$	0.08	0.22	— ^a	3.70
$\text{TiO}_2/\text{Ta}_{0.97}$	0.97	2.08	— ^a	4.59
$\text{TiO}_2/\text{Ta}_{5.25}$	2.25	7.99	3.98	6.80
$\text{TiO}_2/\text{V}_{0.12}$	0.12	0.58	— ^a	3.09
$\text{TiO}_2/\text{V}_{0.47}$	0.47	0.65	— ^a	3.66
$\text{TiO}_2/\text{V}_{1.41}$	1.41	1.72	— ^a	3.62
$\text{TiO}_2/\text{V}_{3.23}$	3.23	2.67	— ^a	3.67
$\text{TiO}_2/\text{V}_{16}$	16.00	15.53	15.27	3.98
$\text{TiO}_2/\text{Nb}_{0.13}$	0.13	0.23	— ^a	0.92
$\text{TiO}_2/\text{Nb}_{0.73}$	0.73	1.16	— ^a	2.18
$\text{TiO}_2/\text{Nb}_{1.33}$	1.33	2.13	— ^a	1.37
$\text{TiO}_2/\text{Nb}_{2.61}$	2.61	4.16	— ^a	1.32
$\text{TiO}_2/\text{Nb}_{6.12}$	6.12	10.04	— ^a	1.23
$\text{TiO}_2/\text{Nb}_{10.24}$	10.24	16.24	— ^a	0.91

—^a = not measured, —^b = not detected.

Mahy et al. [46].

The presence of nitrogen in all samples, including undoped TiO_2 , is shown on Fig. 5 c and quantified in Table 4. The N 1s spectrum reveals a main peak centered around 400 eV, with two secondary peaks observed

near 404 and 407 eV. The latter are attributed to nitrite and nitrate residues resulting from the nitric acid used during synthesis. In the scientific literature, notably in Mahy et al. [11], the presence of an N 1s peak around 400 eV is attributed to various sources including NH_x , NO_x , NHOH groups, which are generally associated with impurities, as well as interstitial Ti–O–N sites. However, in this study, Ti–N–O substitution is excluded, given the systematic absence of the specific peak at around 395 eV. Furthermore, the absence of a peak around 455–456 eV eliminates the possibility of the presence of Ti–N species. Consequently, the low concentration of nitrogen observed in all the samples probably comes mainly from the nitric acid used during synthesis, which corresponds to low doping and may therefore lead to an enhancement of their photocatalytic activity.

In Fig. 5d, the high-resolution XPS spectrum of Ti 2p in the different samples reveals two spin–orbit coupling peaks, labelled 3/2 and 1/2. These characteristic peaks are observed at binding energies of 458.6 eV and 464.3 eV, respectively, with a separation of 5.7 eV, typical of the Ti^{4+} species in TiO_2 . These observations are also highlighted in [11,44,47]. The spectra of the different samples do not show significant differences, except perhaps for higher dopant concentrations, such as in the case of $\text{TiO}_2/\text{V}_{16}$, which shows peaks in the Ti 2p region of slightly lower intensity than in the case of the other samples.

Fig. 5 e shows the XPS spectrum of Ta, where peaks at 26.0 eV and 27.8 eV are associated with Ta 4f orbitals and attributed to a Ta^{5+} oxidation state, suggesting successful doping of Ta, potentially in the

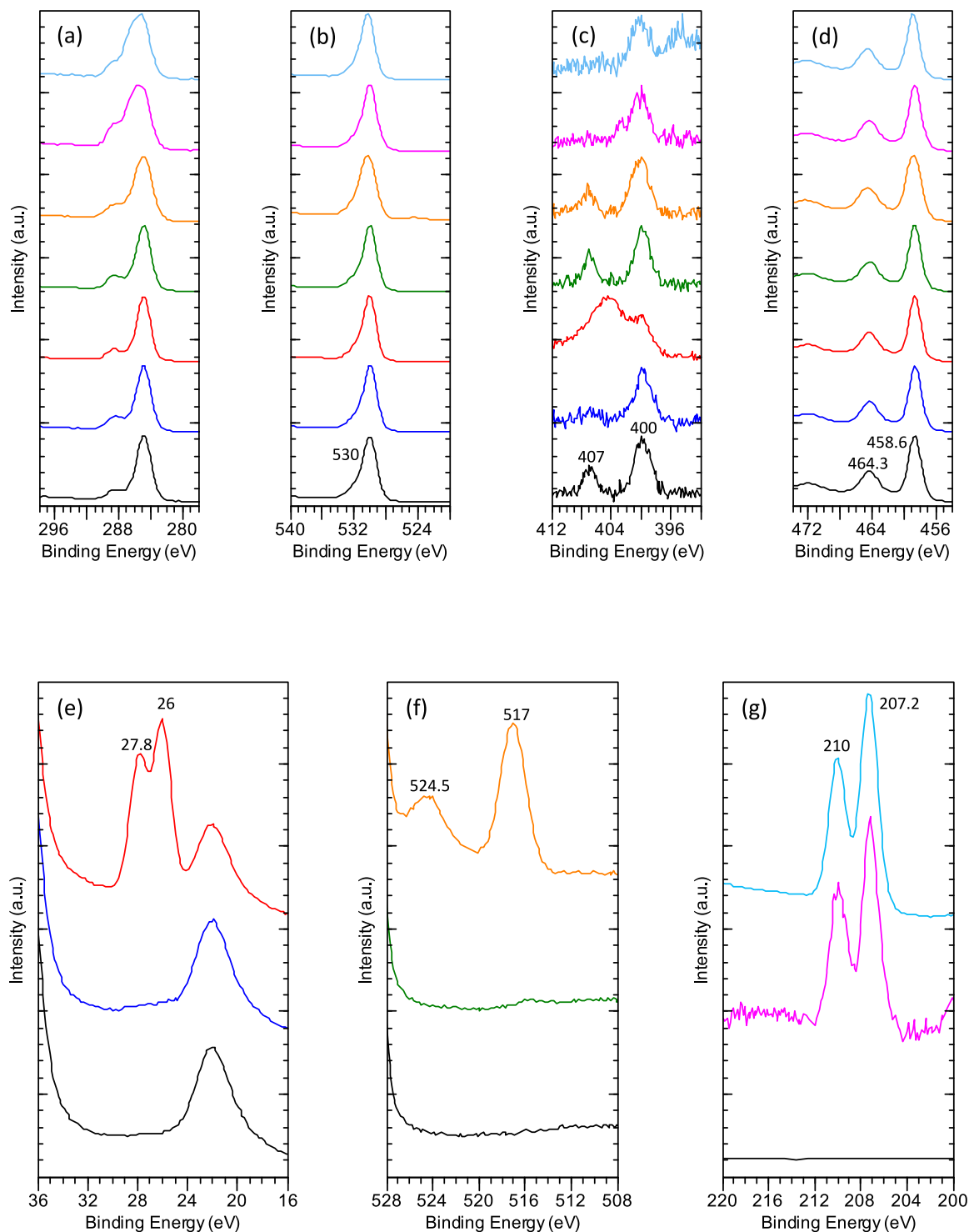


Fig. 5. XPS spectra of undoped TiO₂ (black), TiO₂/Ta_{0.08} (blue), TiO₂/Ta_{5.25} (red), TiO₂/V_{0.12} (green), TiO₂/V₁₆ (orange), TiO₂/Nb_{0.73} (purple), TiO₂/Nb_{10.24} (light blue) samples: (a) C 1s region, (b) O 1s region, (c) N 1s region, (d) Ti 2p region, (e) Ta 4f region, (f) V 2p region and (g) Nb 3d region.

form of Ta₂O₅, into TiO₂. These conclusions are based on discussions established by Cui *et al.* [45]. The binding energy of the Ta 4f photopeak remains constant among all the samples, except for its intensity, which increases with the amount of doping Ta. In the same figure, a small peak observed at around 22 eV is attributed to O 2s.

In Fig. 5 f, the existence of V 2p 3/2 and V 2p 1/2 peaks at binding energies of 517 eV and 524.5 eV, indicates the presence of V⁵⁺ ions in V-doped TiO₂, supposedly in the form of V₂O₅, as proposed by Wang *et al.* [44] and Chen *et al.* [48]. These V⁵⁺ ions, usually exhibiting a

coordination number equal to six, are quite easily substituted at Ti⁴⁺ sites in the TiO₂ lattice due to their similar ionic radii, thus forming substituted structures in vanadium-doped TiO₂.

Finally, Fig. 5g shows two peaks at the binding energies of 207.2 eV and 210 eV for niobium, the difference of 2.8 eV corresponding to the spin-orbit coupling corresponding to the total angular momentum $J = 5/2$ and $J = 3/2$ in the d sublayer of Nb. The presence of niobium in the sample is mainly in its +V oxidation state [49].

As a final remark, it should be noted that, in general, when doping

metal ions in a + V oxidation state, a partial reduction of Ti^{4+} ions to Ti^{3+} ions is anticipated. According to Cui *et al.* [45] this can result in the appearance of a slight shoulder on the low binding energy sides of the Ti^{4+} 2p 3/2 and Ti^{4+} 2p 1/2 peaks (Fig. 5d), respectively. This formation of Ti^{3+} defects could result from an excess of positive charge, inducing a charge imbalance in the crystal lattice, as a consequence of the substitution of Ti by Ta, V or Nb and/or the formation of oxygen vacancies, as indicated by Kumaravel *et al.* [50] and Shukla *et al.* (2023) [51]. Concerning substitution, the atomic radius of Ti^{3+} (0.67 Å) is slightly larger than that of Ta^{5+} and Nb^{5+} (0.64 Å) [50] and slightly smaller than that of V^{5+} (0.68 Å) [52].

The XPS quantifications also made it possible to obtain the atomic percentages of the species present on the surface of the samples and to calculate the dopant surface content in the vanadium-, tantalum- and niobium-doped TiO_2 samples, as presented in Table 4. In the majority of cases, the molar percentage determined by XPS exceeds the actual value measured by ICP-AES, with the exception of the samples $\text{TiO}_2/\text{V}_{3.23}$ and $\text{TiO}_2/\text{V}_{16}$. For the latter, the calculated percentage is slightly lower than the expected theoretical value. A comparison of the dopant contents for two samples measured both by EDX and those obtained by XPS shows that they are similar for the $\text{TiO}_2/\text{V}_{16}$ sample and that they diverge significantly for $\text{TiO}_2/\text{Ta}_{5.25}$. In fact, the XPS measurement of 7.99 % is well above the 3.98 % estimated by EDX. However, it should be kept in mind that these XPS measurements are carried out on the very surface of the samples compared to the EDX which goes deeper in the material. It can result in a surface enriched in dopant compared to the bulk.

3.3. Optical properties

The UV-visible diffuse reflectance spectra, the evolution of the normalized Kubelka-Munk function $F(R_\infty)$ as a function of wavelength (λ), are shown in Fig. 6. Increasing the tantalum concentration in the samples results in a blue shift of the absorption edges, corresponding to higher energies, compared to the undoped sample. This agrees with the

finding made by Alim *et al.* in paper [53].

Vanadium-doped samples show a red shift in the energy gap and an increase in the absorption of visible light proportional to the dopant concentration. This observation is also made in articles [41,47,54]. This shift towards higher wavelengths, and therefore lower energies, can be seen visually in the orange-brown coloration of vanadium-doped samples. A poorly defined absorption band in the 650–700 nm range is also observed in the spectra and is thought to be due to the d-d transition of the V 3d electrons, as reported by Liu *et al.* [54]. The $\text{TiO}_2/\text{V}_{16}$ sample shows the maximum red shift, reaching a wavelength around 550 nm. This suggests that vanadium doping extends the optical absorption range of TiO_2 from UV to visible light, which could potentially increase the efficiency of photocatalytic degradation. According to the analysis of Wang *et al.* [47], this phenomenon can, a priori, be explained by the replacement of Ti by V in the TiO_2 lattices, thus forming an intermediate doping energy level caused by V 3d electrons in the band gap of TiO_2 . In addition, since the radius of V is smaller than that of Ti, the distance between Ti and O is reduced, favoring the transition of photogenerated electrons from O 2p to Ti 3d. In addition, the V^{5+} ion, which has a higher positive charge and a smaller radius than the Ti^{4+} ion, exerts a polarizing effect on O.

The precise values of the direct and indirect bandgap energies determined for the selected samples are listed in Table 3. It appears that the tantalum-doped samples have slightly higher direct and indirect bandgap energies than undoped TiO_2 . This shift can possibly be attributed to the formation of oxides such as Ta_2O_5 , an inorganic compound with a higher bandgap than TiO_2 (~4 versus the 3.2 eV of anatase) [55]. This result would then be comparable to that obtained for ZrO_2 in the paper by Mahy *et al.* [2].

Conversely, the bandgap width, whether direct or indirect, decreases monotonically with increasing vanadium content. The hypothetical presence of crystalline V_2O_5 species, with a band gap of ~2 eV [44], could partly explain this result. Thus, compared to undoped TiO_2 , the visible light absorption properties of V-doped TiO_2 samples could

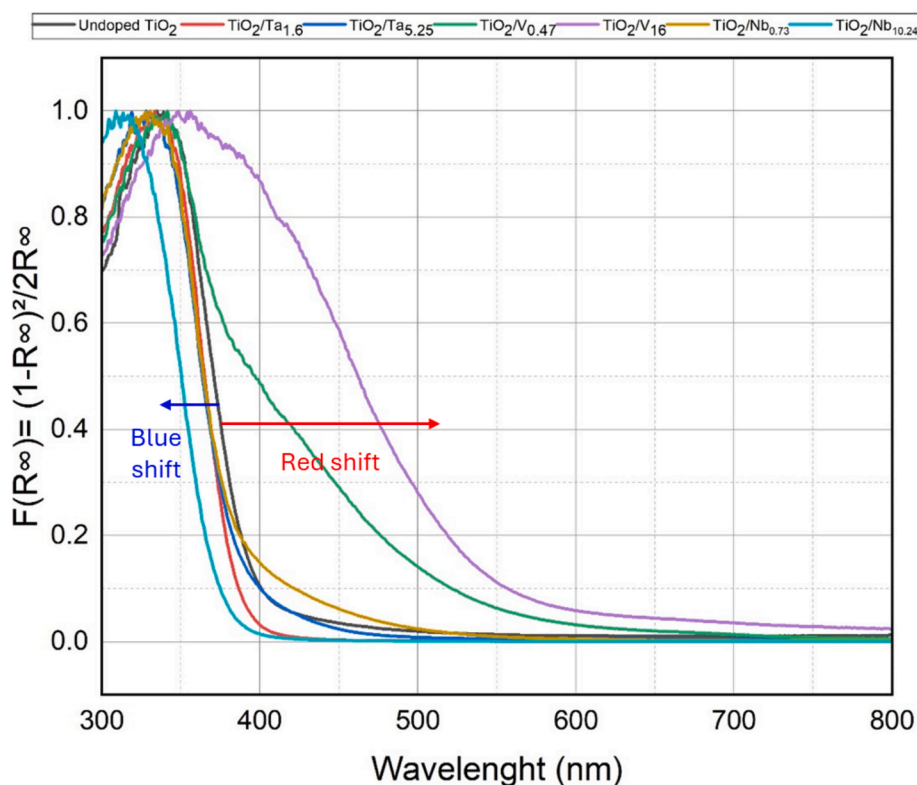


Fig. 6. Normalized Kubelka-Munk function $F(R_\infty)$ calculated from DRUS spectra for undoped TiO_2 (black), $\text{TiO}_2/\text{Ta}_{1.6}$ (red), $\text{TiO}_2/\text{Ta}_{5.25}$ (blue), $\text{TiO}_2/\text{V}_{0.47}$ (green), $\text{TiO}_2/\text{V}_{16}$ (purple), $\text{TiO}_2/\text{Nb}_{0.73}$ (light brown), and $\text{TiO}_2/\text{Nb}_{10.24}$ (light blue) samples.

theoretically be significantly improved.

The niobium-doped samples did not show much difference from the bandgap of undoped TiO_2 . This is because Nb_2O_5 has a bandgap of 3.4 eV [56], which is very close to that of TiO_2 , at 3.2 eV.

3.4. Photocatalytic results

The photocatalytic results for the degradation of PNP are presented

in Fig. 7 both under UV–visible and visible light. Fig. 7 is divided into three, corresponding to each dopant: Fig. 7a for Ta series, Fig. 7b for V series and Fig. 7c for Nb series. The kinetic study of PNP degradation under UV–visible light with undoped TiO_2 , $\text{TiO}_2/\text{Ta}_{0.32}$, $\text{TiO}_2/\text{V}_{16}$, and $\text{TiO}_2/\text{Nb}_{0.73}$ samples is represented in Fig. 8.

3.4.1. Under UV–Visible light

The results of the photocatalytic experiments under UV–visible light

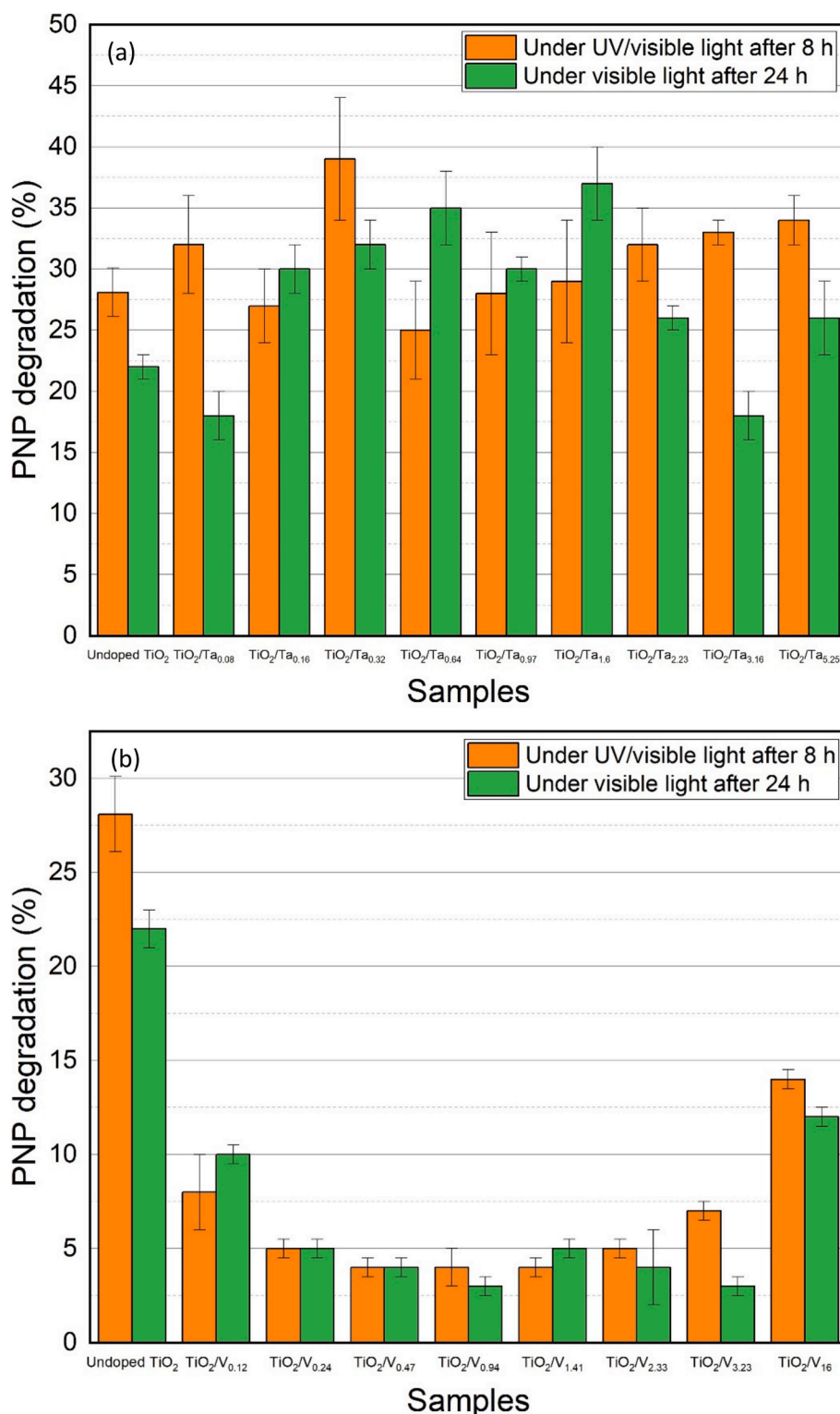


Fig. 7. PNP degradation for (a) the TiO_2/Ta doped, (b) the TiO_2/V doped and (c) the TiO_2/Nb doped samples.

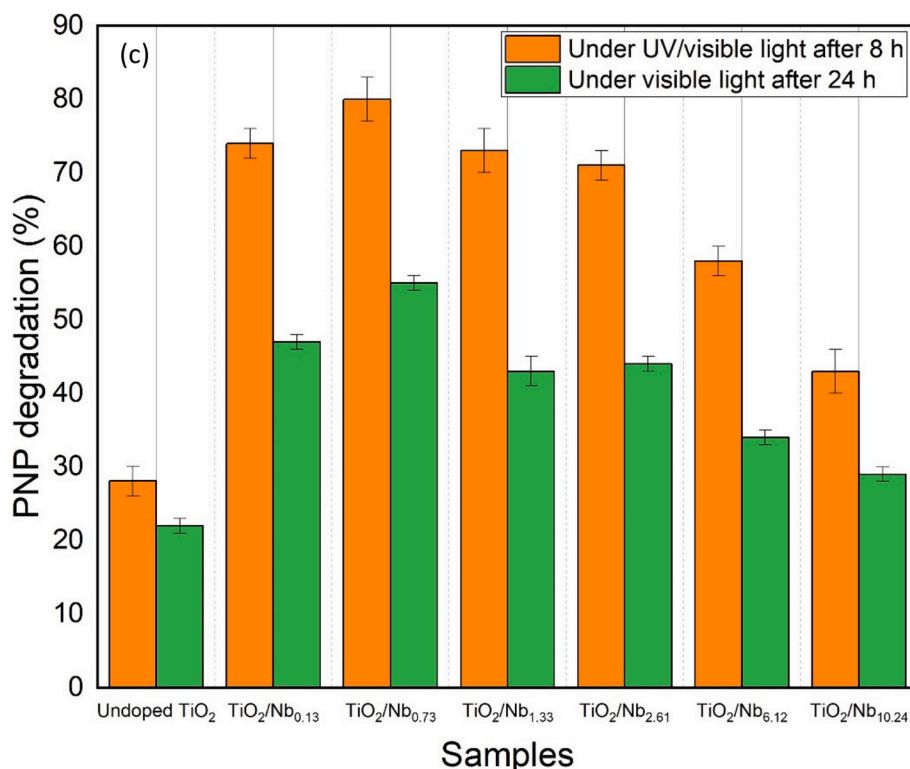


Fig. 7. (continued).

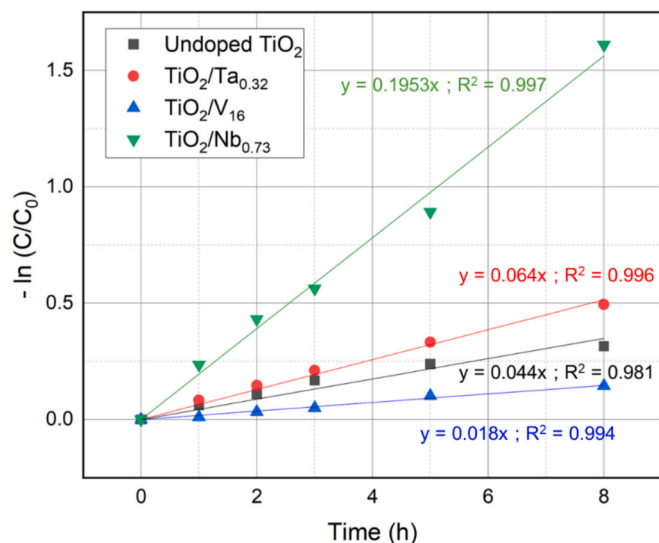


Fig. 8. Experimental determination of kinetic constant of PNP degradation under UV/visible light by sampling at 6 different times for undoped TiO₂ (black), TiO₂/Ta_{0.32} (red), TiO₂/V₁₆ (blue), and TiO₂/Nb_{0.73} (green) samples.

are represented in orange in Fig. 7. Combining the information from Table 3 and Fig. 7a (in orange), it can be seen that for the undoped TiO₂ sample, the PNP degradation rate after 8 h is 27 %. With the introduction of dopants, variations in photocatalytic behavior are observed. In Fig. 7a (orange), Ta-doped samples show overall a higher photocatalytic activity than undoped TiO₂ with the exception of the TiO₂/Ta_{0.64} sample which reaches 25 % degradation compared to 28 % for undoped TiO₂. In particular, the TiO₂/Ta_{0.32} sample stood out by achieving 38 % degradation of PNP, closely followed by TiO₂/Ta_{5.25} with 34 % degradation.

This general improvement in the photocatalytic activity of titanium

dioxide with tantalum doping has also been reported by Paul et al. [29] and Sudrajat et al. [57], particularly in the context of the degradation of pigments such as methylene blue or rhodamine B and endocrine disruptors such as bisphenol A.

On the other hand, in Fig. 7b (in orange), the UV photocatalytic activity decreases drastically with the addition of vanadium as a dopant, compared with undoped TiO₂. This finding is independent of the dopant content incorporated during synthesis. In this series of samples, the TiO₂/V₁₆ sample shows the best photocatalytic activity, degrading only 15 % of the PNP, followed by TiO₂/V_{0.12}, which contains the lowest vanadium content and whose degradation amounts to 8 %. For the other samples, the photocatalytic activity decreases as the vanadium content increases. These observations are partly consistent with the conclusions of Li et al. [54]. Indeed, in this article, it is specified that the highest photocatalytic activity is associated with very low vanadium contents and decreases with increasing vanadium concentrations. It is important to note that the vanadium contents used in the syntheses studied in these articles are sometimes even lower than those tested in this work, ranging from 0.005 to 1.5 mol.%, and thus do not cover percentages as high as 16 %. The only relevant paper reporting such high vanadium contents, by Sanchez Mendez et al. [58], presents contradictory results to those obtained for TiO₂/V₁₆ in this study. Indeed, in this article, the authors observe a quasi-extinction of photocatalytic activity for dopant contents of between 10 and 20 %, which seems, at first sight, to be more in line with the results obtained for the other samples.

Finally, the niobium-doped samples show a maximum degradation for the TiO₂/Nb_{0.73} sample, reaching an excellent 80 % degradation after 8 h exposure, followed by a gradual decrease in photocatalytic efficiency up to the highest doping percentage, showing that an optimum is reached for a low dopant concentration of 0.73 %.

Fig. 8 shows that the kinetics of PNP degradation are first order as the fitted curve of $-\ln(C/C_0)$ vs. time being a straight line for the 4 samples, as previously observed in our studies [12,38]. The kinetic constants can be calculated for each sample and are the slopes of the fitted curves in Fig. 8. The sample with the highest degradation has the highest kinetic

constant (TiO₂/Nb_{0.73} sample, with a kinetic constant of 0.1953 h⁻¹, 2.3 times greater than undoped TiO₂ sample).

3.4.2. Under visible light

The results under visible light are presented in green in Fig. 7. The experimental results of photocatalysis, presented in Fig. 7 a, b and c (in green), reveal a clear difference in degradation efficiency between UV-visible light and visible light alone, for all the samples. In fact, visible light is generally less energetic than UV-visible light, and the filter surrounding the samples also partially reduces the light intensity. This dual effect therefore leads to a reduction in the probability of transfer of photogenerated species, resulting in a proportionally smaller increase in photocatalytic activity for doped samples. Under visible light alone, PNP degradation reached 22 % with the undoped TiO₂ sample for 24 h of illumination, i.e. >50 % less degradation than under UV-visible light after 8 h.

By comparison, according to the article by Mahy et al. [11], the undoped TiO₂ sample, prepared using the same type of synthesis, degrades ~ 25 % PNP, a value similar to that obtained in this work, whereas the commercial Evonik P25 degrades only 12 % of the PNP under visible light. The activity of undoped TiO₂ under visible light probably results, in part, from the nitrogen doping of the samples obtained by synthesis with the use of nitric acid, and is thus higher than that of Evonik P25 containing no trace of nitrogen [11]. Tantalum doping also increases degradation as a function of dopant concentration. Tantalum-doped samples always show slightly higher activity than the undoped TiO₂ sample, reaching a maximum degradation of 37 %. Under visible light, the TiO₂/Ta_{1.6} sample showed the best performance in terms of PNP degradation within all tantalum doped samples. For the vanadium-doped samples, the degradation trend remains similar to that observed in the case of UV-visible illumination, but with even lower degradation percentages. It should be noted that TiO₂/V₁₆ appears to remain the most effective, achieving 12 % PNP degradation, as in the case of Evonik P25. For the niobium doped samples, as for the vanadium, the degradation trend remains similar to that observed in the case of UV-visible illumination, with the same sample (TiO₂/Nb_{0.73}) showing 55 % of degradation after 24 h, achieving the best degradation of all the dopants used in this study.

3.4.3. Doping influence on photocatalytic activity

Various parameters discussed in the previous sections, such as crystalline structure, morphology, specific surface area, micropore volume and bandgap width, are modified in the presence of dopants and can significantly influence the photocatalytic activity of the samples. Firstly, the results of the XRD analysis allow us to conclude that neither the size of the nanoparticles nor their crystalline structure have a prominent impact on the photocatalytic activity of the samples. Indeed, the samples all consist of nanoparticles of similar sizes ~5 nm. Concerning the crystalline structure, anatase is generally recognized as the most active phase for photocatalysis. However, in view of the results presented in Fig. 1, the crystalline proportions in the samples vary only slightly from one sample to another and do not seem to directly account for the better or worse performance of the photocatalysts. Secondly, a larger specific surface area and a well-developed pore structure are usually a major advantage for photocatalytic activity. The specific surface area and micropore volume of doped samples are higher than those of undoped TiO₂. However, the increase in these parameters does not seem to be directly correlated with better photocatalytic activity, since the samples with the largest specific surface area (and the largest micropore volume) are not necessarily the best performing. This observation leads to the conclusion that, although specific surface area may help to explain the increased photocatalytic activity of doped samples, it is not the determining factor responsible for the superior results obtained for certain photocatalysts. In addition, it is important to remember that, when samples are exposed to UV-visible light, TiO₂-based materials become excited, producing photogenerated electrons

(e⁻) and holes (h⁺). However, on analyzing the results, it was suggested that species such as Ta₂O₅, which have a wider band gap than undoped TiO₂, could be present in the synthesized samples. This could explain a shift in the absorbance spectrum towards shorter wavelengths. Therefore, hypothetically, some of the photogenerated h⁺ could be transferred to the valence band of Ta₂O₅. Thus, the separation between e⁻ and h⁺ would be more efficient, leading to increased photoactivity compared to undoped TiO₂, similar to the case of ZrO₂ described in the article by Mahy et al. [2]. In this work, it is assumed that the efficiency of this charge separation increases with higher theoretical Ta contents (between 2.23 % and 5.25 %), under UV-visible illumination. However, it is essential to note that the dopant concentrations used in this study remain relatively low, and that this hypothesis may no longer hold for dopant concentrations >5.25 %. Regarding vanadium doping, the results have shown that the samples exhibit a narrower energy bandgap than undoped TiO₂ (Table 3), and the hypothesis of the formation of the V₂O₅ phase has been proposed (Fig. 5). Thus, although the specific surface area is high and the narrowing of the bandgap initially improves light absorption, it appears from the work of Wang et al. [47] and Lili et al. [58], that the vanadium-doped sites and the V₂O₅ phase can act as electron traps or even as recombination centers for electron-hole pairs. This could explain the significantly lower photocatalytic activity observed compared with undoped TiO₂ under identical conditions. In fact, the recombination of e⁻ – h⁺ pairs, which is already rapid for undoped TiO₂ (only ns [59]), could be further accelerated by the intermediate levels created within the band gap. Similarly to tantalum, niobium, which appears to be the best choice for doping TiO₂ in this study for both UV-Visible and visible PNP degradation, allows better charge separation, maximizing charge lifetime. Indeed, after illumination with a wavelength >395 nm, undoped TiO₂ can form electron/hole pairs, as discussed above. The bandgap of Nb₂O₅, at 3.4 eV, is smaller than that of Ta₂O₅, but slightly larger than that of undoped TiO₂, which could lead to better electron flow between the semiconductors and therefore better charge separation leading to better PNP degradation.

3.4.4. Scavenger experiments

To have information about the species involved in PNP degradation, scavenger experiments are conducted with undoped TiO₂, TiO₂/Ta_{0.32}, TiO₂/V₁₆ and TiO₂/Nb_{0.73} samples both under UV/visible and visible light. The results are presented in Fig. 9 with/without the three scavengers, AO, ISOP and PB. For the four samples, the tendencies are similar. The addition of AO as a hole scavenger prevents water from interacting with the holes formed during illumination, resulting in a drastic reduction in the formation of hydroxyl radicals leading to a huge decrease in PNP degradation both under UV/visible and visible light (Fig. 9). The trend is very similar when ISOP is used as a hydroxyl radical scavenger, with also a huge decrease in PNP degradation both under UV/visible and visible light. This is consistent with the results obtained with AO, which inhibits the upstream production of hydroxyl radicals by interacting with the holes formed. When PB (superoxide scavenger) is used, a smaller decrease in PNP degradation is obtained, concluding that superoxide plays a lower role in PNP degradation than hydroxyl radicals. These results are consistent with our previous study [12,38] where hydroxyl radicals and holes are the most important factors for PNP degradation.

3.4.5. Recycling experiments

To assess the stability of the photoactivity of the TiO₂ materials developed in this study, recycling experiments were performed with four photocatalysts during 5 cycles of PNP degradation: undoped TiO₂, TiO₂/Ta_{0.32}, TiO₂/V₁₆ and TiO₂/Nb_{0.73} samples. The results are presented in Fig. 10.

Each sample showed its constant photoactivity both under UV/visible or visible light proving its stability with time.

The metal ion release was also measured for the 3 doped samples (TiO₂/Ta_{0.32}, TiO₂/V₁₆ and TiO₂/Nb_{0.73}), no metal ion is detected above

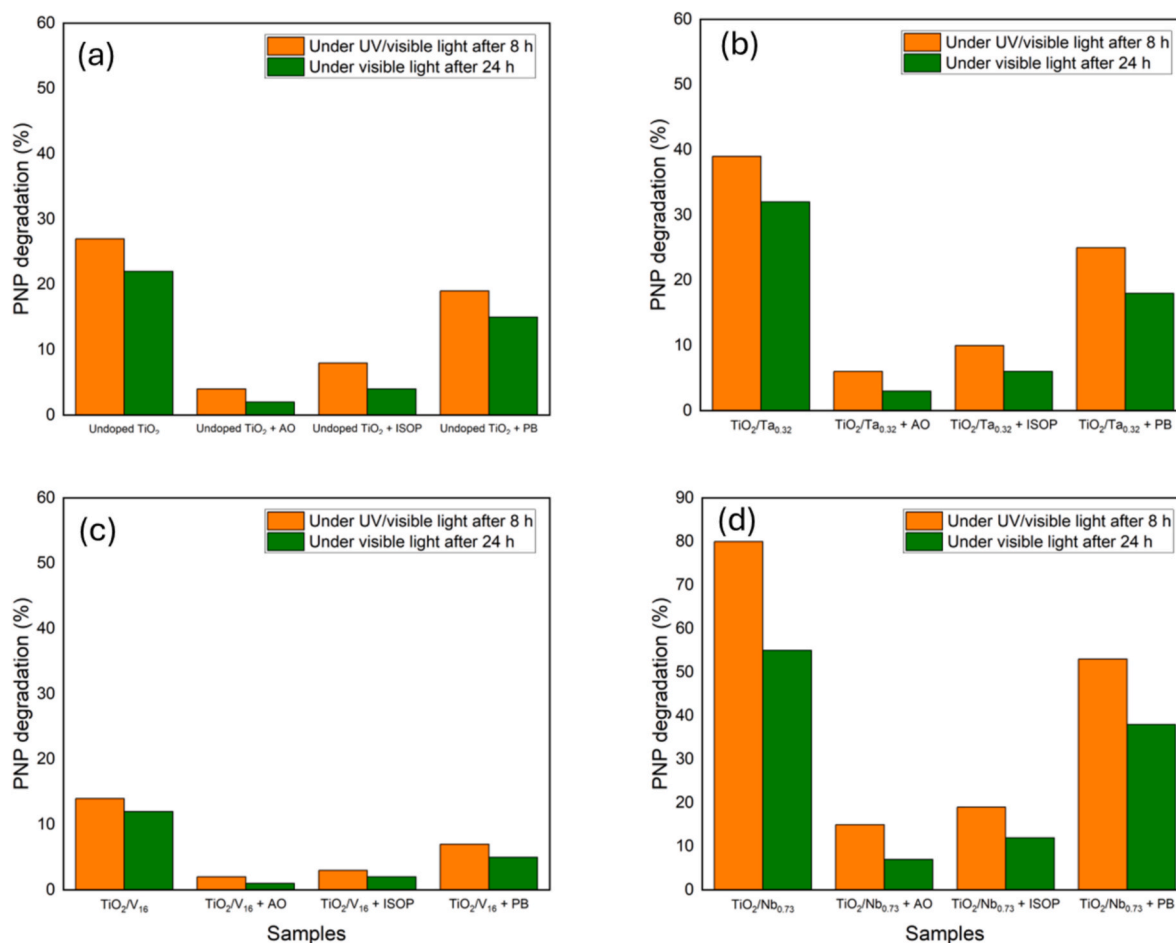


Fig. 9. PNP degradation with and without scavenger during 8 h under UV/visible light (orange) or during 24 h under visible light (green) for (a) undoped TiO₂, (b) TiO₂/Ta_{0.32}, (c) TiO₂/V₁₆, and (d) TiO₂/Nb_{0.73} samples. AO = ammonium oxalate, ISOP = isopropanol, PB = p-benzoquinone.

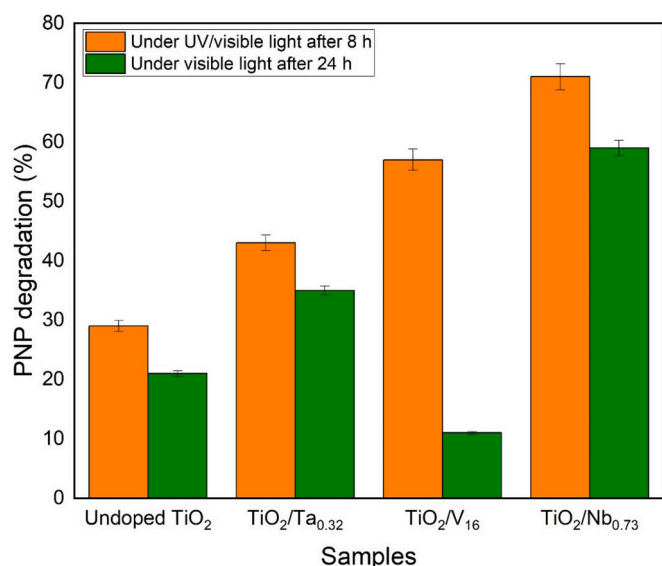


Fig. 10. Mean PNP degradation under UV/visible or visible light for 5 successive photocatalytic tests (120 h of illumination) for undoped TiO₂, TiO₂/Ta_{0.32}, TiO₂/V₁₆ and TiO₂/Nb_{0.73} samples; the mean values correspond to the mean PNP degradation values measured after 8 h of degradation in each of the 5 experiments under UV/visible (orange) or the mean PNP degradation values measured after 24 h of degradation in each of the 5 experiments under visible light (green).

the limit of detection (Table S2).

3.5. Electrophotocatalysis

To finalize this work, an electrophotocatalytic cell was set up (Fig. S1). The aim of this application was to quantitatively determine, by measuring total organic carbon, the impact of the best TiO₂ coatings on the degradation of PNP in solution compared to a system using an uncoated anode or to photocatalysis alone. Indeed, electrophotocatalytic devices are referenced in the literature as being more efficient than a simple photocatalysis or electro-oxidation process thanks to the synergy of these two processes [9]. Indeed, improving the charge separation of the photocatalyst from the movement of electrons with the current combined with electro-oxidation reactions should allow faster elimination of pollutants [9].

It should be emphasized that this experimental device as well as the operating conditions are not optimized here, and that additional research would be necessary to optimize its components, configuration and operating conditions for future developments.

The results of the different experiments are shown in Table 5: for each experiment the TOC is measured in order to have direct information on the mineralization efficiency of each condition.

It is clearly observed in this table that the value of total organic carbon decreases when a current passes through the system and becomes even lower under UV illumination, with 41 and 69 % of mineralization, respectively. The TOC value further decreases when a TiO₂ coating is present on the anode, with a most pronounced effect for the Nb-doped TiO₂ coating (94 % of mineralization). Therefore, it can be concluded

Table 5

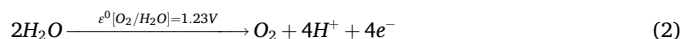
Results of the electrophotocatalytic experiments after 8 h of reaction.

Experiments	TOC (mg/L)	Degradation (%)
Initial PNP	8.37	—
PNP + current	4.96	41
PNP + current + UV	2.59	69
PNP + current + UV + undoped TiO ₂	2.31	72
PNP + current + UV + TiO ₂ /Ta _{0.32}	2.18	74
PNP + current + UV + TiO ₂ /Nb _{0.73}	0.507	94
PNP + current + UV + undoped TiO ₂ + ISOP	3.10	63
PNP + current + UV + TiO ₂ /Nb _{0.73} + ISOP	2.51	70

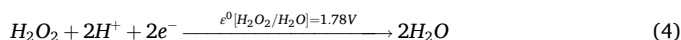
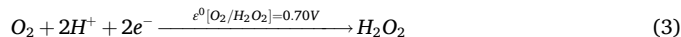
ISOP = isopropanol.

that the mineralization of the solution is enhanced in the presence of UV light and a photocatalyst film on the anode. Indeed, without UV light and photocatalyst, only electrooxidation processes occur [9], many reactions can take place, and many reactive species are produced. Among these reactions, we can cite the following ones:

At the anode, the oxidation of water is [60]:



At the cathode, the reduction of oxygen in two steps [60]:



The production of H₂O₂ (Eq. (3)), among other species, can play a role in organic pollutant (PNP in this case) degradation as it is a powerful oxidizing molecule leading in the present configuration to 41 % of PNP degradation.

When UV light is used during this process, it can help to convert H₂O₂ into hydroxyl radicals (following Eq. (5)) [61] to further enhance the PNP degradation (69 %, Table 5).



With the addition of the photocatalyst, even more hydroxyl radicals are produced. And as observed in the photocatalytic experiments (Fig. 7),

Table 6

Comparison with literature.

References	Photocatalysts (dopant amount) and thermal treatment	Pollutant (concentration)	Illumination	Photocatalyst concentration	Best results of degradation (vs. comparison with undoped TiO ₂)
This present work	TiO ₂ /Ta (0.08–5.25 mol%) TiO ₂ /V (0.12 to 16 mol%) TiO ₂ /Nb (0.13–10.24 mol%) Powder dried at 100 °C	PNP (10 ^{−4} M)	8 h (under UV–visible light, 300–800 nm) Or 24 h (under visible light, 400–800 nm)	1 g/L	Under UV, 39 % with TiO ₂ /Ta _{0.32} 15 % with TiO ₂ /V ₁₆ 80 % with TiO ₂ /Nb _{0.73} (vs. undoped TiO ₂ 26 %) Under visible, 37 % with TiO ₂ /Ta _{0.64} 12 % with TiO ₂ /V ₁₆ 55 % with TiO ₂ /Nb _{0.73} (vs. undoped TiO ₂ 22 %)
R. Doong et al. [27]	TiO ₂ /V (0.5 to 2 wt%) Powder calcined at 500 °C	Methylene blue (MB, 10 ^{−3} M)	1 h under 305 nm Or 350 min under solar light	1 g/L	Under 305 nm, 90 % for V 1 wt % sample (vs. undoped TiO ₂ 95 %) Under solar light, 69 % for V 0.5 wt% sample (vs. undoped TiO ₂ 36 %) 75 % for sample calcined at 800 °C (vs. undoped TiO ₂ not evaluated)
G. C. Falk et al. [65]	TiO ₂ /Nb Powder calcined between 500 and 800 °C resulting in TiNb ₂ O ₇	MB (20 mg/L)	150 min under UV (365 nm)	0.25 g/L	Under solar light, 75 % for V 0.15 mol% sample (vs. undoped TiO ₂ 25 %)
G. Zhao et al. [62]	TiO ₂ /V (0.05 to 0.25 mol%) Powder dried under IR lamps	Methyl orange (MO, 10 ^{−4} M)	12 days under real solar light	0.66 g/L	Under UV LED, 96 % for V 0.036 mol% sample BUT at V 0.18 mol% fell to 36 % (vs. undoped TiO ₂ 80 %)
O. Sacco et al. [63]	TiO ₂ /V (0.036 to 0.18 mol %) Powder dried at 25 °C	Caffeine (25 mg/L)	360 min under UV LED (365 nm)	3 g/L	Under UV, 88 % for Ta 3 wt% sample (vs. undoped TiO ₂ 43 %)
R. Paul et al. [29]	TiO ₂ /Ta (3–9 wt%) Powder dried at 200 °C	MB (10 ppm)	120 min under UV (365 nm)	0.6 g/L	Under visible, 76 % (vs. undoped TiO ₂ 36 %)
N. M. Safiay et al. [28]	TiO ₂ /Nb (1 mol%) Film calcined at 500 °C	MB (10 ppm)	3 h under visible light	1 film deposited on glass/25 mL	Under UVc, 45 % for Ta 2 mol% sample (vs. undoped TiO ₂ 20 %)
H. Sudrajat et al. [57]	TiO ₂ /Ta (2–4–8 mol%) Powder calcined at 390 °C	MB (10 mg/L)	2 h under UVc (254 nm)	1 g/L	Under UV, 90 % for Ta 7.5 wt% sample (vs. undoped TiO ₂ 60 %)
C. Wang et al. [64]	TiO ₂ /Ta (2.5–7.5 wt%) Powder calcined at 500 °C	PNP (25 mg/L)	1 h under UV (313 nm)	0.8 g/L	Under UV, 70 % for Nb 0.5 mol % sample (vs. undoped TiO ₂ 80 %)
M. C. Wu et al. [37]	TiO ₂ /Nb (0.25–10 mol%) Powder calcined at 600 °C	MO (10 mg/L)	4000 s under UVb Or 4000 s under visible light	0.66 g/L	Under visible, 50 % for Nb 0.5 mol% sample (vs. undoped TiO ₂ 35 %)
With commercial Evonik P25, with the condition of the present study	Undoped TiO ₂	PNP (10 ^{−4} M)	8 h (under UV–visible light, 300–800 nm) Or 24 h (under visible light, 400–800 nm)	1 g/L	Under UV, 55 % Under visible, 3 %

the photocatalyst with the highest activity ($\text{TiO}_2/\text{Nb}_{0.73}$) lead also to the highest mineralization of PNP (Table 5). A synergy between the different processes is clearly demonstrated in these experiments.

•OH radicals seem to play an important role in the PNP degradation as its degradation falls consequently when •OH scavengers are present during the experiments (Table 5).

These experiments highlight the interest in combining different processes to improve pollutant degradation efficiency, which is even more necessary for recalcitrant micropollutants such as pharmaceutical compounds or endocrine disruptors.

3.6. Comparison with literature

Table 6 summarizes results from the literature for the development of TiO_2 material doped with Ta, V or Nb compared to the present study. The commercial Evonik P25 material was also tested in the same conditions as the present study and added at the end of Table 6. Globally, it is difficult to have a direct comparison because, as observed in Table 6, many parameters differ from one study to another, such as the type of pollutant, its concentration, the lamp used for illumination, the duration of the photocatalytic experiments, the concentration of photocatalysts. Nevertheless, some conclusions can be drawn.

In the majority of the other studies, a dye is mainly used as model pollutant (usually MB or MO). These pollutants are more easily degraded than PNP. In the papers where V doping is studied [27,62,63], some improvements of the photoactivity were observed compared to our present work where this doping was not successful. Nevertheless, the doping level of their best photocatalysts was quite low compared to what was tested in the present paper, for example in O. Sacco *et al.* [63] it was 0.036 mol.%. Some authors also observed a decrease in activity with this V doping [27,63]. For the Ta doping, improvement of photoactivity was reported by some authors [29,57]. Especially, in Wang *et al.* [64], where the same model pollutant was used as us (PNP) but with very different photocatalytic conditions (lamp, concentration, duration), very similar improvement of activity was obtained with their best photocatalysts (Table 6). Indeed, by Ta doping, up to a relative 50 % of improvement was reached in both cases. Concerning Nb doping, the results of this present study were better than in [28,37,65].

To have a better comparison, the commercial Evonik P25 TiO_2 was evaluated in the same conditions as our doped photocatalysts (Table 6). The best Nb-doped sample performed better than this commercial material showing the potential of this synthesis to produce highly efficient photocatalyst both under UV and visible light. Finally, it can be added also that the synthesis process of the present study is cleaner, using water as solvent and no calcination to crystallize TiO_2 .

4. Conclusions

Several Ta, V and Nb doped titania samples were prepared by a soft sol-gel procedure. From a crystalline point of view, the syntheses resulted in relatively similar compositions, with a predominance of the anatase phase and a relatively stable amorphous proportion between 47 % and 60 %. The presence of the brookite phase was also observed, in smaller proportions, while the rutile phase was not detected. The photocatalysts synthesized consisted of TiO_2 nanoparticles of 5–6 nm. This size was determined from diffractograms of the doped and undoped samples and confirmed by transmission electron microscopy (TEM) images. In terms of textural properties, the high specific surface area of the samples, as determined by BET analysis, ranged from 182 to 292 m^2/g . The nitrogen adsorption/desorption isotherms of all the doped samples show type IVa characteristics, with a hysteresis typical of mesoporous materials, and a final saturation plateau. The presence of a kink, indicating a significant increase in the volume of nitrogen adsorbed at low pressure, also suggests the existence of some microporosity. In addition, TEM images reveal a similar morphology between doped and undoped samples, composed of aggregates of spherical TiO_2

nanoparticles. Overall, an increase in specific surface area, as well as microporosity and mesoporosity, was observed for all the doped samples compared with the undoped TiO_2 sample. ICP-AES, EDX and XPS analyses confirmed the presence of the elements Ti, O and Ta, V or Nb in the samples. In addition, the XPS spectra highlighted the incorporation of nitrogen into the TiO_2 materials due to the use of nitric acid during synthesis, constituting a form of additional doping, and suggested the formation of species such as Ta_2O_5 , V_2O_5 and Nb_2O_5 . With regard to the optical properties assessed by DRUS, the vanadium-doped samples show a reduction in their bandgap compared with the undoped sample, which is close to that of anatase (3.2 eV). By opposition, the bandgap increases slightly for tantalum-doped samples, while the niobium doped ones showed little change due to the bandgap of Nb_2O_5 3.4 eV, close to that of TiO_2 . In parallel with these characterizations, the photocatalytic activity of undoped and doped photocatalysts was evaluated through the degradation of p-nitrophenol under UV-visible light and visible light only. The results highlight the significant influence of the nature and content of the dopant on photocatalytic activity. Photoactivity tests reveal an improvement in the activity of tantalum-doped photocatalysts, while a drastic decrease is observed with vanadium doping. Samples doped with niobium show much better activity, with an almost 3-fold increase in UV-visible and visible activity. This observation can be explained by the increase in bandgap associated with niobium and tantalum doping favoring the separation of photogenerated charge carriers, whereas vanadium doping leads to the creation of intermediate levels within the TiO_2 bandgap that act as electron traps or recombination centers for 'electron-hole' pairs, resulting in a reduction in photocatalytic performance. Scavenger experiments have also shown that holes and •OH radicals are the most important species implied in the PNP degradation. Recycling experiments demonstrated the stability of the best photocatalysts during 120 h of illumination.

Finally, to complete this work, a first experimental setup was established, under non-optimized conditions, showing an improvement in the mineralization of the p-nitrophenol solution when the anode is coated with Nb-doped TiO_2 compared to an uncoated anode. This observation opens the way for future investigations aimed at optimizing components, configuration and conditions of the operating system in order to prevent, among other things, the degradation of the electrodes and the appearance of secondary reactions. These perspectives suggest the potential viability of a sustainable combined process of water pollution control, allowing in particular a satisfactory degradation of refractory organic compounds.

CRedit authorship contribution statement

Antoine Farcy: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Stéphanie D. Lambert:** Writing – review & editing, Resources, Project administration, Funding acquisition, Formal analysis. **Maxine Mathy:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Conceptualization. **Louise Lejeune:** Writing – review & editing, Investigation, Formal analysis. **Pierre Eloy:** Writing – review & editing, Investigation, Formal analysis. **Sophie Hermans:** Writing – review & editing, Investigation, Formal analysis. **Julien G. Mahy:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jphotochem.2025.116453>.

Data availability

The raw/processed data required to reproduce these findings can be shared on demand.

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