Characterization of a highly efficient N-doped TiO₂ photocatalyst prepared via factorial design†

Karen A. Borges,† Lidaine M. Santos,† Roberto M. Paniago,‡ Newton M. Barbosa Neto,§ Jenny Schneider,† Detlef W. Bahnemann,*de and Antonio Otavio T. Patrocinio*a

The preparation of titanium dioxide nanoparticles doped with nitrogen for application as a photocatalyst in the decomposition of azo dyes was optimized by factorial planning. Five variables were evaluated and the results showed that the stirring method of the reaction medium, the nitrogen source and the calcination temperature are the determining parameters that affect the photocatalytic activity. With this methodology, it was possible to obtain an optimized photocatalyst (K1) with high surface area and high mineralization efficiency (100%) of the dye Ponceau 4R under solar irradiation. K1, its non-doped version and the worst photocatalyst obtained by the factorial planning (K2) were characterized by several techniques to rationalize the different behaviors. The observed mineralization rate constants under artificial UV-A radiation were in the order of 10⁻², 10⁻¹ and 10⁻³ min⁻¹, respectively, for K1, K2 and the non-doped oxide. As shown by N₂ sorption isotherms, the powders exhibited large variations in porosity as well as in the specific surface area, with values ranging from 63.03 m² g⁻¹ for K1 to 12.82 m² g⁻¹ for K2. Infrared spectra showed that the calcination of the doped oxides between 300 and 500 °C leads to considerable loss of the nitrogen content, which is corroborated by XPS measurements that also indicate the presence of oxygen vacancies on their surfaces. Nanosecond transient absorption measurements show that the electron–hole half-lifetime in K1 is 870 ns, ca. two times longer than that observed for the other photocatalysts. Additionally, dye degradation studies under solar radiation reveal that K1 is ca. 28% faster than the non-doped TiO₂ under similar conditions. This higher photocactivity for K1 is attributed to its extended visible light absorption and the optimized morphological and electronic properties.

1. Introduction

Nanostructured titanium dioxide (TiO₂) has attracted interest in several research areas, including photoelectrochemical applications.¹⁻⁴ The photocatalytic efficiency of TiO₂ depends on its structural and morphological characteristics, which are related to the method of synthesis used in its preparation.⁵⁻⁸ Typically, the crystalline structure needs to be controlled (anatase is ascribed as the most active one) along with high specific surface area and adequate pore size to allow the diffusion and adsorption of the reacting species.⁹,¹⁰

One of the main limitations of TiO₂ is its band gap energy (3.2 eV), which limits its use under solar radiation.¹¹,¹² However, doping and other alternatives¹³⁻¹⁷ can introduce new intra-band gap electronic states in TiO₂, enabling light harvesting in the visible region.¹⁸⁻²¹ Among the different dopants typically employed, the use of nitrogen arises as a viable possibility.²²⁻²⁴ Being less electronegative than oxygen (3.0 and 3.5 eV respectively), the incorporation of nitrogen introduces electronic states above the valence band of TiO₂, causing the reduction of its band gap excitation energy.²⁵ Nitrogen doped oxides can be produced by thermal treatment under ammonia flow or by wet methodologies using different sources such as NH₄OH, NH₄Cl, thiourea or urea.²⁶⁻³¹

Although there is a considerable number of studies involving the doping of TiO₂ by nitrogen³²⁻³⁵ systematic studies on the
relation between the variables involved in the synthesis and the 
photocatalytic activity were found only in a reduced number.\textsuperscript{36-38} 
As the different parameters may interact between themselves, 
multivariate data analysis appears as a powerful tool to obtain 
highly efficient photocatalysts. Chemometrics methods have been 
largely applied in chemical analysis, spectroscopy and process 
optimization.\textsuperscript{39-41} In photocatalysis, they have been used mainly 
on the investigation of the synergetic interactions of key physico-
chemical parameters that affect the photocatalytic efficiency (pH, 
reaction times, relative concentrations etc.).\textsuperscript{42-47} Only in a few 
works in the literature, chemometrics tools have been used to 
evaluate the synthetic parameters employed in the photocatalyst 
preparation.\textsuperscript{48}

In the present study, we have used experimental factorial 
design (screening and response surface experiments) to identify 
the most important synthetic variables that affect the photo-
catalytic activity of N-doped TiO\textsubscript{2} catalysts. The photocatalytic 
activity of the synthesized materials was quantified using the 
Ponceau 4R (P4R) dye as the target compound. Different charac-
terization techniques were employed to establish direct relations-
ships between the structure and photocatalytic efficiency.

2. Materials and methods

2.1. Synthesis

TiO\textsubscript{2} powders were prepared by the precipitation method.\textsuperscript{49,50} 
Briefly, 5 mL (17 mmol) of the metal precursor, titanium(IV) 
isopropoxide (Aldrich, 97%), was dissolved in 13 mL of 
2-propanol (HPLC grade, VETEC). The resulting solution was 
kept under stirring, while 50 mL of deionized water was slowly 
dropped to yield a white precipitate using a jacketed addition 
funnel. The water temperature was controlled using a cooling 
thermocouple bath connected to the funnel. Two different stirring 
methods were employed by using a magnetic stirrer or an 
ultrasound bath (70 W, 40 Hz). The precipitate was washed 
with deionized water, centrifuged at room temperature, and 
dried at 70 °C.

Nitrogen doping was carried out by suspending the powder 
into 30% m/m urea (pH = 7) or 30% m/m NH\textsubscript{4}OH solution 
(pH = 8). The system was kept under stirring for 24 h and then 
let to rest in the dark for two days. After that, the precipitate 
was washed with deionized water, centrifuged at room temperature, 
and dried at 70 °C. The samples were submitted to a thermal 
treatment at two different temperatures (400 °C and 500 °C) for 
3 hours.

The influence of the synthesis conditions and thermal treat-
ment on the photocatalytic activity of TiO\textsubscript{2} powders was analyzed through 
a multifunctional experimental design. The defined variables, 
as well as their low and high values are summarized in Table 1. 
Such values were selected based on our previous studies and 
also on different works in the literature, in which one or more 
parameters were studied individually. The software package 
Statistica 7.0 (StatSoft, Inc. Tulsa, USA) was used to generate the 
experimental matrix, obeying a 2\textsuperscript{5-1} fractional factorial design. 
The response of interest was defined as the Ponceau 4R 
mineralization rate. After evaluation of the multivariate analysis 
results, a central composite design (CCD)\textsuperscript{36} was applied to 
analyze the relationship between the sintering temperature 
and time on the N-doped TiO\textsubscript{2} photocatalytic activity.

2.2. Methods

The samples were characterized by X-ray diffraction, using a 
Shimadzu XRD-6000 diffractometer, with a CuK\textsubscript{α} (\(λ = 1.54148 \) nm) 
monochromatic source. Crystalline silicon was used as the 
diffraction standard. The diffractograms were collected between 
19° and 90° at 0.5° min\textsuperscript{-1}. Rietveld analyses of the 
XRD data were done using the FullProf software. Fit parameters 
can be found in the ESI† (Table S1). As fitting criteria, the ratio 
between the weight factor (\(R_{\text{wp}}\)) and the expected factor (\(R_{\text{exp}}\)) 
was employed, which should be closer to 1 (\(R_{\text{wp}} = R_{\text{exp}}\)).

The specific surface area, volume and pore diameter were 
measured towards N\textsubscript{2} adsorption/desorption isotherms using the 
BET methodology\textsuperscript{31} and a Micrometrics ASAP 2020 surface 
 analyzer. Scanning transmission electron microscopy (STEM) 
was carried out using a FEI Inspect F50 microscope located 
at the Brazilian Nanotechnology National Laboratory (LNNano) 
and operated at 30 kV.

Diffuse reflectance spectra of the synthesized oxides were 
acquired at room temperature using a double beam Shimadzu 
UV-1650 spectrophotometer equipped with an integration 
sphere. Barium sulfate was used as blank. The band gap energy 
was estimated by the Kubelka–Munk function.\textsuperscript{52} FTIR spectra 
were acquired in the range between 500 and 4000 cm\textsuperscript{-1} on a 
SHIMADZU IR Prestige-21 spectrometer, using potassium 
broxide pellets with the synthesized oxides. XPS spectra were 
obtained as previously described\textsuperscript{53,54} using a VG Scientific 
ESCALAB 220 iXL surface analysis system equipped with an 
Mg/K\textsubscript{α} double anode monochromator and an electron spherical 
 analyzer. C1s peak at 284.6 eV was employed as the internal 
reference.

Transient absorption spectroscopy (TAS) was carried out 
employing a LKS80 nanosecond laser flash photolysis spectro-
 meter (Applied Photophysics) equipped with the proper diffuse 
reflectance accessory as described previously.\textsuperscript{55} The samples 
were excited in a quartz cuvette using a LPX 200 excimer laser 
from Lambda Physics (XeF; \(λ_{\text{exc}} = 351 \) nm; 14 mJ per pulse, 
illumination area of laser beam: 0.5 cm\textsuperscript{2}). The transient signals 
were collected using a PMT connected to a computer interfaced 
to a DSO9064A oscilloscope (Agilent). The transient decay was 
then recorded using the oscilloscope as the voltage changes,

| Table 1 | Experimental variables and their low and high values employed in the 2\textsuperscript{5-1} fractional factorial design |
|---------|-----------------------------------------------------------|
| Variable | Low (-1) | High (+1) |
| (1) Water temperature | 3 °C | 25 °C |
| (2) Stirring method | Ultrasound | Magnetic |
| (3) Nitrogen source | NH\textsubscript{4}OH | Urea (CH\textsubscript{3}N\textsubscript{2}O) |
| (4) Peptizing time | 1 hour | 2 hours |
| (5) Sintering temperature | 400 °C | 500 °C |
and the data points were recalculated to the final signal $\Delta J$ according to eqn (1), in which $I_o$ is the incident intensity of the analyzing light; $J_o$ is the diffuse reflected light without the laser pulse (ground light level); and $J_x$ is the diffuse reflected light with the laser pulse. It has been reported that for TiO$_2$ the $\Delta J$/value can be correlated with the transient absorption if $\Delta J$ is less than 0.3,$^{56,57}$ thus to describe the results obtained by detection of the diffuse reflected light, the term transient absorption will be referred to.

$$\Delta J = \frac{J_o/I_o - J_x/I_o}{J_o/J_0} = \frac{J_o - J_x}{J_o} \quad (1)$$

Raman spectra were acquired at room temperature using a triple-grating Jobin Yvon T64000 spectrometer, collecting the scattered light with backscattering configuration. Samples were excited at 514 nm, delivered by an argon laser and the spectrometer slits were set for a resolution of 0.6 cm$^{-1}$.

2.3. Lab-scale photodegradation tests

The photocatalytic activity of the as prepared N-doped TiO$_2$ was evaluated through degradation of the azo-dye Ponceau 4R (P4R) using UV-A radiation. A detailed description of the experimental setup can be found elsewhere.$^{58}$ Briefly, 100 mg L$^{-1}$ of the P4R dye and 100 mg L$^{-1}$ of the catalyst were exposed to solar irradiation in closed borosilicate glass vessels with an active area of 57 cm$^2$. A vessel was protected from light to be taken as a reference, with the others being irradiated. When the accumulated dose of UV-A was equal to 200 kJ m$^{-2}$, one vessel was taken for analysis and the others remained under irradiation. The UV-A radiation was monitored using a radiometer equipped with a PMA 2100 UV-A detector. The second vessel was taken after a 400 kJ m$^{-2}$ UV-A dose and, finally, the last one at 600 kJ m$^{-2}$. The discoloration and the mineralization rates were probed, respectively, by spectrophotometry and DOC analyses. During the irradiation time, the temperature of the vessels varied from 25 to 35 °C. All photocatalysts were tested simultaneously, allowing direct comparisons on their respective photoactivities.

3. Results and discussion

3.1. Experimental factorial design applied to the preparation of N-TiO$_2$

The mineralization of P4R solutions, expressed as percentages of dissolved organic carbon ($100 \times \frac{DOC}{DOC_0}$), after 140 minutes under artificial UV-A irradiation in the presence of different N-doped TiO$_2$ photocatalysts and the corresponding preparation conditions selected in the multivariate design are presented in Table 2. In the ESI,$^\dagger$ it can be found that the DOC decays as a function of irradiation time for the catalysts studied, as well as for the direct photolysis of dye solution in the absence of a photocatalyst. The percentages of mineralization mediated by the photocatalysts synthesized in this work are systematically higher than that obtained by direct photolysis, when only

| Catalyst | Water temperature | Stirring method | Doping source | Peptization time | Sintering temperature | Mineralization (±2%) |
|----------|------------------|----------------|---------------|-----------------|-----------------------|---------------------|
| 1        | −1               | −1             | −1            | −1              | +1                    | 28.93               |
| 2        | +1               | −1             | −1            | −1              | −1                    | 33.13               |
| 3        | −1               | +1             | −1            | −1              | −1                    | 53.00               |
| 4        | +1               | +1             | −1            | −1              | +1                    | 45.00               |
| 5        | −1               | −1             | +1            | −1              | −1                    | 29.13               |
| 6        | +1               | −1             | +1            | −1              | +1                    | 19.30               |
| 7        | −1               | +1             | +1            | −1              | +1                    | 24.15               |
| 8        | +1               | +1             | +1            | −1              | −1                    | 41.77               |
| 9        | −1               | −1             | −1            | +1              | −1                    | 41.83               |
| 10       | +1               | −1             | −1            | +1              | +1                    | 19.30               |
| 11       | −1               | +1             | −1            | −1              | +1                    | 40.73               |
| 12       | +1               | −1             | −1            | +1              | −1                    | 56.23               |
| 13       | −1               | −1             | +1            | +1              | −1                    | 15.13               |
| 14       | +1               | −1             | +1            | +1              | +1                    | 18.23               |
| 15       | −1               | +1             | +1            | +1              | −1                    | 43.33               |
| 16       | +1               | +1             | +1            | +1              | +1                    | 27.73               |
12.70% of mineralization was achieved after 140 minutes of irradiation.

From the Pareto’s chart, obtained by the analysis of the multivariate data, Fig. 1, it is possible to evaluate the influence of each variable and determine the best conditions of synthesis for obtaining an optimized N-doped TiO\textsubscript{2} photocatalyst.

The analysis reveals that the stirring method (2), nitrogen source (3) and sintering temperature (5) exert significant influence on the photocatalytic efficiency of the N-doped TiO\textsubscript{2} samples. The stirring method (2) has a positive correlation with the dye mineralization, which means that the photocatalytic process is favored when this variable is selected to be of high level. On the other hand, the variables (3) and (5) have a negative effect on mineralization. Therefore, the photocatalytic activity is favored if they are selected to be of low level. The variables water temperature (1) and peptizing time (4) by themselves have little influence on mineralization.

The multivariate analysis allows estimating the influence of the interaction between two variables on the efficiency of the photocatalytic process. It can be observed that the interactions between the variables 1 and 2 (1:2) and 1 and 5 (1:5) are significant and positive. It means that such variables when kept at a high level favor dye degradation. The interaction between variables 1 and 4 (1:4) is significant, but the result is negative for mineralization. The inversion of the level for one of these variables tends to cause a positive response. Variable 4 (peptizing time) was chosen to be inverted since it is less significant by itself. Then, it was set to the high level. Therefore, the best conditions for the preparation of N-doped TiO\textsubscript{2} powders with high photocatalytic activity are summarized in Table 3.

Photodegradation tests employing a catalyst prepared under the conditions shown in Table 3 resulted in (53 ± 2)% mineralization of the organic dye. This result is experimentally similar to that observed for the catalysts #12 and 3 (Table 2). So far, these results corroborate the conclusion taken from the multivariate analysis, since the difference in the preparation between the best catalyst defined by the statistical methodology and the catalysts #3 and #12 is related to the variables 1 and 4, which have a small influence on the photoresponse. The statistical method indicates what is physically expected: with lower water temperatures, a longer peptizing time is required and should yield more homogeneous and smaller particles, leading to improvements in the photocatalytic activity.

Additionally to the multivariate analysis, the central composite design (CCD) method was employed to identify the best conditions (temperature and time) for the thermal treatment of N-doped TiO\textsubscript{2} catalysts. For this, the other variables (1 to 4) have been maintained as shown in Table 3. The estimated ranges for temperature and time were, respectively, 300–450 °C and 3–5 hours, based on the results of the $2^{5-1}$ fractional factorial design. The fit of the mineralization efficiency as a function of sintering temperature and time resulting in the response surface is shown in Fig. 2 (experimental data can be seen in Table S2, ESI†).

The CCD data allowed determining the optimum sintering temperature and time regarding P4R degradation by N-doped TiO\textsubscript{2}, which are, respectively, 333 °C and 4.2 hours. Nevertheless, it can be concluded from the surface response that catalysts treated at 330–400 °C for 4–5 hours should exhibit higher photocatalytic activities.

### 3.2. Morphological and electronic characterization of the as-prepared N-TiO\textsubscript{2} photocatalysts

Different characterization techniques were employed on the as-prepared catalysts in order to correlate their photocatalytic activity.
activity and preparation conditions with the morphological, structural and electronic properties. As a matter of comparison, the catalysts named as K1 and K2 were selected from the multivariate analysis, since the former exhibits the best mineralization of P4R (64%), while K2 furnished poor photocatalytic activity (~8%). In Table 4, the preparation conditions of K1 and K2 are presented, along with their respective photocatalytic performances. To clearly show the role of nitrogen as a modifier, a TiO2 sample was obtained under the same conditions of K1, but without the addition of NH4OH to the reaction medium. The apparent rate constants were determined following the Langmuir–Hinshelwood kinetics model.59

Firstly, N2 adsorption/desorption isotherms were obtained in order to determine the specific surface area and other surface parameters, accordingly to the B. J. H. methodology,51 Table 4. The isotherms of K1, K2 and also that for the bare TiO2 can be classified as type IV according to IUPAC,60 which is typical for mesoporous materials (the N2 sorption isotherms as well as the pore size distribution curves can be found in Fig. S3 of the ESI†). The specific surface area of K1 is about five times higher than the one of K2, while its pore volume is 75% larger. The results indicate that, in K1, there are more available adsorption sites outside the pore walls, which can be related to the presence of less aggregated particles. Looking at the preparation conditions, Table 4, the higher surface area of K1 should be a consequence of the smaller sintering temperature, which avoids the particle necking. This behavior can be seen in the STEM images of K1 and K2, Fig. 3. Additionally, the different shapes of the hysteresis in N2 adsorption/desorption isotherms obtained for K1 and K2 indicate distinct surface textures (pore size, geometry, connectivity etc.). The better morphological parameters of K1 favor the adsorption of P4R and water molecules and should yield a higher density of active sites.61

It is noteworthy to observe that the surface area of a TiO2 powder prepared under the same conditions of K1 but without the addition of NH4OH exhibits higher surface area. This is likely due to the catalytic effect of OH− ions on the hydrolysis of the Ti4+ precursor that leads to a higher particle growth. Nevertheless, as shown in Table 4, the higher surface area of bare TiO2 does not lead to a higher P4R mineralization. Interestingly, two distinct dye degradation rate constants are observed in the presence of the K1 photocatalyst, Fig. 4. At longer times, the rate constants tend to increase, mainly for $k_{\text{miner}}$, which can be related to the increase in the concentration of reactive oxygen species (ROS) produced by the excited photocatalyst as the reaction takes place, since the concentration of the organic species is continuously decreasing.62

The results are suggestive of the positive effect of doping with nitrogen on the photocatalytic activity. Neither the discoloration nor the mineralization efficiencies achieved using the bare TiO2 reach the values obtained using K1. The best results for discoloration and mineralization achieved by the bare TiO2 correspond, respectively, to 76% and 45% of the results reached using K1. On the other hand, the mineralization achieved by the catalyst K2 corresponds to about 12% of that reached using K1.

The K1 photocatalyst was also more effective under solar irradiation than the non-doped TiO2. 15 mg L$^{-1}$ of the P4R dye solutions were exposed to solar radiation in the presence of 100 mg L$^{-1}$ of K1 and the bare TiO2 photocatalysts. The discoloration and mineralization efficiencies were measured

| Variable                        | Processing conditions | TiO2 |
|---------------------------------|-----------------------|------|
| Water temperature (1)           | 3 °C                  | 3 °C |
| Stirring (2)                    | Magnetic              | Urea |
| Doping (3)                      | NH4OH                 | Urea |
| Sintering temperature (4)       | 2 h                   | 2 h  |
| Reaction time (5)               | 4.2 h                 | 3.0 h|
| Specific surface area (m2 g$^{-1}$) | 63.03                | 12.82|
| Total pore volume (cm3 g$^{-1}$) | 0.14                  | 0.08 |
| Average pore size (nm)          | 6.45                  | 19.4 |
| Discoloration (%)               | 100                   | 68   |
| $k_{\text{disc}}$ (min$^{-1}$)  | $2.2 \times 10^{-2}$  | 7.6 \times 10^{-3}$ |
| Mineralization (%)              | 64                    | 8    |
| $k_{\text{miner}}$ (min$^{-1}$) | $4.5 \times 10^{-3}$  | 29   |

It was not possible to accurately determine $k_{\text{miner}}$ for K2 due to the low mineralization observed and the high dispersion of the experimental values.

![Fig. 4](image-url) Kinetics of discoloration (A) and mineralization (B) of a P4R solution in the presence of 100 mg L$^{-1}$ of bare TiO2 (●), K1 (●) and K2 (●).
as a function of the cumulative UV-A dose. After a 200 kJ m\(^{-2}\) UV-A dose in the presence of K1, the total discoloration of the dye solution was observed, while complete mineralization of the organic matter is observed after 600 kJ m\(^{-2}\). Using the bare TiO\(_2\), complete discoloration is observed only after 600 kJ m\(^{-2}\) of UV-A radiation, corresponding to 78% mineralization efficiency.

X-ray diffraction patterns of the three catalysts are presented in Fig. 5. For all samples the diffraction peaks can be indexed according to the anatase polymorph (JCPDS 89-4921). A small peak at 30 °C observed for the bare TiO\(_2\) can be associated with the brookite metastable TiO\(_2\) phase (JCPDS 89-4921). Rietveld analyses of the XRD data (Fig. S4 and Table S3, ESI\(^{†}\)) allow estimating the amount of brookite as ca. 17%. In relation to the bare TiO\(_2\), the lattice parameters of K1 do not vary significantly. Just a small reduction in the anatase cell volume is observed. In relation to K2, the K1 photocatalyst exhibits broader diffraction peaks, which is indicative of poorer crystallinity and smaller particle size. This behavior was expected since the sintering temperature of K1 was lower than that applied for K2. The crystallite size estimated by the Scherrer equation was 14, 23 and 8 nm, respectively, for K1, K2, and bare TiO\(_2\).

Raman spectroscopy was employed to evaluate the structural disorder of the different oxides prepared, Fig. 6. At first view, it is observed that all investigated samples present the well-known Raman bands for anatase TiO\(_2\) nanoparticles.\(^{63}\) The more intense E\(_g\) mode is located at 144 cm\(^{-1}\), and the other three B\(_{1g}\), A\(_{1g}\) and E\(_g\) modes are located at 398, 517 and 640 cm\(^{-1}\), respectively. A small peak is also observed at around 200 cm\(^{-1}\) and it is assigned to the other E\(_g\) frequency mode.

It is noticeable, from the inset of Fig. 6(a), that K1 exhibits a significant reduction of the width for the more intense band in relation to the bare oxide prepared under the same conditions. Such a narrowing is not expected for a doped sample, in which a higher disorder degree is presumed. However, it is clear from XRD data that the bare oxide contains ~17% of brookite content. Brookite TiO\(_2\) exhibits an intense Raman peak at 152 cm\(^{-1}\),\(^{64}\) which can be deconvoluted to the anatase peak at 144 cm\(^{-1}\) for the bare TiO\(_2\) sample by using Lorentzian curves, Fig. 6(b). Thus, it is not possible to obtain further information about the influence of nitrogen on the oxide structure from the Raman data since the peak widths of the samples are influenced by the presence of a second phase in the bare oxide. Nevertheless, the absence of large shifts between the samples indicates that the nitrogen probably is being adsorbed at the surface of the TiO\(_2\) structure.

XPS spectroscopy was employed to provide experimental evidence of the chemical states of nitrogen in the samples. XPS data of the K1 photocatalyst reveal the presence of only titanium, oxygen and nitrogen in the surface along with traces of carbon (as typically observed for samples that had contact with air). The high resolution XPS spectra of the K1 photocatalyst before and after the sintering step in the respective N1s, Ti2p and O1s peak regions are shown in Fig. 7.

Before the sintering step at 330 °C, one can observe a broad peak at the N1s region, which can be deconvoluted into two peaks centered at 398.2 and 401.2 eV. Previous XPS studies on N-doped TiO\(_2\) have identified different chemical states for the nitrogen species on TiO\(_2\). N1s peaks with binding energies between 396 and 397 eV are correlated with substitutional nitrogen on oxygen sites, i.e. nitride species (Ti–N).\(^{19,31,65}\).

![X-ray diffraction patterns of TiO\(_2\) (---), K1 (---) and K2 (---). * indicates the presence of brookite in the bare TiO\(_2\).](image)

![Raman spectra, at room temperature, for K1 (black line), K2 (blue line) and bare TiO\(_2\) (red line) and (b) theoretical fitting (red line), employing Lorentzian curves (blue lines), of experimental data obtained for the bare TiO\(_2\) (open circles). The inset of (a) shows a zoom of the spectral region between 100 and 240 cm\(^{-1}\).](image)
On the other hand, peaks in the range of 398–401 eV are related to NO and NH species adsorbed on the TiO₂ surface. Based on the preparation method employed for K₁, the N₁s peaks observed before sintering can be associated mainly with NH₃ species adsorbed on the oxide surface. Additional experimental evidence for this conclusion is taken from FTIR spectra (Fig. S5, ESI†), whereas typical N–H stretching modes at 3186 and 1396 cm⁻¹ are observed. The N₁s XPS peak at higher energies (401.2 eV) can be attributed to NH₄⁺ cations adsorbed to Ti–O⁻ bonds. This attribution is corroborated by the high resolution spectrum in the O₁s region, Fig. 7. The peak at 532.5 eV is shifted in relation to typical Ti–OH signals at 531.5 eV (seen in the spectrum of the sintered sample) and is related to Ti–O–N bonds. The main peak at 530.4 eV is due to lattice oxygen (Ti–O–Ti) in the anatase nanocrystals.

The second N₁s peak at 398.2 eV can possibly be related to NH₃ molecules coordinated to Ti⁴⁺ ions in the surface of the oxide to yield O–Ti–N bonds. The K₁ photocatalyst is prepared at pH = 8, in which ca. 10% of NH₃ remains non-ionized. Thus, they can act as Lewis bases and coordinate to the Ti⁴⁺ ions in the oxide surface. The high resolution XPS spectrum in Ti₂p confirms such assignment. One can observe two components in each peak of the Ti₂p doublet. Taking Ti₂P₃/2, a main peak can be seen at 458.8 eV, characteristic of Ti⁴⁺ ions in anatase, with a shoulder at 457.1 eV, which is related to electron-richer titanium centers (Ti³⁺). During the preparation of K₁, it is not reasonable to expect the reduction of Ti⁴⁺ ions, and so, this lower energy 2P₃/2 peak is likely related to Ti³⁺ ions coordinated to NH₃, which acts as a sigma donor. This change in the electronic environment of some Ti³⁺ ions should also be responsible for a third well-resolved O₁s peak at 528.4 eV. After the thermal treatment at 330 °C in air, N₁s signals could not be detected, showing that most of the adsorbed species are removed, probably as gaseous NO or NO₂. Thus, from XPS, it can be concluded that less than 2% of the oxide surface is composed of nitrogen species. This low incorporation of nitrogen in the sample agrees with the literature in which the reported nitrogen content in the N-doped TiO₂ varies vastly from 0.08 to 8%. Low concentrations of nitrogen have been generally observed to be all interstitial, which is the case in K₁. Concomitantly to the disappearance of the N₁s signal, the additional peaks initially observed in the Ti₂p and O₁s regions also vanish, confirming the previous assignments. In the Ti₂p doublet region, a small contribution (~10%) of a higher energy component is identified and can possibly be related to non-stoichiometric TiOₓ species (x < 2).

Although XPS data show that most nitrogen species are removed after sintering, different techniques provide clear evidence about its effect on the electronic properties of a TiO₂ matrix. In the diffuse reflectance spectra of K₁, K₂ and bare TiO₂, Fig. 8, one can observe that K₁ exhibits an additional absorption band in the 390–500 nm region. In fact, K₁ is a yellow powder, different from the typical white TiO₂ (Fig. 8, inset). This new absorption feature leads to an improvement in the light-harvesting efficiency and, consequently, in the production of reactive oxygen species, responsible for dye degradation. The K₁ spectrum resembles the one calculated for TiO₂–Nₓ by Asahi and co-workers. The new absorption feature in the visible region is attributed to the creation of intermediate electronic levels between the valence and conduction bands of TiO₂ as a result of the interaction between the 2p states of nitrogen and oxygen and also due to the creation of oxygen vacancies during the sintering step that is favored in the presence of nitrogen species.
The presence of intra-band gap states in the form of oxygen vacancies below the conduction band or N 2p localized states slightly above the valence band edge changes the electron–hole dynamics in K1 in relation to the bare TiO2, as can be inferred from ns-transient absorption measurements. In Fig. 9(a–c), the transient absorption spectra of both photocatalysts at different time-delays as well as data for K2 are shown. The samples exhibit similar transient absorption features with a band at 380–500 nm and a broad band between 500 and 700 nm. In a previous work, we have intensively discussed the origin of these features as a sum of transient absorption signatures that originated from trapped holes and electrons. The trapped electron absorption occurs between 400 and 650 nm, while below 400 nm the transient absorption spectra seem to be dominated by the trapped holes.

The transient absorption intensities between 450 and 600 nm for the bare oxide and for K2 are higher than those observed for K1, especially, which is indicative of multiple trapping sites. For the K1 photocatalyst, it seems that preferential trapping sites are populated upon excitation, leading to narrower bands. Looking at the decay traces at 400 nm, Fig. 9(d), one can observe that K1 exhibits slower recombination rates than the bare oxide and K2. The calculated half-lives are 490, 530 and 870 ns, respectively, for the bare TiO2, K2 and K1. Thus, the electron–hole lifetime in K1 is almost twice that in K2 and the bare TiO2.

Therefore, the higher efficiency of K1 as a photocatalyst seems to be originated from its greater light harvesting and slower recombination rates, which are both related to the modification of the TiO2 matrix caused by nitrogen species. Despite most of them being removed during the sintering processes, they induce the formation of oxygen vacancies at the oxide surface that reduce the band gap energy and, upon excitation, work as electron traps.

4. Conclusions

Factorial experimental planning was successfully employed to obtain N-doped TiO2 photocatalysts by the precipitation
method with enhanced activity under solar radiation. The homogeneity of the reaction medium as well as the nitrogen source employed are key variables to obtain samples with suitable morphological properties for photocatalysis. Further thermal treatment is also necessary to ensure the crystallinity of the material and an optimized range of 330–400 °C for 3–5 hours was identified based on the photocatalytic test made using Ponceau 4R dye solutions. Photodegradation tests performed under UV-A irradiation showed that the best N-TiO₂ photocatalyst (K1) can mineralize the P4R dye with rate constants up to 10⁻² min⁻¹. This catalyst also exhibited a 28% improvement in relation to the non-doped oxide under solar irradiation. Surface characterization techniques show that the nitrogen content in the best photocatalyst is below 2%. Nevertheless, the powder contains oxygen vacancies that introduce intra-gap electronic states allowing visible light absorption and result in an electron–hole half-lifetime of 870 ns, as measured by transient absorption studies. This value is two times higher than the half-lifetime measured for the non-doped oxide. The results presented here provide new insights into the application of factorial design to obtain efficient systems for photocatalysis and can be used for other oxides and dopants.

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