

## Research Article

# N-TiO<sub>2-x</sub> Nanocatalysts: PLAL Synthesis and Photocatalytic Activity

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N-TiO<sub>2-x</sub> nanocatalysts are developed by the pulsed laser ablation in liquid (PLAL) technique, a simple and surfactant-free preparation method. The PLAL approach allows synthesizing chemical-morphological fine-tuning water TiO<sub>2</sub>-based nanomaterials, starting from targets of different nature (powders and commercial high purity targets). The catalytic activity was investigated using methylene blue (cationic dye) and methyl orange (azo dye). A different photocatalytic response was found for the various kinds of N-TiO<sub>2-x</sub>. In the first 20 min, under UV and visible light, about 50% and 10% of the methyl orange were removed using the N-TiO<sub>2-x</sub> and TiO<sub>2</sub> colloids, respectively. In addition, we observe that the response towards the methylene blue is comparable in all the synthesized samples under UV irradiation while differing by about 30% under a visible lamp. The enhanced photocatalytic response of the N-TiO<sub>2-x</sub> nanocatalysts with respect to the TiO<sub>2</sub> one is dependent on the content of the nitrogen dopant, surface area, and nitrogen-oxygen bonding configurations.

## 1. Introduction

TiO<sub>2</sub> is extensively studied in view of photocatalytic applications thanks to its low cost, high photogenerated hole oxidizing power, and long lifetime of electron/hole pairs when irradiated with light. Such photoinduced electron-hole pairs have been utilized to generate electricity in solar cells, to split water into hydrogen and oxygen, and to oxidize and degrade inorganic/organic/biological compounds in environments as well as to create superhydrophilicity [1].

The first reliable paper on photocatalytic activity of TiO<sub>2</sub> was published in 1938. It has been shown that UV absorption produced active oxygen species on TiO<sub>2</sub> surfaces, causing photobleaching of dyes [2]. Subsequent works to this have shown the oxidation of organic solvents and the formation of H<sub>2</sub>O<sub>2</sub> under an UV irradiation of a mercury lamp under ambient conditions while the water photolysis was demon-

strated for the first time in 1969 on TiO<sub>2</sub> semiconductors [3]. Fundamental processes of TiO<sub>2</sub> photoelectrochemistry have been studied intensively, mainly analyzing the behavior of TiO<sub>2</sub> nanomaterials, interesting for their high surface-volume ratio. TiO<sub>2</sub> nanostructures provide increased surface area at which photoinduced reactions may occur, enhancing the light absorption rate, increasing the surface photoinduced carrier density, enhancing the photoreduction rate, and resulting in higher surface photoactivity. At the same time, the high surface-volume ratio of the nanoparticles enhances the surface absorption of OH<sup>-</sup> and H<sub>2</sub>O, increasing the photocatalytic reaction rate [4, 5]. Based on the basic research results, industrial applications of photocatalytic TiO<sub>2</sub> have been achieved since the end of the 1990s and will develop further in the 21st century. Among them are photocatalytic water splitting [6], purification of pollutants [7], photocatalytic self-cleaning [8], photocatalytic antibacteria,

and photoinduced super hydrophilicity [9], as well as photo-voltaics and photosynthesis [10] (see Figure 1).

However, the large bandgap of  $\text{TiO}_2$  (3.2 eV for anatase and 3 eV for rutile) limits its light absorption only to the UV region [11]. Thus, pure  $\text{TiO}_2$  works as a photocatalytic material under UV light (4-5% of solar light), but it has very low photocatalytic activity in visible light (45% of solar spectrum). Some efforts have been made to overcome this limitation. Some aspects have been identified as essential to resolve the issue such as to tailor  $\text{TiO}_2$  bulk/surface electronic structures and the interfaces in order to tune surface band-bending, surface state distribution, and charge separation, which could significantly influence  $\text{TiO}_2$  photocatalysis response in the visible spectral range. The main requirements are (1) a high surface/volume ratio and a controlled anatase-rutile ratio to provide a large number of active sites for the degradation reaction and (2) shifting the absorption limit of the material in the visible range, searching for an increase in reaction rate of photocatalysis and hydrogen production.

Doping appears as a good alternative for changing the activity of  $\text{TiO}_2$  catalysts through the optoelectrical modification of this material by the introduction of dopants with different energy levels between the conduction and valence bands. The applied dopants can be (1) noble metals (such as Ag, Au, Pd, and Pt), which absorb the visible light due to the surface plasmon resonance, but the high cost associated with these materials should be considered a disadvantage [12]; (2) transition metals cheaper than noble metals, but their leaching behavior leads to the fast deactivation of the catalyst and constitutes a second source of pollution [13]; and (3) nonmetals (N, B, S, F, and C) able to extend optical absorption of  $\text{TiO}_2$  to the visible light region and then to improve visible-light-driven photocatalytic processes [14, 15]. Among the above-mentioned nonmetals, the most suitable and commonly used is nitrogen.

Nitrogen, as sulfur and fluorine species, is an anionic dopant which confers greater stability to the catalyst with respect to the conventional transition-metal dopants and also determines a significant red shift of the band gap into the visible range. According to theoretical modelling [16], the p-orbitals of the nitrogen dopant extensively overlapped, favouring the transfer of photogenerated charge carriers to the  $\text{TiO}_2$  surface, in turn increasing its photocatalytic activity [17]. It was proven that both in the anatase and rutile phases of  $\text{TiO}_2$ , the N2p states were located just above the top of the O2p valence band, which means a red shift of the absorption band edge to the visible region [18].

Despite the potential, data about the main changes provided by nitrogen doping in  $\text{TiO}_2$  is not well established. Moreover, for large scale usage of  $\text{TiO}_{2-x}\text{N}_x$  nanomaterials in all the solar radiation ranges, none of the results actually reached are satisfactory due to their low nitrogen/oxygen content, low chemical-physical stability, and increased carrier trapping.

There are multiple and assorted methods to prepare N- $\text{TiO}_2$  catalysts. Physical vapor deposition (PVD), reactive sputtering, cathodic arc deposition, plasma-gas reaction, and Chemical Vapor Deposition (CVD) are the common methods used to deposit N-doped titania films. However,

all these techniques allow the deposition of low level N-doped titania with micron-sized structures only at high vacuum conditions ( $10^{-8}$ - $10^{-9}$  Pa) and at high temperature (1200-1500°C) to avoid sample reoxidation. The methods based on plasma-gas phase reactions with the use of TiN powders seem to be a good and low cost alternative to obtain films with a small particle size (about 10 nm). However, these samples show a high oxygen content (ca. 15–20 at.%) [19]. Recently  $\text{TiO}_2$ , loading a different percentage of nitrogen, was prepared by nitridation of a nano- $\text{TiO}_2$  powder in a mixed ammonia/argon atmosphere at a range of temperatures from 400 to 1100°C [17]. According to the results obtained by Zhang et al. [20], the samples prepared at 700°C are oxygen deficient, which may be partly responsible for the shifting band gap and for the significant photocatalytic activity. On the other hand, nanocolloid production generally involves the use of surfactants and derivatives which cause secondary pollution to the environment.

For all these reasons, further studies will be useful mainly to (1) clarify whether oxygen deficiency has a bigger effect on photocatalytic activity than N-doping at low levels, (2) give a systematic and complete characterization of the chemical-morphological and optical properties of the synthesized N- $\text{TiO}_{2-x}$  nanomaterials, and (3) identify green methods and define a synthesis protocol in order to produce nanocolloids. This latter should be usable directly in the liquid phase in an innovative photocatalytic device, with a high degradation time (even in extreme conditions).

In this work, we presented and discussed the results obtained using the potentiality of the pulsed laser ablation in liquid (PLAL) technique to prepare N- $\text{TiO}_{2-x}$  nanocolloids. The syntheses were carried out in water to favour the formation of (Ti-O-N), ( $-\text{NH}_2$ ),  $\text{NO}_2^-$ ,  $\text{N}_2$ ,  $\text{NH}_x$ , and ( $-\text{OH}$ ) species, inducing their incorporation into the  $\text{TiO}_2$  lattice as nitride through dehydration. To this aim, the optimal PLAL deposition parameters (i.e., laser fluence and irradiation time) were found as well as the optimal composition of the targets ( $\text{TiO}_2$  mixed to TiN powders or TiN rod purchased from Matek Srl). PLAL processes were performed in ambient condition (room temperature) using the water as solvent, with the advantage to obtain nanocolloids, without by-products, suitable for mechanical deposition on photoanode materials or to be incorporated in integrated solar water-splitting devices.

All the synthesized colloids were characterized by scanning transmission electron microscopy (STEM), X-ray photoelectron (XPS), and conventional optical spectroscopies, providing complementary information which allows drawing a picture of the compositional, morphological, and optical properties of the nanocomposites, constituting the starting point for their successive photocatalysis applications which require moderate operating temperatures and limited energy consumptions.

## 2. Experimental Section

$\text{TiO}_{2-x}\text{N}_x$  powders, pressed into a disk at room temperature, were prepared starting from powders of TiN and  $\text{TiO}_2$  (P25), mixed at the TiN/ $\text{TiO}_2$  mass ratios of 75/25, 50/50, and

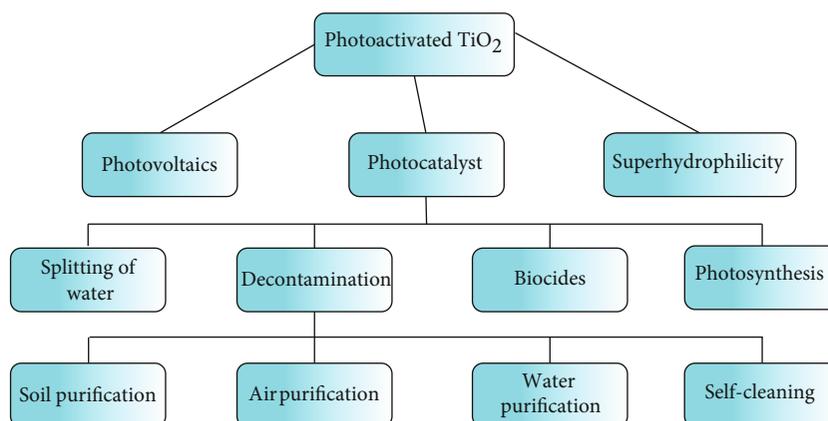


FIGURE 1: Dependence graph of photo-activated  $\text{TiO}_2$  materials applications. The flow goes from the top to the bottom direction.

25/75. Then, the compacts were maintained in a furnace at around  $250^\circ\text{C}$  for 1 hour. Pulsed laser ablation in liquid (PLAL) processes of the pressed powders as well as of commercial TiN and  $\text{TiO}_2$  rod targets (synthesized by Matek Srl at  $1200^\circ\text{C}$ ) were carried out in deionized water ( $\text{H}_2\text{O}$ ). The targets were irradiated at the laser fluence of  $0.5\text{ J}/\text{cm}^2$  for an irradiation time of 15 min (samples labelled TION3-5 and TION1P-5P-17P-12P) and of  $1.5\text{ J}/\text{cm}^2$  for 30 min (TION4), by the 532 nm radiation coming from a Nd:YAG laser source, operating at the repetition rate of 10 Hz and at the pulse width of 6 ns. The scheme of the PLAL setup and an overview of the sample set are shown in Figure 2.

Scanning transmission electron microscopy (STEM) images were acquired using a Zeiss electronic microscope which operates at an accelerating voltage of 30 kV. Samples for the STEM analysis were prepared by dropping a suspension of the sonicated colloids on a 400 mesh holey-carbon support sputter-coated with chromium.

A PerkinElmer (Lambda 750) spectrometer, working in the 300-900 nm range, was used to collect optical absorbance spectra.

The crystalline phase of the oxide was also investigated by analyzing Raman scattering data. Raman spectra have been excited with the 532 and 638 nm diode laser lines mounted in the XploRA spectrometer coupled with an Olympus microscope. Spectra have been collected with a 50x objective (spot size of about  $2\ \mu\text{m}$ ) and a Charged Coupled Device (CCD) used as a sensor. An acquisition time of 80 s granted a sufficient S/N ratio.

The chemical bonding states and the relative atomic content in the nanocomposites were investigated by X-ray Photoelectron Spectroscopy (XPS), using the Thermo Scientific K-Alpha system equipped with a monochromatic Al-K $\alpha$  source (1486.6 eV) and operating with a pass energy of 50 eV in the CAE mode.

Some aqueous solutions of methyl orange (MO) and methylene blue (MB) (Sigma-Aldrich) were prepared by dissolving the analytical grade dyes in the synthesized colloids at a  $1.5 \cdot 10^{-5}\text{ M}$  concentration.

MO and MB were used as probe molecules for a first evaluation of the photocatalytic activities of N- $\text{TiO}_2$  nanostruc-

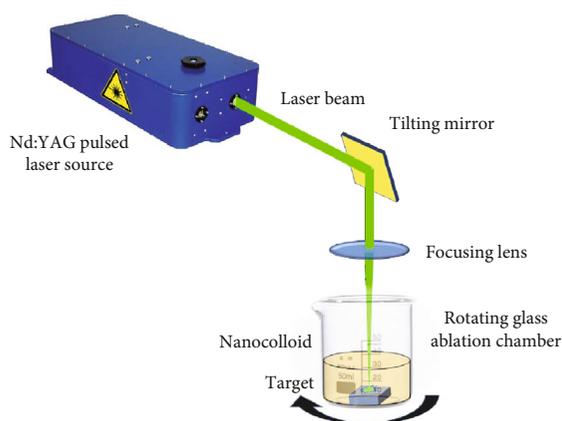
tures. The reaction was conducted in 3 ml of aqueous solution containing the dye, previously maintained in a beaker for 30 min at a temperature of about  $10^\circ\text{C}$ . The photocatalytic reaction was carried out under stirring. 0.5 mg of catalyst was dispersed in 3 ml of dye aqueous solution placed in an ice bath; in this way, the temperature of aqueous dispersion was maintained at around  $14 \pm 2^\circ\text{C}$ .

A 40 W Hg lamp (for UV irradiation) and a 450 W xenon lamp (as a visible light source blocking UV radiation by a 400 nm glass filter) were used as light sources placed at a distance of about 15 cm. Prior to irradiation, the dye catalyst suspensions were kept in the dark for 30 min to ensure an adsorption/desorption equilibrium. Then, the photodecolourization of MO and MB was studied.

Analytical samples were filtered through a  $0.2\ \mu\text{m}$  Millipore<sup>®</sup> filter to remove the solid, at well-defined time intervals during the irradiation, and placed into a 0.35 ml microquartz cuvette. Then, the residual dye concentrations in the filtrates were analyzed by UV-visible spectrophotometer (PerkinElmer 750) at maximum absorption wavelengths ( $\lambda_{\text{max}}$ ) of 464 and 664 nm for MO and MB, respectively. Direct photolysis decolourization of the respective dye was estimated by performing blank experiments.

### 3. Results and Discussion

**3.1. Sample Characterization.** In Figure 3 are shown representative STEM images of the samples obtained ablating in water targets of different nature. Specifically, the colloids, obtained ablating the (25/75) TiN/ $\text{TiO}_2$  powder targets, show a porous morphology with some spherical nanostructures with a mean diameter of about 50 nm (Figure 3(a)). It is to be noted that the observation of perfectly rounded submicrometer particles, probably associated with  $\text{TiO}_2$  species, is in agreement with what was observed by Felice et al. [21]. On the other hand, a high density of nanoparticles with a spherical shape and size mainly below 30 nm characterizes the colloids prepared ablating the high purity (99.99%) commercial TiN rod target (Figure 3(c)). An analogous morphology is shown by the colloids prepared ablating the TiN powder target (Figure 3(b)). More details can be observed



Sample	Preparation conditions
TION1P	From TiN powder ( $F = 0.5 \text{ J/cm}^2$ ; $t = 15 \text{ min}$ )
TION5P	From TiN/TiO <sub>2</sub> powder at 25/75 mass ratio ( $F = 0.5 \text{ J/cm}^2$ ; $t = 15 \text{ min}$ )
TION12P	From TiN/TiO <sub>2</sub> powder at 75/25 mass ratio ( $F = 0.5 \text{ J/cm}^2$ ; $t = 15 \text{ min}$ )
TION17P	From TiN/TiO <sub>2</sub> powder at 50/50 mass ratio ( $F = 0.5 \text{ J/cm}^2$ ; $t = 15 \text{ min}$ )
TiON3	From TiN target ( $F = 0.5 \text{ J/cm}^2$ ; $t = 15 \text{ min}$ )
TiON4	From TiN target ( $F = 1.5 \text{ J/cm}^2$ ; $t = 15 \text{ min}$ )
TiON5	From TiN target ( $F = 0.5 \text{ J/cm}^2$ ; $t = 30 \text{ min}$ )

FIGURE 2: Scheme of PLAL setup and synthesis parameters for each adopted target.

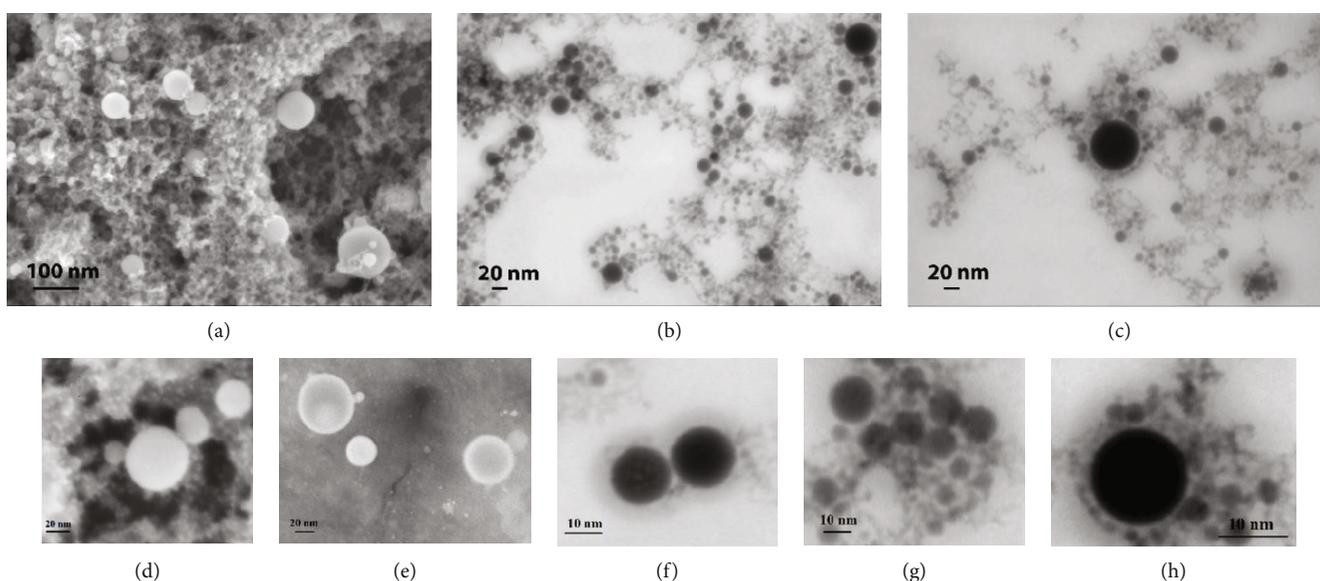


FIGURE 3: STEM images of the samples obtained ablating the (25/75) TiN/TiO<sub>2</sub> powder targets (a, d, e), the TiN powder target (b, f), and the high purity (99.99%) commercial TiN rod target (c, g, h).

from images d–h collected for the samples obtained ablating the (25/75) TiN/TiO<sub>2</sub> powder targets and the TiN rod and powder targets.

The sample obtained from the (25/75) mixed TiN/TiO<sub>2</sub> powders show Raman features typical of the anatase-rich TiO<sub>2</sub> material [6]. It is important to highlight that first-order Raman features of TiN (at 225 cm<sup>-1</sup> (TA), 310 cm<sup>-1</sup> (LA), and 540 cm<sup>-1</sup> (TO)) are almost absent, suggesting that nitrogen could be incorporated as a defect in the crystalline TiO<sub>2</sub> lattice. Samples, obtained from TiN powder (red line) and rod (blue line) targets, showed very similar Raman spectra; in this case, TiN vibrational features are well observable (see Figure 4(a)) as indicated by the pronounced peak at about 550 cm<sup>-1</sup> related to the TiN-TO mode [22]. Moreover, we observe that the E<sub>g</sub> (associated to the anatase phase) signal below 200 cm<sup>-1</sup> is totally absent and that the intensity ratio between the observed peaks at 200 and 290 cm<sup>-1</sup> is very similar to that of a possible formation of a rutile TiO<sub>2</sub> phase. Unfortunately, TiN and rutile features overlapped in this

region, so a correct attribution for the rutile is not possible exclusively from Raman analyses. All this evidence indicates a tendency towards an anatase-rutile conversion and/or an oxygen replacement by nitrogen with the formation of Ti-N bonds [22]. Interstitial nitrogen species are expected as a result of the ablation of a TiN target in water.

In Figure 4(b) are shown the optical absorbance spectra of the synthesized nanocolloids. We observe that (1) the colloid obtained by a TiN rod target is transparent (over 90%) in the visible range with a sharp absorption edge at about 350 nm, (2) a broad band at around 420 nm characterizes the sample prepared from the TiO<sub>2</sub> powder target, and (3) a slight blue shift is evident in the colloids prepared using the pressed and sintered target with a (75/25) TiN/TiO<sub>2</sub> mass ratio; for these samples, the 420 nm band is totally absent, while a significant visible light absorption contribution up to 600 nm is evident, probably due to the electronic transition from the localized N doping level to the conduction band of TiO<sub>2</sub> (see also the scheme reported in Figure 5).

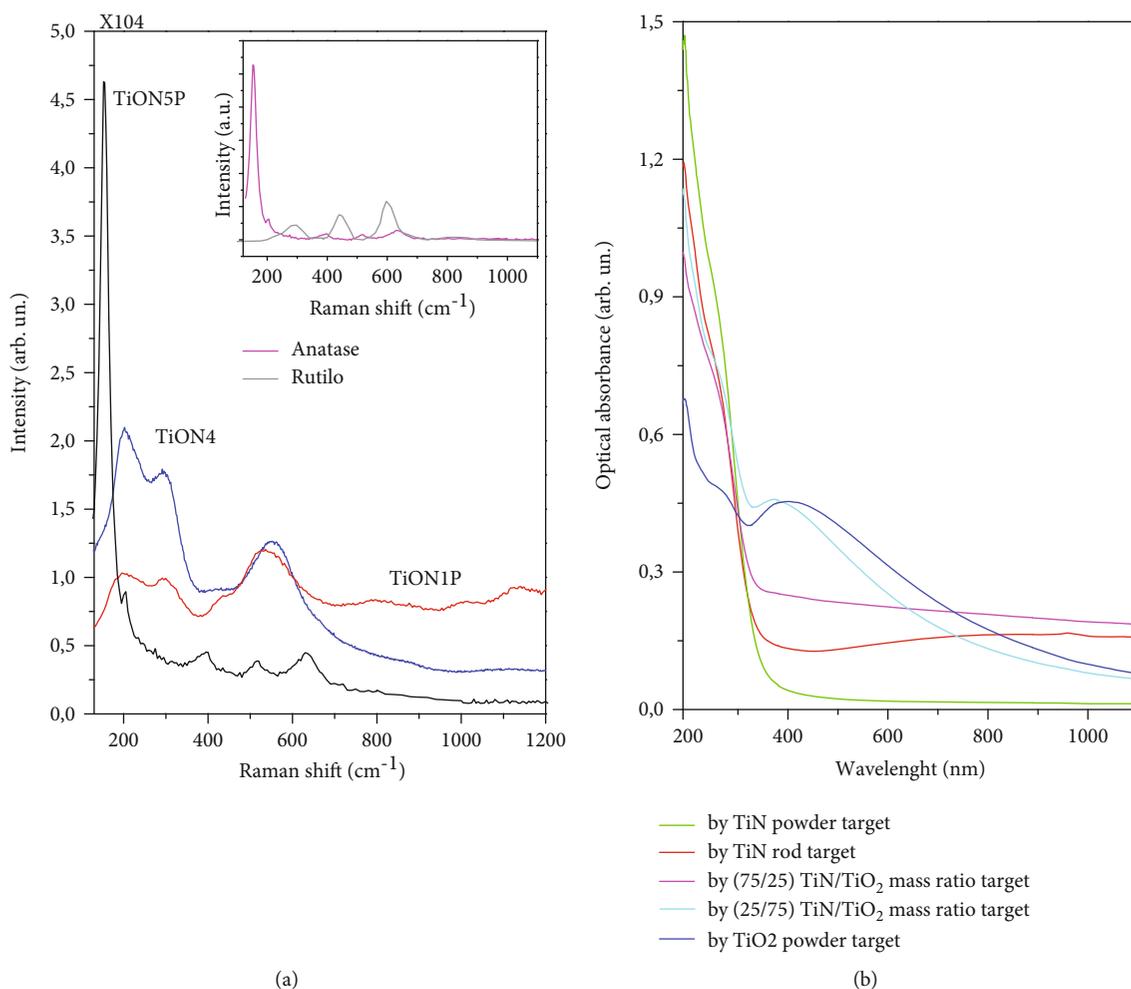


FIGURE 4: (a) Raman and (b) optical absorbance spectra of the synthesized samples.

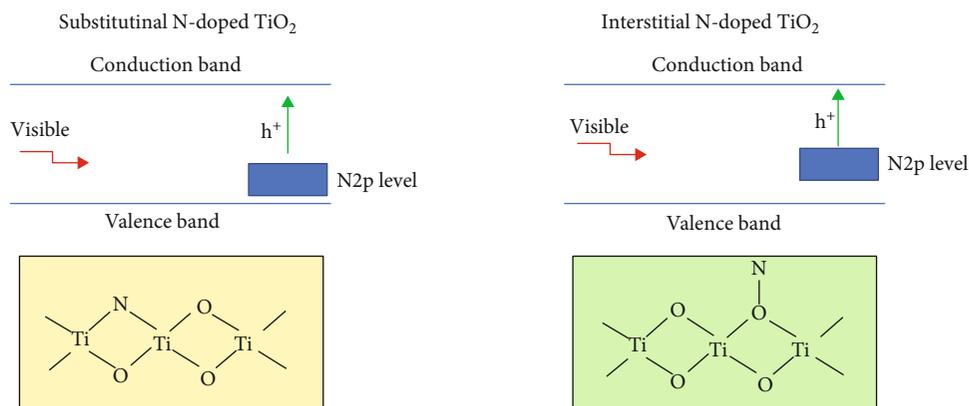


FIGURE 5: Schematic diagram showing the valence and conduction bands of N-doped  $\text{TiO}_2$ .

The incorporation of nitrogen into the  $\text{TiO}_2$  lattice leads to the formation of a new midgap energy state, i.e., the N2p band above the O2p valence band. So, upon a visible light irradiation, the electrons can migrate from the valence band to the conduction band (Figure 5) and from here the

expected visible light activity of N-doped  $\text{TiO}_2$  or  $\text{TiO}_{2-x}\text{N}_x$  materials (see Catalytic Activities). Nitrogen can replace one or more oxygen atoms (“substitutinal doping”), or nitrogen can be positioned in interstitial  $\text{TiO}_2$  sites (“interstitial doping”). In both cases, as shown in Figure 5, N doping

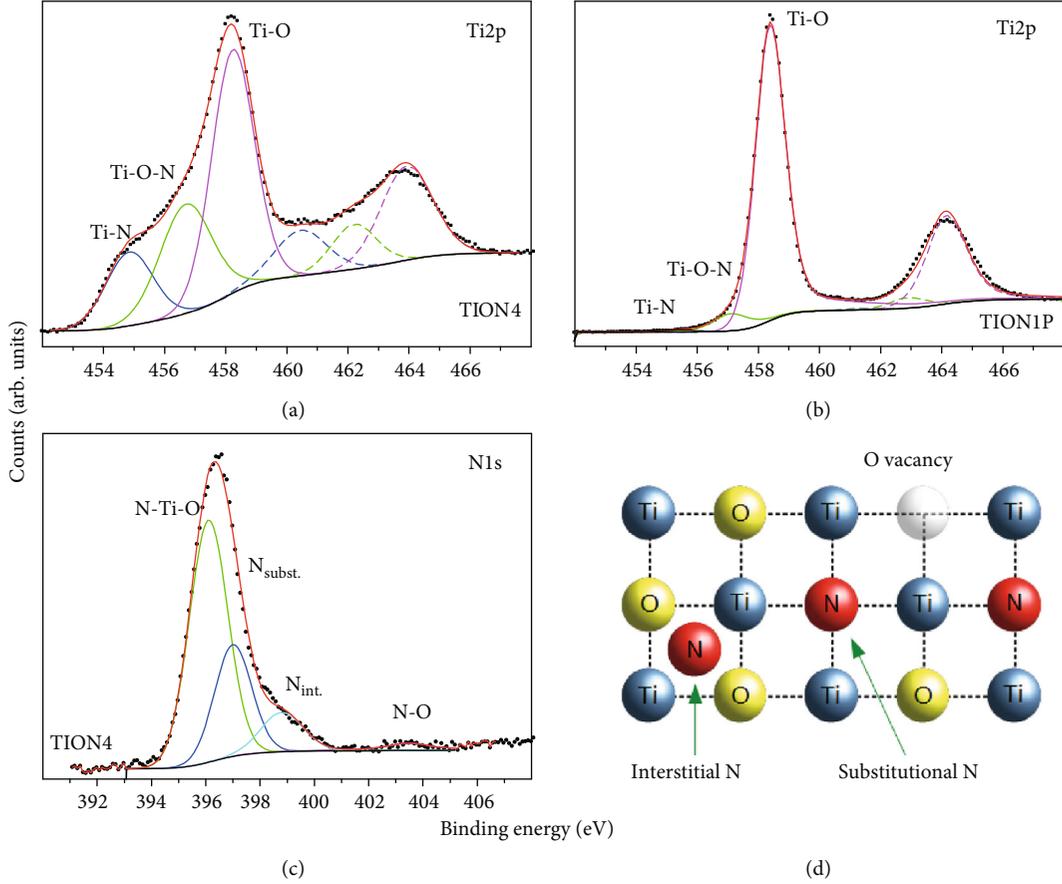


FIGURE 6: Ti2p (a, b) deconvoluted profiles of the samples obtained from the TiN rod and TiN powder targets, respectively. We outline that all the samples obtained from the mixed powders show Ti2p line shapes similar to those of the sample starting from the TiN powder. The N1s deconvoluted profile of the sample obtained starting from the TiN rod target (c) and a scheme of the potential nitrogen allocation into the TiO<sub>2</sub> structure (d).

TABLE 1: Atomic surface chemical composition and bonding fraction estimated by the deconvoluted XPS spectra.

Sample	Chemical composition (%)			Bonding configurations (%)						
	N (%)	Ti (%)	O (%)	Ti-N	Ti2p Ti-O-N	Ti-O <sub>2</sub>	N-Ti-O	N <sub>subst.</sub>	N1s N <sub>int.</sub>	NO/NO <sub>2</sub>
TION1p	1.1	28.8	70.1	0.8	6.4	92.8	—	—	100	—
TION5p	0.7	28.4	71.0	0.5	3.5	96.0	—	—	100	—
TION12p	5.9	23.8	70.3	0.9	3.4	95.7	—	—	100	—
TION17p	4.6	19.8	75.6	0.0	3.7	96.3	—	—	100	—
TION3	12.2	28.8	59.1	15.5	26.0	58.5	67.4	18.5	9.5	4.6
TION4	17.8	24.1	58.1	17.8	29.1	53.1	59.7	26.6	10.7	2.9
TION5	14.8	25.7	59.6	17.4	30.1	52.6	65.5	22.0	9.9	2.7

leads to a change in the electronic behavior of the nanoparticle due to a change in the electronic band structures and/or a decrease of electron-hole recombination [23].

XPS analysis allows investigating the surface chemical composition and bonding configurations of our samples, in which it is known that the surface chemical coordination greatly influences the catalytic response [24]. In Figures 6(a)–6(c) are shown representative Ti2p and N1s deconvoluted profiles, while the chemical atomic percentage

of the detected species and the relative surface bonding configurations are reported in Table 1. Two different Ti2p profiles characterize our samples: those obtained starting from the TiN rod target (Figure 6(a)) show a broad band whose features are ascribed to the titanium nitride, the titanium dioxide (TiO<sub>2</sub>), and the intermediate phase of titanium oxynitride [25, 26]. Otherwise, in the samples obtained by the TiN powder (Figure 6(b)), narrower profiles are obtained and the binding energy of the Ti2p<sub>3/2</sub> peak is brought closer

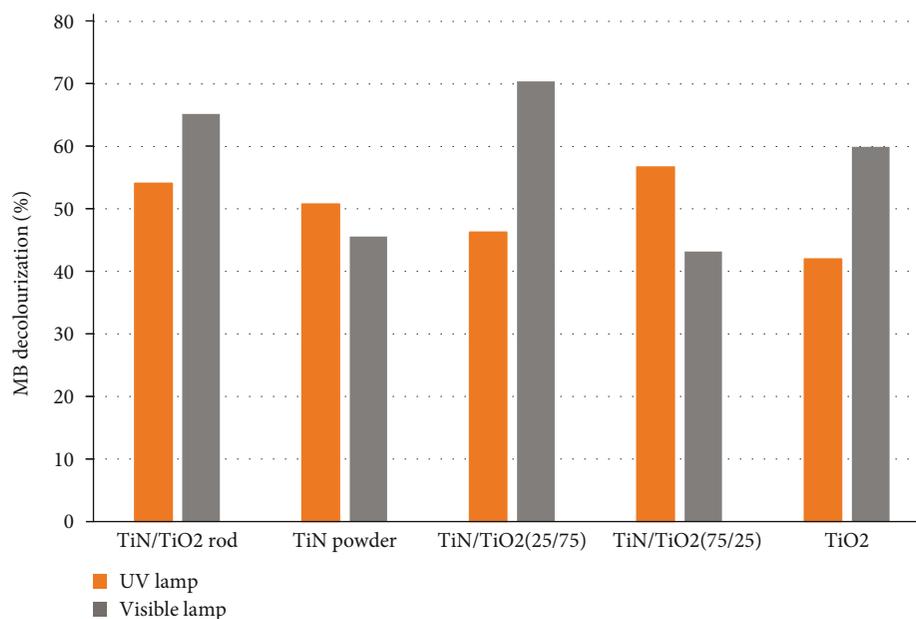


FIGURE 7: Photocatalytic activity towards the methylene blue (MB) dye molecule under UV and visible irradiation (60 min exposure time).

to 458.5 eV (typical of TiO<sub>2</sub> compound), while the binding energies of the other phases still fall within the possible ranges. Interestingly, no resolved N1s signal was collected from the powder targets while the N1s profile is well structured and defined for samples obtained from the rod targets (Figure 6(c)). The main components are located at around 396 and in the 397–400 eV range. These features are ascribed to the titanium oxynitride phase and to the nitrogen in substitutional and interstitial positions [26–31]. The NH<sub>x</sub>, NO/NO<sub>2</sub>, and NO<sup>3-</sup> contributions are generally reported at a binding energy higher than 400 eV [29–31] but, in our case, are less pronounced (see Figures 6(c) and 6(d)).

**3.2. Catalytic Activities.** All the photocatalytic reactions were undertaken in air as the photobleaching of MB is irreversible in an oxygen-saturated aqueous solution such as ours, and in an ice bath to avoid degradation effects due to light irradiation-induced heating. The photodegradation was monitored by recording UV-visible extinction spectra as a function of light irradiation exposure time. The percentage of MB decolourization under ultraviolet and visible radiation for the synthesized and TiO<sub>2</sub> reference samples is shown in Figure 7. Under UV and visible irradiation, all the produced nanostructures show a photocatalytic activity towards the degradation of methylene blue (MB) dye molecule. However, the response is comparable in all the samples under UV irradiation while, under the visible lamp, the estimated percentages differ by about 30%. In fact, for the samples obtained by ablating TiN powder and TiN/TiO<sub>2</sub>-mixed powder in 75/25 ratio, MB decolourization is about 45% but increases in the samples obtained from the TiN rod or from the TiN/TiO<sub>2</sub>-mixed powders at the 25/75 ratio. Photocatalytic decolourization behavior of MB dye (during visible irradiation, over the 1 h time frame of the experiment) seems to be influenced by the amount of N, Ti, and O and their bonding coordina-

tion and by the increasing absorption in the visible light region [32].

In Figure 8 is shown the percentage of MO decolourization under UV and visible lamp for the synthesized and reference samples. MO is an azo dye characterized by a N=N linkage, which is anionic in aqueous media and absorbs light in the visible region (450–550 nm) with an absorption maxima at 464 nm [33]. The samples obtained by TiN rod or TiN powder targets as well as those in which the TiN fraction is higher than the TiO<sub>2</sub> one (75/25 ratio) are the most active nanocomposites, both under UV and visible irradiation. For the colloids going from the TiN rod, we observe that, in the first 20 min, 50% and 60% of the dye were removed under UV and visible light, respectively, while only about 10% of the dye is removed for the TiO<sub>2</sub> colloid. Moreover, 70% of MO decolourization occurs within 80 min under visible irradiation while the other samples, for which Ti-O chemical bonds dominate in comparison to TiN/Ti-O-N ones, show significantly less efficiency in the same range of time.

In order to have a quantitative estimation of the photocatalytic activity, we carried out a simple fitting procedure already adopted to test photodegradation efficiency of MB using zinc oxide nanocolloids, prepared by picosecond pulsed laser ablation, as catalysts [34]. If a semilogarithmic scale of the relative absorbance as function of irradiation time is employed, it is possible to obtain a pseudoorder constant rate for all analyzed samples (see Table 2). In detail, by following the equation

$$\ln \left( \frac{A}{A_0} \right) = -k_c t, \quad (1)$$

with  $A_0$  and  $A_t$  as the starting absorbance and the absorbance at the time  $t$ , respectively, a linear fitting procedure, limited

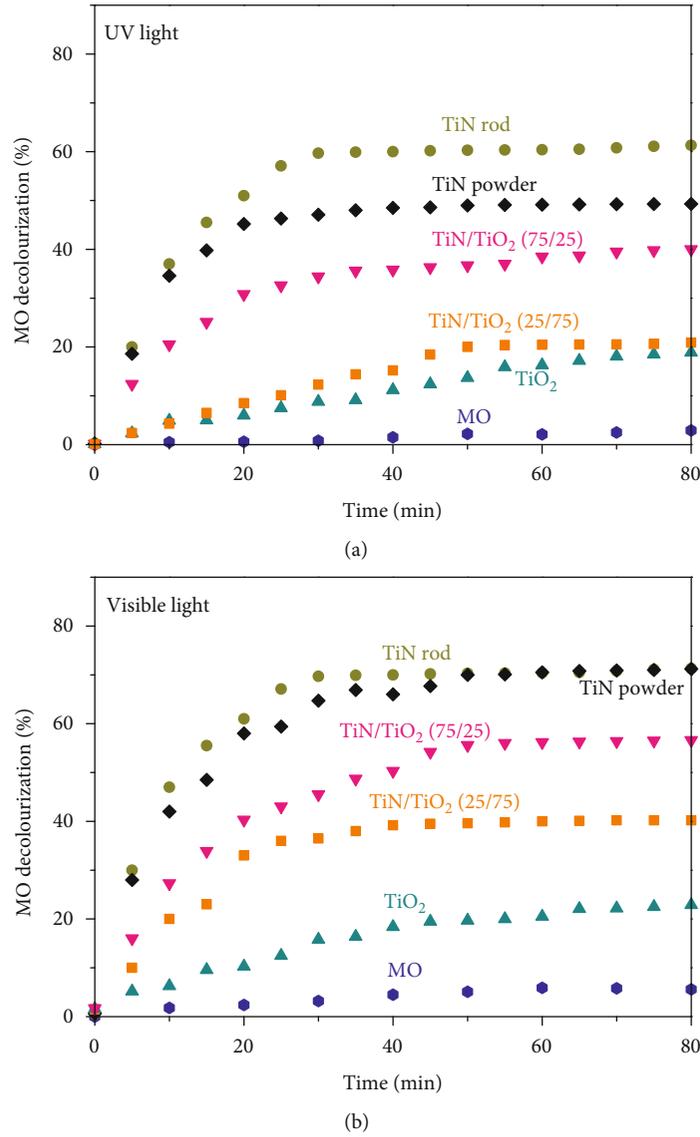


FIGURE 8: Photocatalytic activity towards the methyl orange (MO) dye molecule under UV and visible irradiation (60 min exposure time).

TABLE 2: Photodegradation rate constants of MB and MO with different catalysts using  $\ln(A/A_0) = -k_c t$  as the fitting equation model.

Sample	$k_c$ ( $\text{min}^{-1}$ )			
	UV lamp	MB	Visible lamp	MO
TION5 (TiN rod target)	-0.0118	-0.0211	-0.0333	-0.0426
TION1P (TiN powder target)	-0.0129	-0.0126	-0.0300	-0.0326
TION5P (TiN/TiO <sub>2</sub> (25/75) target)	-0.0103	-0.0242	-0.0043	-0.0176
TION12P (TiN/TiO <sub>2</sub> (75/25) target)	-0.0139	-0.0113	-0.0153	-0.0158
TiO <sub>2</sub> target	-0.0091	-0.0211	-0.0026	-0.0046

to the first 30 minutes of irradiation, is evidence that both dyes degrade faster under the visible source and that the highest  $k_c$  value is obtained with nanocatalysts from the TiN rod target.

Hence, on the basis of the obtained results, we suggest that the sample obtained from TiN characterized by the

higher N content could be photosensitized by the “N-doping.” In this case, oxygen vacancies promoted the charge recombination, resulting in weak reduction power. Otherwise, the high activity of the sample synthesized from the TiN/TiO<sub>2</sub> mixed powder in 25/75 ratio was attributed to the abundance of hydroxy groups in its porous structure

(see STEM image), which provided more active sites for the degradation reaction as well as to the high available surface/volume ratio of the catalyst, since this sample shows a porous structure (Figure 3(a)). Nevertheless, no clear correlation between the MB or MO photocatalytic activity and the chemical-structural properties of the synthesized nanocolloids is found, since dye decolorization is also affected by the ionic nature, structure and stability, adsorption, and orientation of the dye molecules on the surface of the catalyst [35, 36]. The synthesized N-TiO<sub>2</sub> nanocatalysts should be further investigated in depth to improve their catalytic response in the visible spectral region by a more rational and environment-friendly PLAL approach.

#### 4. Conclusions

In this work, the potentiality of the pulsed laser ablation in liquid (PLAL) technique to prepare N-TiO<sub>2-x</sub> nanocolloids, suitable for mechanical deposition on photoanode materials by conventional spraying technique, or to be incorporated in integrated solar water-splitting devices was reported. Synthesis processes were carried out in water, using targets with different nature and composition, to favour the formation of (Ti-O-N), (-NH<sub>2</sub>), NO<sup>2-</sup>, N<sub>2</sub>, NH<sub>x</sub>, and (-OH) species, and the nitrogen incorporation into the TiO<sub>2</sub> lattice as nitride through dehydration. PLAL processes were performed in ambient condition (room temperature) using the water as solvent, without the need to provide high temperature (T) and pressures (P), thus preparing nanocolloids, ready to use without by-products. The observed photoactivity response of the synthesized nanocatalysts is explained in terms of their surface composition and bonding configurations and optical and morphological properties, which has been tuned changing the incorporation of nitrogen into the TiO<sub>2</sub> lattice, beneficial for potentially separating the photogenerated carriers in space.

#### Data Availability

The data used to support the reported findings are available from the corresponding authors upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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