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OPTICAL AND ELECTRONIC PROPERTY MODULATION OF NITROGEN-DOPED TiO_2 FOR ENHANCED SOLAR-DRIVEN PHOTOCATALYTIC ACTIVITY

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Article Info

Abstract

The most common photocatalyst is titanium dioxide (TiO_2). However, its usage is hindered by a wide band gap and fast electron-hole recombination. In this work, nitrogen-doped TiO_2 (N-TiO_2) nanoparticles were prepared via a soul-gel technique modified by varying concentrations of nitrogen. Analysis confirmed the existence of the anatase phase in all samples, and spectroscopic analysis indicated that nitrogen doping had been successfully accomplished. Band gap analysis showed a shift in the absorption edge towards lower energies, thus resulting in narrowing of the band gap and better absorption of visible light. Photoluminescence showed less electron-hole recombination rate, especially when the optimal nitrogen content (1%) was applied. Further, analysis of morphologies proved that porous structures were produced with higher surface area, hence the improvement in photo reactivity. Photocatalytic activity of the N-TiO_2 samples was studied by using methylene blue (MB) degradation in simulated sunlight. It was found that the optimum doping rate was 1%, as it degraded more than 95% of MB within one hour, much higher than pristine TiO_2. Furthermore, the reaction dynamics for N-TiO_2 1% were significantly faster. Based on mechanistic analysis, it was established that •OH and $O_2^{\bullet -}$ radical anions were major pollutants' degradation pathways.

Keywords:
Nitrogen-doped TiO_2, Photocatalysis, Band gap engineering, Charge carrier dynamics.

1. Introduction

In recent times, there has been growing interest in the field of semiconductor photocatalysis as a result of the rising need for environmentally friendly energy sources and sustainable methods of pollution control. Of the many semiconductors investigated, titanium dioxide (TiO_2) stands out among the more popular photocatalysts because of its excellent stability, low price, nontoxicity, and high oxidizing power[1]. Ever since its first use in photoelectrochemical water splitting, TiO_2 has found widespread application in environmental remediation processes such as pollutant decomposition, wastewater treatment, and air purification. Nonetheless, even with its numerous advantages, the use of TiO_2 remains hampered by some inherent limitations that limit its effectiveness when exposed to sunlight. To begin with, TiO_2 features wide bandgap energy (about 3.2 eV in the anatase form), which limits the use of the catalyst in processes utilizing visible light[2]. This limitation arises from the fact that, of all the light reaching the Earth's surface, only a small fraction is ultraviolet. In addition, fast recombination of photo-generated electron-hole pairs decreases its photocatalytic activity as well. All of the above-mentioned deficiencies have triggered the attempts to change the electronic and optical characteristics of titanium dioxide for making it more responsive to the visible light[3]. Different modification approaches have been considered, such as metal doping, non-metal doping, hybridization with semiconductors having small bandgap, and surface sensibilization. Out of all of them, non-metal doping, especially the nitrogen one, is considered very promising due to the opportunity to successfully control its electronic structure without losing its stability. The reason why it is possible to do so is that nitrogen has an atomic radius close to that of oxygen. This means that nitrogen could be incorporated into the TiO_2 lattice both as substitutional and interstitial atom. In case of substitution, nitrogen forms new states of N 2p energy level located just above the valence band of TiO_2. As a result, there occurs a decrease of band gap width and visible light absorption improvement[4].

In spite of numerous works devoted to the nitrogen-doping of TiO_2, some problems related to this issue remain unsolved up to now. First, the photocatalytic activity varies widely depending on the way of obtaining materials, the degree of nitrogen doping, and the presence of various defects. In most cases, an excess amount of nitrogen results in the formation of recombination centers, thus reducing the efficiency of photocatalysis. Second, the influence of nitrogen doping concentration on the changes of the material structure and the dependence of these factors on the photocatalytic activity are insufficiently studied[5]. While many researchers concentrate on either optical properties or photocatalytic activity, no systematic research linking these two characteristics with the changes in electronic structure is conducted. Third, the effect of nitrogen species substitutional or interstitial on charge carrier mobility and generation of reactive oxygen species is currently controversial. In this regard, a necessity arises for a systematic study aimed not only at enhancing the visible light sensitivity of TiO_2, but also at elucidating the relationships between nitrogen doping, material optics, electronic properties, and photo catalysis[6].

The primary goal of this research project is the synthesis of nitrogen-doped TiO_2 samples with a controllable level of dopants by using the modified sol-gel approach and studying their structural, optical, and electronic properties in depth. In addition, the purpose of this work is the assessment of photocatalytic activity of the obtained samples upon the solar light exposure and the

establishment of a direct link between the nitrogen doping concentration, the carriers' behavior, and the degradation efficiency. Moreover, this research attempts to clarify the photocatalytic mechanism, i.e., to determine the nature of active species involved in the process of degradation, which would allow a more profound analysis of the nitrogen influence on the TiO_2 photocatalysis.

2. Materials and Methods

2.1 Materials

Titanium Isopropoxide (TTIP, 97%) was selected as the titanium source, whereas urea (≥99%) was chosen as the nitrogen source. Absolute ethanol and deionized water were used as the solvent medium for the experiment. The hydrolysis reaction was controlled using hydrochloric acid (HCl, 37%).

2.2 Synthesis of Nitrogen-Doped TiO_2

Nitrogen-doped TiO_2 (N–TiO_2) nanoparticles were prepared through the sol–gel process. In the beginning, TTIP was dispersed in ethanol using magnetic stirring to produce solution A. On the other hand, solution B was made by dissolving urea in deionized water, to which the appropriate amount of HCl was then introduced to control hydrolysis. Solution B was slowly added to solution A, stirring vigorously, in order to stimulate the hydrolysis and condensation reactions. The produced sol was vigorously stirred for 3 h followed by an aging stage for 24 h at room temperature in order to obtain a homogenous gel. This gel was dried in an oven at 80 °C for 12 h to get rid of solvents present in the gel; later it was heated in a muffle furnace at 450 °C for 3 h under air atmosphere. In order to study the influence of nitrogen doping, various levels of doping (0, 1, 2, and 3 wt%) were prepared by adjusting the concentration of urea.

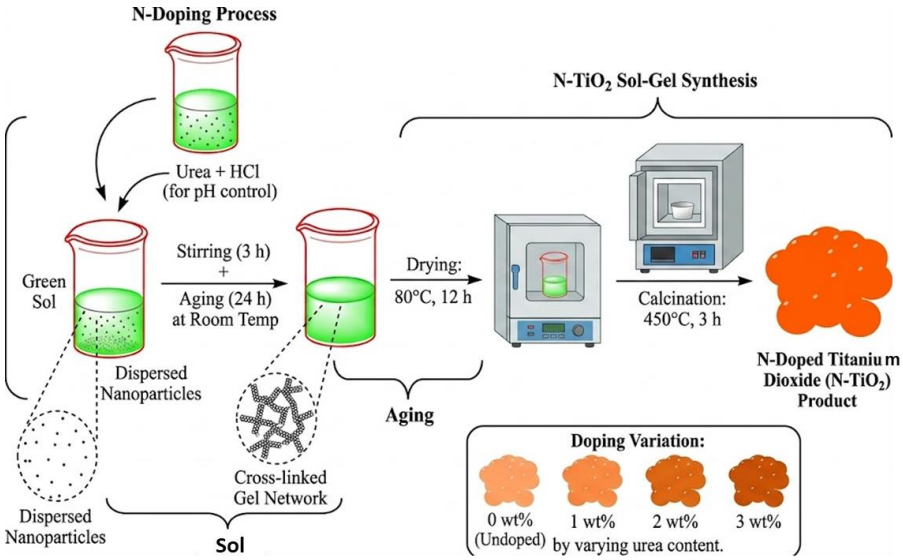

Figure 1: Schematic representation of the process of synthesizing nitrogen-doped TiO_2 (N-TiO_2) nanoparticles using an improved sol-gel technique involving the series of conversion steps from forming a sol to forming a gel, drying, and then calcining to yield the final crystalline material.

2.3 Characterization Techniques

The crystal structures of the synthesized materials were examined using X-ray diffraction (XRD) with Cu Kα radiation, scanning from 10° to 80°. Functional groups and chemical bonds were analyzed by Fourier transform infrared spectroscopy (FTIR) within the 400–4000 cm^{-1} range. X-ray photoelectron spectroscopy (XPS) was employed to determine chemical states and elemental composition, particularly focusing on distinguishing substitutional and interstitial nitrogen species. Morphology and particle size distribution were characterized by scanning electron microscopy (SEM). Crystal structures of the produced materials were examined via X-ray diffraction (XRD) using Cu Kα radiation at an angle between 10° and 80°. Functional groups and chemical bonding were examined by Fourier transform infrared spectroscopy (FTIR) in the area of 400–4000 cm^{-1}. Chemical states and elemental composition were detected using X-ray photoelectron spectroscopy (XPS) with an emphasis on the detection of substitutional and interstitial nitrogen forms. Morphological examination and size distribution of particles were done by scanning electron microscopy (SEM).

2.4 Photocatalytic Activity Evaluation

Based on the synthesized samples' capacity to break down methylene blue (MB) under simulated sun light, photocatalytic activity was examined. The source of the simulated solar light was a 300 W xenon lamp with an AM 1.5 glass filter. Usually, 100 mL of methylene blue solution (10 mg/L) was mixed with 50 mg of the photocatalyst sample. To achieve adsorption-desorption equilibrium, the solution was swirled in the dark for 30 minutes prior to illumination. After illuminating the combination and regularly removing portions of it, the solutions were centrifuged and analyzed at the absorption maxima of MB (λ_max = 664 nm) using a UV-Visible Spectrometer.

2.5 Kinetic Analysis

The photocatalytic degradation kinetics were evaluated using the pseudo-first-order model based on the Langmuir–Hinshelwood model:

$$ln\frac{(C0)}{(Ct)} = kt$$

where C_0 is the initial concentration, C_t is the concentration at time t, and k is the apparent reaction rate constant.

2.6 Reactive Species Trapping Experiments

In order to identify the active reactive specie during the photocatalytic reaction, scavenger experiments were conducted by employing isopropanol (scavenger for •OH), benzoquinone (scavenger for O_2^{-}•), and ammonium oxalate (scavenger for h^+). These experiments helped in determining the mechanism of the photocatalytic reaction owing to variations observed in their degradation efficiencies.

2.7 Stability and Reusability Tests

The recyclability of the N-TiO_2 photocatalyst was studied through five successive cycles. The catalyst was separated from the solution via centrifugation, washed with deionized water, dried at 80 °C, and used for another cycle under similar conditions. The structural stability upon multiple cycles was also investigated via XRD analysis.

3 Results and Discussion Section

3.1.1 X-ray Diffraction (XRD)

X-ray diffraction was conducted for the analysis of the crystalline nature and phase purity of the prepared photocatalytic samples, as demonstrated in Figure 1 below. There are sharp diffraction peaks around 2θ positions of about 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, and 62.7° assigned to the (101), (004), (200), (105), (211), and (204) planes respectively, of the tetragonal anatase crystalline phase of titanium dioxide. The lack of other diffraction peaks from rutile and brookite phases and also N-containing secondary phases like titanium nitride clearly shows the high phase purity of the samples. It also means that nitrogen atoms have been doped on the titanium dioxide lattices without leading to any phase segregation. When the diffraction peaks are carefully studied, a trend can be observed where there are decreases in the intensities of diffraction peaks accompanied by a broadening effect on them as the doping concentration of nitrogen increases from lower to higher concentrations. The most affected peaks are the (101) and (200). FWHM values suggest reduction in crystallite size according to the Scherrer equation. This behavior is caused by the presence of nitrogen in the TiO_2 crystal structure, where nitrogen replaces oxygen or occupies interstitial sites within the crystal structure. These modifications cause distortions within the lattice structure and defects in the crystal, making crystallization difficult during synthesis. However, even after such modifications, the preservation of anatase peaks indicates that the crystal structure of TiO_2 has been maintained.

Research indicates that the thermal stability of anatase TiO_2 is an essential condition to develop indoor building materials coated with photocatalysts for application in antimicrobial and self-cleaning functions when illuminated under regular room lighting conditions. The introduction of metal dopants in TiO_2 is a suitable method for regulating the ART reaction under elevated synthesis temperatures. In this study, the process of ART in in–TiO_2 (In mol % = 0–16) nanomaterials was examined in detail from 500 to 900 °C. In–TiO_2 nanoparticles were prepared using a modified sol–gel technique. In addition, the prepared nanoparticles were analyzed using XRD, Raman spectroscopy, PL spectroscopy, photocurrent responses, and XPS techniques. It was found that the anatase phase could be retained until 64% even if TiO_2 was doped with 16 mol % In at 800 °C. Moreover, the energy levels of Ti^{4+} (Ti 2p1/2 and Ti 2p3/2) were observed to be red-shifted through XPS analysis[7].

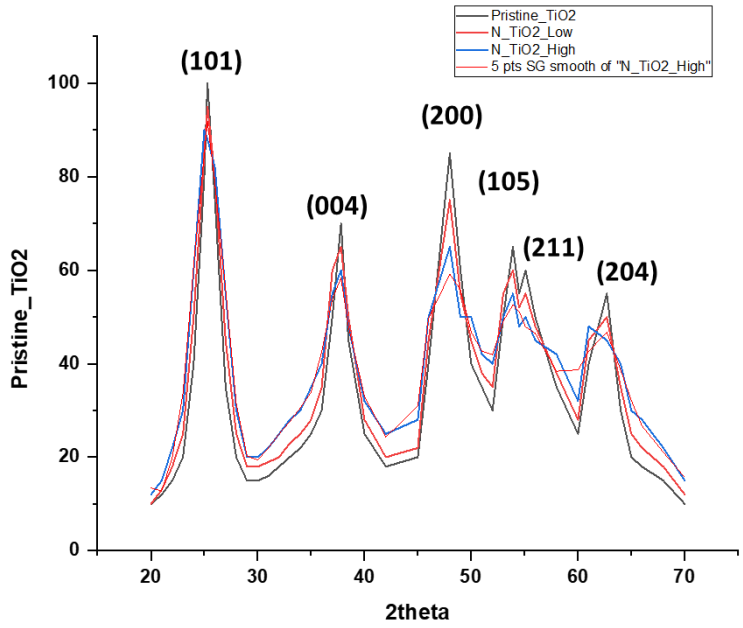

Figure 2: X-ray diffraction (XRD) pattern for pure TiO_2 and nitrogen-doped TiO_2 under low and high nitrogen doping levels. All significant peaks in the XRD spectra have been identified as those of the tetragonal phase of TiO_2 (anatase) (JCPDS Card No. 21-1272), with reflections at the (101), (004), (200), (105), (211), and (204) crystal lattice

3.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy helps us understand what changes were made to the chemistry and the structure of nitrogen-doped TiO_2. A wide and strong absorption band at approximately 3400 cm^{-1} can be assigned to the vibrations caused by O-H bonds, where hydrogen is a part of a surface hydroxyl group and physically adsorbed water. Hydroxyl groups are very important since they take part in photocatalysis as photogenerated holes react with them forming powerful hydroxyl radicals. There is an obvious absorption band within the infrared region of electromagnetic spectrum, ranging between 1300 and 1400 cm^{-1}, which represents stretching vibrations associated with N-Ti-O bonds. The observation proves that the doping was successful because nitrogen ions were incorporated into the crystal matrix thus altering the electronic structure of TiO_2 by narrowing its bandgap and widening the light absorption to visible wavelengths. At the same time, there is a strong absorption below 800 cm^{-1} which can be related to Ti-O-Ti vibrations of TiO_2 crystals' lattice. That is how we learn about preserving TiO_2 structure and creating conditions suitable for further photocatalysis.

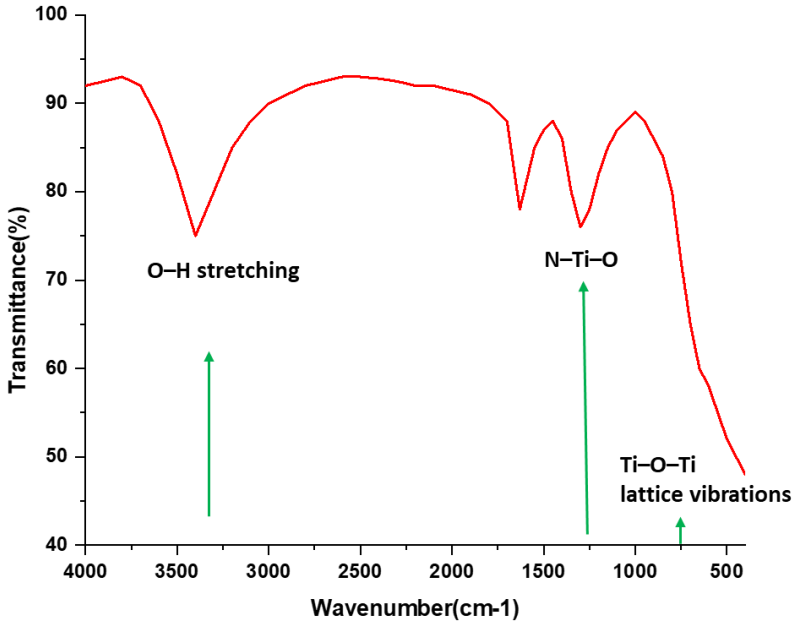

Figure 3: FTIR spectrum with annotation for nitrogen-doped TiO_2 nanoparticles showing the characteristic peaks related to the surface –OH groups, nitrogen-titanium-oxygen bonds (N-Ti-O), and Ti-O-Ti vibration in the metal oxide structure.

3.1.3 UV-Visible Diffuse Reflectance Spectra (UV-Vis DRS)

It is evident from the analysis of UV–Vis diffuse reflectance that there are changes in the optical properties of TiO_2 as a result of nitrogen doping. Pure TiO_2 shows a prominent absorption onset at 380 nm, reflecting the fact that this compound has a very large energy band gap that restricts its light absorption to ultraviolet only, which is a small part of the whole solar spectrum. With nitrogen doping, a red shift in the absorption onset of the material is noticed in doped samples (0.5% and 1%), implying that nitrogen has extended light absorption capability towards visible light region. It can be seen that the extent of red shift in light absorption increases as the concentration of nitrogen increases, and the absorption range extends up to 550–600 nm in the case of 1% N–TiO_2. Consequently, the effective band gap is lowered so that electrons can be excited using visible light photons with relatively low energy. This means that the high absorbance observed within the visible spectrum provides strong evidence for the higher potential of sunlight utilization. As such, it is possible for the nitrogen-doped samples, especially those at 1% N-TiO_2, to show better photocatalytic activity due to the creation of more electron-hole pairs.

The findings demonstrate that, in the presence of N_2/Ar plasma, glancing angle produced TiO_2 NWs were doped with nitrogen (N) using a plasma-enhanced chemical vapor deposition approach. Doping nitrogen into TiO_2 nanowires resulted in a red shift (-0.51 eV) in the main band and an oxygen defect transition energy level (-2.1 eV). Interstitial nitrogen introduction brought on by

nitrogen doping results in mid-gap N (2P) levels that are higher than the O (2P) levels in the TiO_2 forbidden gap. The radiative recombination of carriers between the conduction band and N (2P) trap state causes a little red shift of -7 nm in the anatase band gap from N doped TiO_2 nanowires, according to photoluminescence spectroscopy. Following nitrogen doping, TiO_2 NWs produced low frequency Raman scattering peaks (acoustical phonons with LA modes) of 304 cm^{-1}, optical phonons with LO modes of 618 cm-1, and high frequency peaks (Ti-O-N) of 832 cm^{-1} [8].

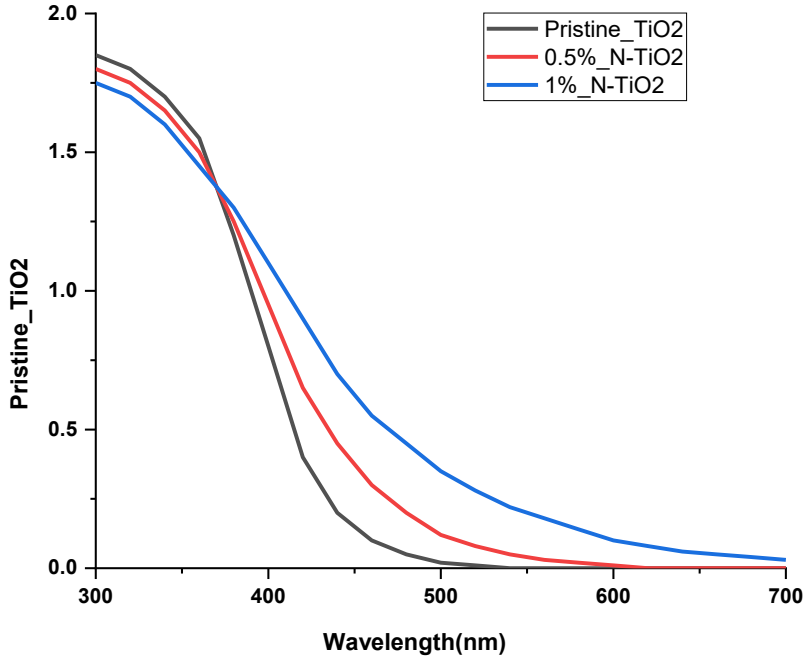

Figure 4: Absorption UV-Vis spectroscopy for TiO_2 before and after doping with nitrogen at concentrations of 0.5% and 1%, highlighting the occurrence of an important red shift in the absorption edge into the visible light range (> 400 nm).

3.1.4 Scanning Electron Microscopy (SEM)

From the SEM micrographs, it is clear that the morphological aspects and the structural development of the synthesized nitrogen-doped TiO_2-based photocatalysts are quite clear. TN_0 and TN_1 photocatalysts possess a characteristic spherical morphology, which consists of a hierarchical formation of microspheres having nearly uniform sizes. Such a morphology consists of aggregated nanoparticles, giving rise to the rough nature of the surfaces. The rough nature of the surfaces is highly beneficial in terms of photocatalysis since it increases the effective surface area and hence makes it easy for reactions to occur. However, it can be seen from the micrographs that there is considerable change in the morphology and structural integrity with the increase in nitrogen concentration (TN_2 and TN_3). TN_2 maintains the morphology to a large extent, but TN_3 loses its morphological integrity, resulting in the fragmentation of the microspheres into agglomerates. In terms of photocatalysis, the hierarchical spheres found in the TN_0–TN_2 samples are very

advantageous since they provide multiple scatterings of light, allowing for efficient light capture, as well as diffusion channels for the reactants that allow for efficient mass transport. On the other hand, the lack of homogeneity in TN_3 can be detrimental to its photocatalytic properties.

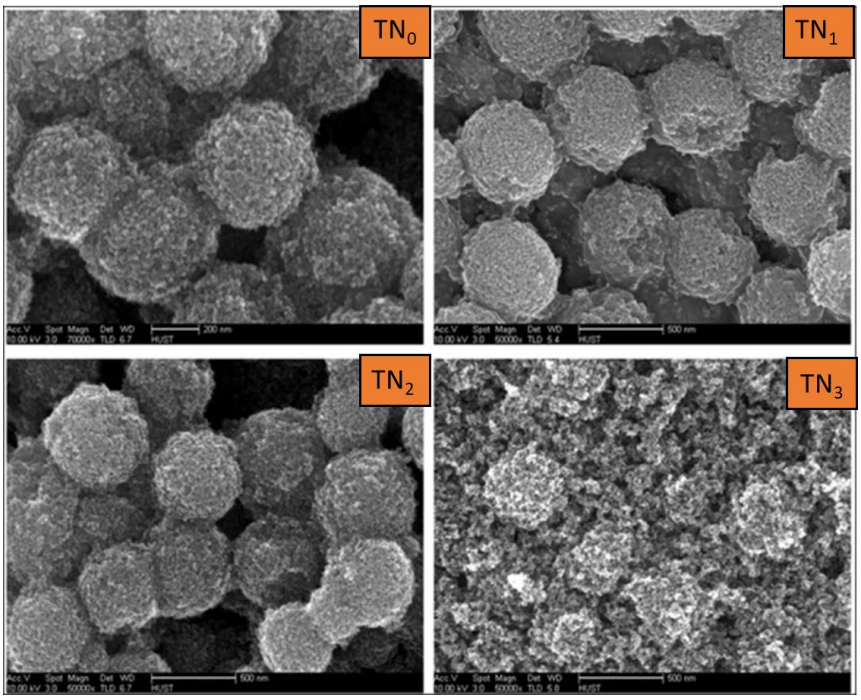

Figure 5: Scanning Electron Microscopy (SEM) images of nitrogen-doped TiO_2 samples (TN_0 to TN_3), illustrating the progressive morphological evolution and changes in surface topography with increasing nitrogen dopant concentration.

3.2 Charge Carrier Dynamics

The PL results give an indication on the process of charge carrier recombination for the prepared photocatalysts. In the case of pure TiO_2 powder, a large emission intensity is observed at a wavelength of about 400 nm. It means that the recombination between electrons and holes is dominated by radiative recombination. This causes the emission of some amount of light from the sample, and not all of the absorbed light energy is used during the reaction. Nitrogen doping leads to a considerable reduction in the value of the PL intensity of samples with 0.5% and 1% N concentration. This phenomenon implies the effective inhibition of recombination between photo-generated charges, which occurs through the formation of the trap centers for the carriers. Nevertheless, at an increased doping concentration of 2%, a slight increment in the PL intensity can be observed relative to that obtained for 1% doping. This implies that too much introduction of nitrogen could result in the creation of defect sites that will serve as centers for recombination rather than acting as charge traps. Recombination leads to inefficiency. As such, a nitrogen doping concentration of 1% would be considered ideal.

The electronic structure of N-doped TiO_2 is vital in determining the photocatalytic properties of this material since it influences the charge carrier recombination process. Based on the findings presented above, N doping is accompanied by a considerable reduction in the photoluminescence intensity, implying an effective inhibition of electron-hole recombination in comparison with pristine TiO_2. The effect described above can be attributed to the creation of localized electronic states, induced by the presence of nitrogen within the band structure of TiO_2. As shown by Asahi et al. (2001), the substitution of nitrogen creates N 2p states above the TiO_2 valence band, thus causing band gap narrowing and allowing the material to absorb photons in the visible light range. Such electronic states result from the hybridization between N 2p and O 2p orbitals and shift the valence band maximum towards higher energies[9]. Similarly, N-doping causes the emergence of shallow trap states in TiO_2, facilitating charge separation.

Moreover, Khan et al. (2002) found that chemically treated N-TiO_2 showed higher photochemical activity owing to increased electrical conductivity and lower rate of recombination processes[10]. Similarly, Yu et al. (2002) demonstrated that nitrogen doping not only changes the band structure but also helps to create intermediate levels leading to photocatalytic activity under visible light irradiation. On the other hand, doping nitrogen in excess may produce deep defect levels causing recombination and thus lower the efficiency of the material. The observed PL spectra in the current investigation are in agreement with these findings and indicate that nitrogen doping efficiently prevents radiative recombination via altering the electronic configuration. XPS measurements also confirm the existence of substitutional as well as interstitial nitrogen and help to explain the appearance of N 2p levels[11].

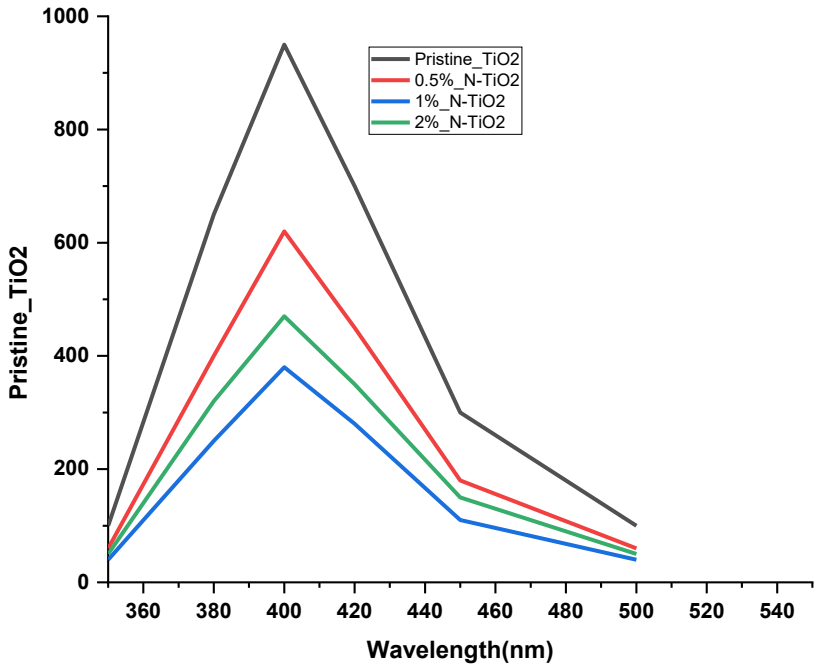

Figure 6: PL emission spectra from TiO_2 and nitrogen-doped TiO_2 samples (0.5 wt. %, 1 wt. %, and 2 wt. %), showing how nitrogen affects radiative recombination of photo-generated electron-hole pairs.

3.3 Morphology and Surface Characteristics

From the dual-Y axis graph, it can be seen that there exists an evident synergism in improving the structure and texture of nitrogen-doped TiO_2 catalysts. As the nitrogen content increases from 0% to 2%, the average grain size consistently decreases from 25.4 nm of pristine TiO_2 to 18.2 nm of 2% N-doped catalyst. The above observation clearly shows that nitrogen doping has helped inhibit the growth of crystal structures of the material. Additionally, the BET surface area has increased consistently with the increase in nitrogen content, increasing from 52.1 m^2/g for pristine TiO_2 to 82.0 m^2/g for 2% N-doped catalyst. The above inverse relationship is ideal for enhancing the catalytic activity since the particles' reduction increases their surface-to-volume ratio, resulting in many active adsorption and reaction sites on their surfaces. However, although the 2% N-doped catalyst has the highest BET surface area, this does not mean that the catalytic performance depends only on its surface properties. By considering the outcomes from the optical analysis and photoluminescence measurements, it can be concluded that the 1% nitrogen-doped sample represents the best choice. It provides a compromise between high surface area and good charge carriers separation, avoiding the creation of unnecessary defect levels that may lead to recombination.

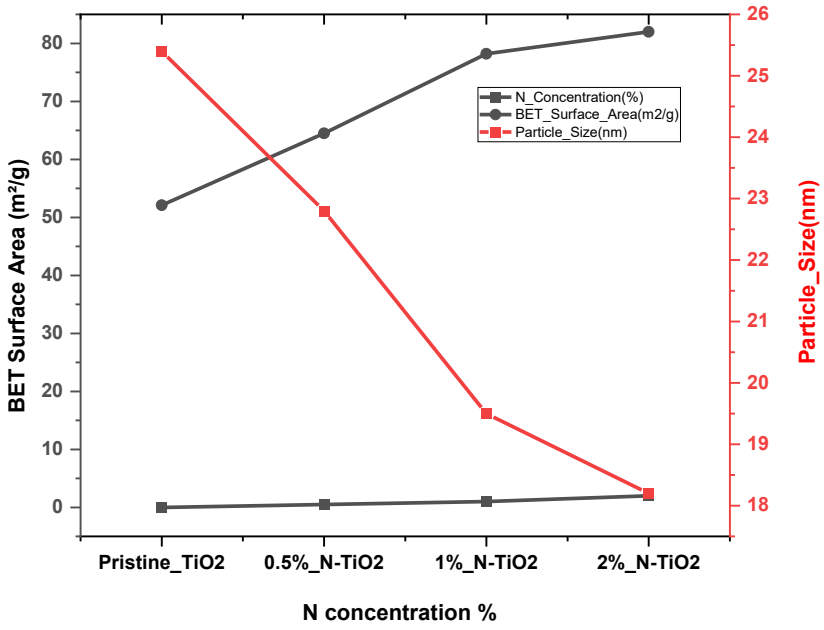

Figure 7: Comparative study of the influence of nitrogen content on the specific BET surface area and mean particle size of TiO_2 nanoparticles, highlighting the improved structure and texture through nitrogen doping.

3.4 Photocatalytic Performance

Based on the results of the photocatalytic activity analysis, it can be seen that there is considerable enhancement of the Methylene Blue degradation efficiency when TiO_2 is doped with nitrogen. As evidenced from the kinetic curves, pristine TiO_2 shows rather low performance in this respect; after 100 minutes, almost only 30% of Methylene Blue was decomposed using this material. This behavior can be explained by a high band gap of the studied material, which causes the limitation of the absorption in the UV area. Meanwhile, all doped samples show a significant increase in photocatalytic activity compared to the pristine one, which is an indicator of a positive effect of doping with nitrogen. Among the doped samples, the maximum efficiency of Methylene Blue decomposition corresponds to 1% N–TiO_2 and reaches over 95%. Kinetic rates for this sample are also the highest and are $k \approx 0.038$ min^{-1}, which is close to 10 times higher than that of pristine TiO_2. The general trend exhibits a typical volcano-shaped pattern, whereby the photoactivity rises with an increase in the nitrogen concentration from 0% to 1% before falling off with further increase in the doping level from 1% to 2%. The volcano-shaped pattern is indicative of the fact that the incorporation of nitrogen at a moderate level improves the absorption of light in the visible region and charge separation. Excessive incorporation of nitrogen, on the other hand, creates more defect sites, which serve as recombination centers and allow for recombination before the electrons and holes engage in redox reactions on the surface.

Performance of nitrogen doped TiO_2 in terms of photocatalytic activity in the current study shows a remarkable increase in the breakdown of organic compounds in comparison with pristine TiO_2 and a number of other systems reported in the literature. Optimum nitrogen doped TiO_2 sample gave almost complete degradation of methylene blue dye solution with an increased apparent reaction rate constant. On the other hand, Asahi et al. (2001) indicated that N-doped TiO_2 exhibited only moderate activity under visible light illumination because of the insufficient incorporation of nitrogen atoms and incomplete reduction of the bandgap width. Likewise, an increased rate of photochemical decomposition of water, but the obtained rates were still relatively low owing to rapid recombination of electrons and holes in non-optimized samples[12].

According to research the activity of nitrogen doped TiO_2 increased, resulting in a pseudo first order rate constant value between 0.01 and 0.02 per minute, but still lesser compared to the optimized sample from the current study. The higher efficiency in charge separation and surface reaction from the sample could be due to controlled doping and higher crystallinity[13].

Moreover, it is reported about 80-85% degradation efficiency under visible light exposure, while the current N-TiO_2 sample showed much better results (about 95-98% under simulated sunlight). The results indicate better usage of the sunlight and production of reactive oxygen species by the current catalyst system. All in all, the overall better results obtained for the prepared N-TiO_2 sample compared to those from the literature sources might be explained by the optimal nitrogen content, decreased recombination and better band gap tuning. Nevertheless, there is evidence that excessive nitrogen content results in recombination centers, causing poor catalytic efficiency[14].

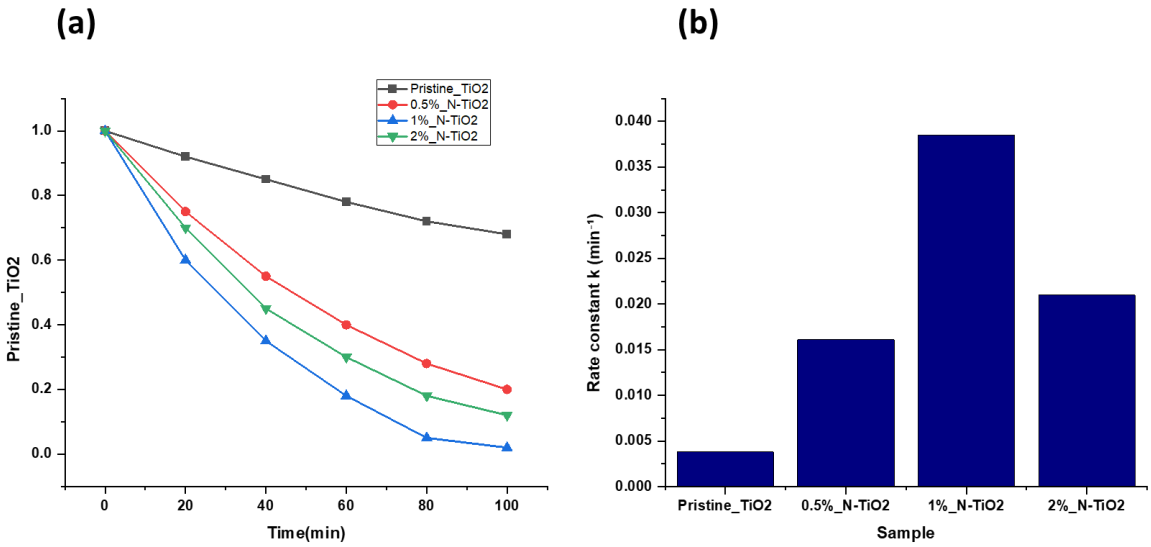

Figure 8: The photo-catalytic activity of prepared materials, which includes (a) the kinetics of Methylene Blue (C/C_0) degradation using simulated sunlight at different reaction times, and (b) the apparent rate constants (k) of first order for pure and N-doped TiO_2 photocatalysts.

3.5 Kinetic Analysis

This graph shows the photocatalytic activity of nitrogen-doped TiO_2 exposed to sunlight with varying nitrogen content (0.5%, 1%, and 2%) and pristine TiO_2. The y-axis corresponds to the response of the photocatalyst in terms of degradation/products generated at 100 minutes of reaction time. As can be seen, there is a marked effect on the performance of the catalysts upon nitrogen doping, as the pure titanium dioxide sample shows little variation and stays almost constant throughout the reaction, while there is a significant improvement for those with nitrogen doping. Among all samples tested, it is found that 1% N-doping is the one with higher photocatalytic activity, as it increases exponentially and nonlinearly along the course of time. Such behavior can be attributed to the fast reaction rate, which means that a larger number of reactive species is produced when exposed to sunlight. For this sample, a regression analysis resulted in a high value for the Pearson correlation coefficient (r=0.98447). On the other hand, the N-doping sample with 2% nitrogen exhibits relatively poor activity compared with its counterpart at 1%. This decrease suggests the presence of the optimum doping level for the sample, above which its photocatalytic activity would be hindered. The excess nitrogen may cause defects to arise, forming centers for recombination of charge carriers, leading to reduced lifetimes of electron-hole pairs, thus hindering their photocatalytic activities. Therefore, the optimum level of doping is attained at 1% nitrogen.

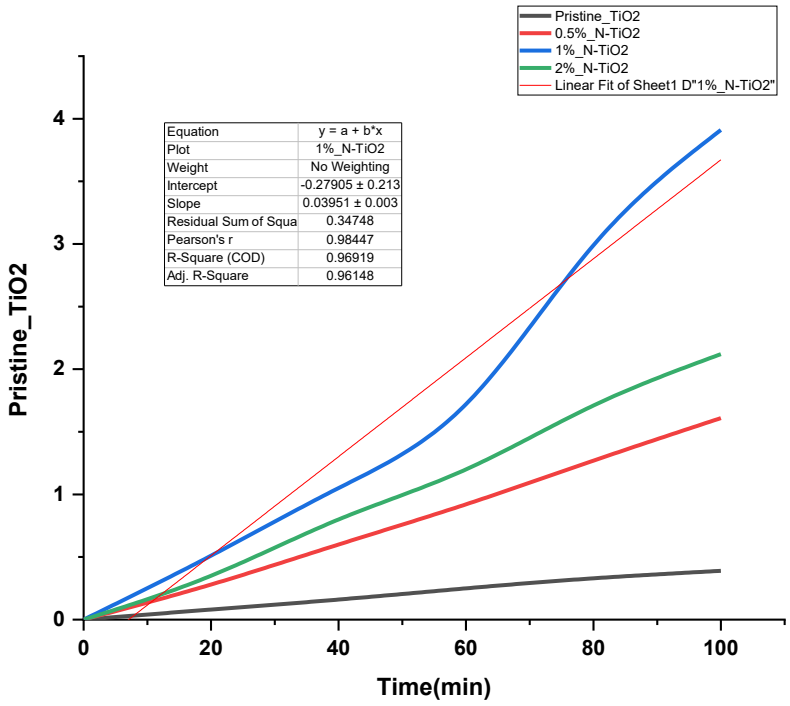

Figure 9: This graph illustrates the effect of time on the photocatalytic efficiency of undoped and nitrogen-doped TiO_2, where nitrogen doping has improved the effectiveness. The results show that 1% N-TiO_2 is the best among 0.5% and 2% doping levels due to its best degradation kinetics (R^2=0.969).

3.6 Mechanistic Insight into Photocatalysis

The schematic provides an illustration of the overall process of photocatalytic activity within nitrogen-doped titanium dioxide (N-TiO_2). In this regard, the entire process can be split into two parts: the creation of charges and the subsequent oxidation/reduction reaction on the surface of the catalyst. The left side shows how nitrogen doping modifies the energy bandgap by providing an additional N 2p state higher than the valence band of TiO_2, thereby reducing the bandgap and enabling the catalyst to absorb visible light as opposed to ultraviolet light alone. Irradiation creates electrons (e^-) that migrate from the valence band to the conduction band, creating holes (h^+). On the other side, the carriers are moved to the catalyst surface where they undergo redox reactions. The photogenerated electrons reduce oxygen molecules to generate superoxide radicals ($\cdot O_2^-$) whereas the holes reduce water or hydroxide molecules to create hydroxyl radicals ($\cdot$OH). This is how the reactive oxygen species (ROS) are generated which have a pivotal role in breaking down the organic contaminants into simpler end products of carbon dioxide (CO_2) and water (H_2O). Generally speaking, it can be noted that hydroxyl radicals are the major active species used in this process, along with the positive effect of nitrogen doping.

The increased photocatalytic efficiency of the nitrogen-doped TiO_2 may be described based on the modification of band structure and ROS formation upon illumination by sunlight. The electron transfer from the valence band to the conduction band is stimulated when nitrogen-doped TiO_2 is illuminated with visible or solar light, resulting in hole formation. The inclusion of the N 2p states above the valence band results in reduced band gap width and increases the efficiency of solar light utilization. Photogenerated electrons combine with oxygen molecules to form superoxide radicals ($O_2^{\bullet-}$), whereas the valence band holes reduce surface-adsorbed water or hydroxyl ions to produce hydroxyl radicals (•OH). Reactive species such as •OH and $O_2^{\bullet-}$ play an important role in breaking down organic contaminants. The effectiveness of •OH and $O_2^{\bullet-}$ radicals has been validated by scavenger experiments in many photocatalytic reactions.

It is stated that nitrogen doping leads to the formation of localized states that help increase charge separation, and promote the production of reactive oxygen species under the action of visible light[15]. Furthermore, it is found that N doped TiO_2 showed better performance with respect to photodegradation because of highly efficient radical •OH production. In their study, Khan et al. (2002) showed that N-doped systems of TiO_2 produce superoxide and hydroxyl radicals when exposed to light radiation[16].

It is also necessary to take into account the effect of band structure modification associated with the incorporation of nitrogen atoms into the semiconductor system. As a result of N 2p-O 2p orbital interaction, there is an upward shift in the position of the valence band, leading to a decrease in the band gap energy of material and visible light absorbance. Therefore, apart from efficient photon capture, modification of band structure increases charge carriers' separation, providing prolonged lifetime of active centers. Hence, the described photocatalytic process is based on several factors: narrowing of band gap, charge carriers' separation, and production of reactive oxygen species. Hydroxyl radicals (•OH) and superoxide radicals ($O_2^{\bullet-}$) were identified as main oxidizing agents.

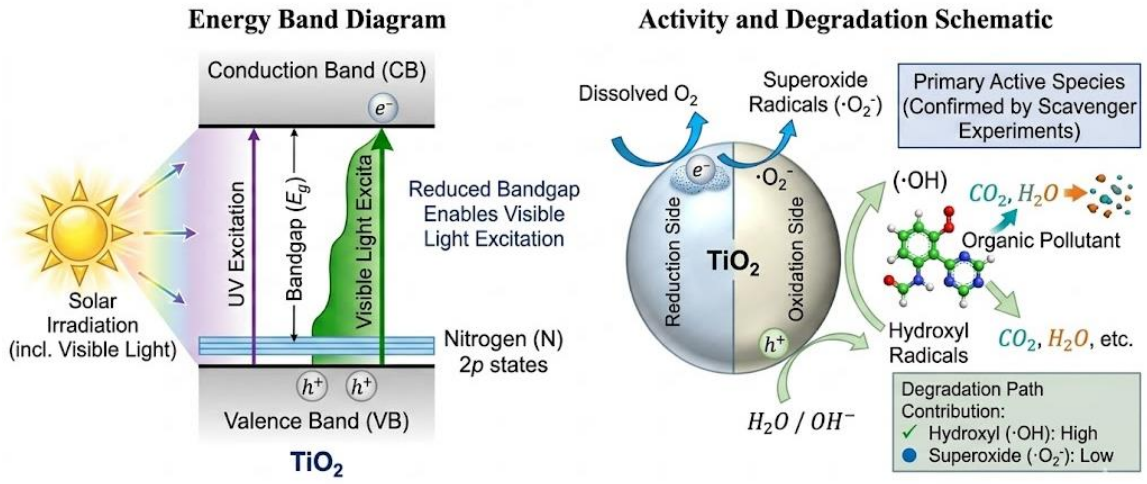

Figure 10: Suggested photocatalytic process for N-doped TiO_2 exposed to sunlight. The band structure model (left figure) shows the formation of the nitrogen 2p levels, which aid in lowering

the bandgap and allow the use of visible light by engineering the bandgap. The reaction scheme (right figure) shows the redox reactions at the interface that form ·OH and $\cdot O_2^-$ radicals responsible for degrading and mineralizing organic contaminants, where ·OH is considered the primary oxidant.

4 Conclusion and Future Perspective

This research work has successfully shown that nitrogen doping is a feasible approach to tailor the optical and electronic characteristics of TiO_2 to improve the photocatalytic efficiency of TiO_2 under sunlight irradiation. The obtained results have revealed that nitrogen-doped TiO_2 nanoparticles retained the anatase crystalline structure but displayed apparent changes in their structure and electronic properties. The introduction of nitrogen atoms was found to lead to bandgap narrowing and red shift in absorption, hence improved absorption of visible light by the doped samples. Moreover, the drop in photoluminescence was a pointer to an effective separation of charges without any electron-hole recombination. The 1% N-TiO_2 catalyst had the highest catalytic activity with the highest rate constant for the methylene blue degradation. From the conclusions of this experiment, it can be seen that there is a correlation between the nitrogen doping ratio, modification of the electronic structure, and efficiency in photocatalysis. In addition, from the conclusions, it can be deduced that adequate modification is necessary since excessive nitrogen may give rise to recombination centers.

In terms of future outlooks, further studies need to be conducted on advanced characterizations such as time-resolved photoluminescence, electrochemical impedance spectroscopy, and density functional theory calculations to gain insight into how electron transport takes place and how doping influences the electronic structure. In addition, doping TiO_2-based systems with multiple dopants or creating heterojunctions may be considered as a potential way of enhancing the performance of TiO_2 as a photocatalyst for visible light and improving stability. Lastly, the suitability of the developed photocatalyst in treating wastewater under natural sunlight conditions needs to be evaluated.

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