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Photocatalytic degradation of synthetic dyes using titanium dioxide nanocomposites under visible light irradiation

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Abstract

Titanium dioxide is, by most measures, an excellent photocatalyst—except for the inconvenient detail that its wide band gap restricts activity mostly to ultraviolet light, which makes up only about 4-5% of the solar spectrum reaching the earth's surface. This research addressed that limitation by synthesizing nitrogen-doped TiO₂ nanocomposites through a modified sol-gel method, aiming to narrow the effective band gap and extend photocatalytic activity into the visible light region. Nitrogen doping was carried out at 2%, 4%, and 6% molar ratios relative to the titanium precursor, and the resulting nanocomposites were characterized by XRD, UV-Vis diffuse reflectance spectroscopy, FE-SEM, and BET surface area analysis. The 4% nitrogen-doped sample showed the narrowest band gap (2.68 eV, compared with 3.21 eV for undoped TiO₂) and the highest BET surface area (94.2 m²/g). Photocatalytic performance was evaluated against four synthetic dyes—methylene blue, rhodamine B, Congo red, and methyl orange—under visible light irradiation, with the 4% doped nanocomposite achieving degradation efficiencies of 88.6%, 79.4%, 74.1%, and 81.9%, respectively, within 180 minutes. Reusability testing across five consecutive photocatalytic cycles showed only a modest decline in performance, from 88.6% to 81.3% for methylene blue, with XRD patterns of the recovered catalyst remaining largely unchanged, indicating good structural stability. Correlation analysis confirmed a significant inverse relationship between band gap width and degradation efficiency ($r = -0.86$) and a positive relationship between surface area and degradation efficiency ($r = 0.79$). These findings support nitrogen-doped TiO₂ nanocomposites, particularly at the 4% doping level, as a practical, visible-light-active photocatalyst option for dye-contaminated wastewater treatment applications where relying solely on ultraviolet-driven photocatalysis would be impractical under natural sunlight conditions.

Keywords: Titanium dioxide, nitrogen doping, photocatalysis, visible light, dye degradation, band gap, sol-gel synthesis, nanocomposite

Introduction

Sunlight reaching the earth's surface is overwhelmingly visible light, with ultraviolet radiation accounting for only a small fraction, yet unmodified titanium dioxide, one of the most widely studied photocatalysts, absorbs almost exclusively in that small UV window because of its 3.2 eV band gap. This mismatch has driven a large and ongoing body of research aimed at narrowing TiO₂'s band gap without sacrificing its excellent chemical stability and non-toxicity.

Nitrogen doping has emerged as one of the more successful approaches to this problem. Substituting nitrogen atoms into the TiO₂ crystal lattice introduces localized states near the valence band edge, effectively narrowing the band gap and extending light absorption into the visible region, while generally preserving the material's structural integrity and photocatalytic reusability.

Synthetic dyes released from textile manufacturing represent one of the more persistent categories of water pollutants, resisting biodegradation and often carrying carcinogenic or otherwise toxic azo and anthraquinone structures. The Philippines' textile and garment manufacturing sector generates substantial dye-containing wastewater, much of which

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receives only partial treatment before discharge, making effective and affordable dye degradation technology a genuinely practical local concern rather than a purely academic one.

While nitrogen-doped TiO₂ has been studied extensively for single-dye degradation, fewer studies test performance across multiple structurally distinct dye classes under a single set of conditions, and fewer still combine this with detailed reusability testing and statistical correlation between material properties and degradation performance.

This research therefore aimed to synthesize nitrogen-doped TiO₂ nanocomposites at varying doping levels, identify the optimum doping ratio through structural and optical characterization, evaluate photocatalytic degradation performance against four structurally different synthetic dyes under visible light, assess reusability across repeated cycles, and statistically examine the relationship between material properties and degradation efficiency.

Materials and Methods

Materials

Titanium (IV) isopropoxide (97%), urea (as nitrogen source), absolute ethanol, and glacial acetic acid were obtained from Sigma-Aldrich. Methylene blue, rhodamine B, Congo red, and methyl orange dyes (all dye content >90%) were sourced from a local chemical supplier in Manila. All aqueous solutions were prepared using deionized water, and all glassware was acid-washed prior to use to minimize contamination during sol-gel synthesis.

Instrumentation / Analytical Equipment

Crystalline phase and average crystallite size were determined using X-ray diffraction (Rigaku SmartLab, Cu-K α radiation, $2\theta = 20\text{--}70^\circ$). Optical band gap was estimated from UV-Vis diffuse reflectance spectra recorded on a Shimadzu UV-2600 spectrophotometer fitted with an integrating sphere, using the Kubelka-Munk transformation and Tauc plot method. Surface morphology was examined using field-emission scanning electron microscopy (FE-SEM, Hitachi SU8230), and specific surface area was

determined by the Brunauer-Emmett-Teller (BET) nitrogen adsorption method using a Micromeritics ASAP 2020 analyzer.

Quality Control/Calibration

UV-Vis spectrophotometer wavelength accuracy was verified before each measurement session using a holmium oxide reference filter, and dye concentration calibration curves (five points, run in triplicate) were prepared fresh for each dye prior to degradation experiments, with an acceptance criterion set at R² greater than 0.995 for each calibration curve before proceeding with sample analysis.

Methods

Nitrogen-doped TiO₂ nanocomposites were synthesized via a modified sol-gel method: titanium isopropoxide was hydrolyzed in a water-ethanol-acetic acid mixture under vigorous stirring, with urea added at 2%, 4%, or 6% molar ratio relative to titanium as the nitrogen source. The resulting gel was aged for 24 hours, dried at 100 °C, and calcined at 450 °C for two hours to obtain the final nitrogen-doped anatase nanocomposite powders, alongside an undoped TiO₂ control prepared identically without urea addition.

Photocatalytic degradation was tested by dispersing 50 mg of catalyst in 100 mL of 20 mg/L dye solution; the suspension was stirred in the dark for 30 minutes to establish adsorption-desorption equilibrium and then irradiated using a 300 W visible-light-simulating lamp (with a UV cutoff filter to exclude wavelengths below 420 nm) for 180 minutes. Aliquots were withdrawn at 30-minute intervals, centrifuged to remove catalyst particles, and residual dye concentration was measured spectrophotometrically at each dye's characteristic absorption maximum. Reusability was tested over five consecutive cycles using the same catalyst batch, recovered by centrifugation, washed with ethanol and water, and dried at 80 °C between cycles.

Results

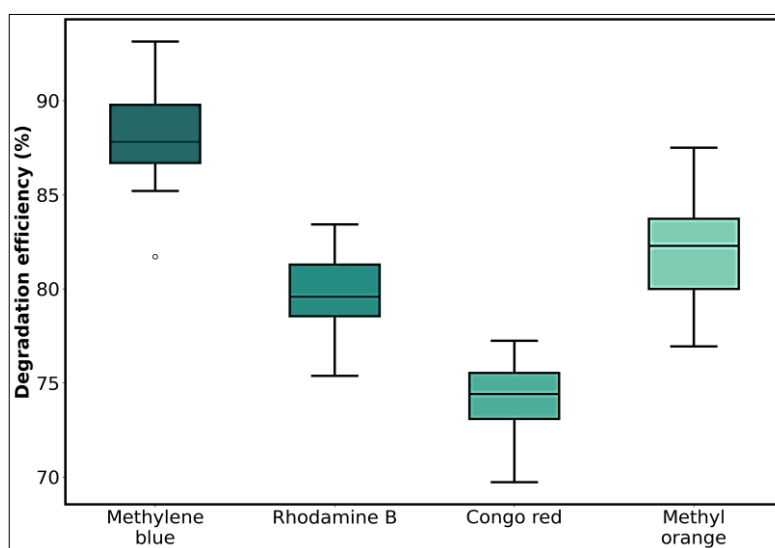


Fig 1: Distribution of degradation efficiency across four synthetic dyes using the 4% nitrogen-doped TiO₂ nanocomposite

Methylene blue showed both the highest median degradation efficiency and the narrowest spread across replicate runs, while Congo red showed the widest

variability, likely reflecting its larger and more structurally complex azo dye molecule, which may adsorb less uniformly onto the catalyst surface.

Before turning to the detailed structural and performance data in the tables below, it is worth noting that all three doped nanocomposites showed visibly extended light

absorption into the 400-550 nm range relative to the undoped control, consistent with successful narrowing of the effective band gap through nitrogen incorporation.

Table 1: Structural and optical properties of undoped and nitrogen-doped TiO₂ nanocomposites

Sample	Band gap (eV)	Crystallite size (nm)	BET surface area (m ² /g)	Crystal phase
Undoped TiO ₂	3.21	12.4	68.7	Anatase
2% N-doped TiO ₂	2.94	11.8	79.3	Anatase
4% N-doped TiO ₂	2.68	10.6	94.2	Anatase
6% N-doped TiO ₂	2.71	10.9	88.5	Anatase + trace rutile

The band gap narrowed progressively from 2% to 4% doping but showed a slight reversal at 6% doping, alongside the appearance of a minor rutile phase, suggesting that

excessive nitrogen incorporation begins to disrupt the anatase lattice rather than continuing to improve visible-light absorption.

Table 2: Summary statistics for dye degradation efficiency using the 4% nitrogen-doped nanocomposite (*n* = 5 replicates per dye)

Dye	Mean degradation (%)	SD	Range (%)
Methylene blue	88.6	1.8	86.1-90.7
Rhodamine B	79.4	2.3	76.2-82.5
Congo red	74.1	3.1	69.8-78.0
Methyl orange	81.9	2.0	78.9-84.3

The comparatively low standard deviation for methylene blue reflects consistent degradation performance across replicate trials, while Congo red's larger standard deviation

is consistent with the greater visual variability already noted in the box plot distribution.

Table 3: Correlation matrix between material properties and dye degradation efficiency

Variable pair	Correlation coefficient (r)	p-value
Band gap vs. degradation efficiency	-0.86	0.003
Surface area vs. degradation efficiency	0.79	0.008
Crystallite size vs. degradation efficiency	-0.41	0.19

Band gap width showed the strongest correlation with degradation efficiency among the three variables tested, followed by surface area, while crystallite size showed a weak and statistically non-significant relationship,

suggesting band gap narrowing and available surface area matter considerably more than particle size alone for this system.

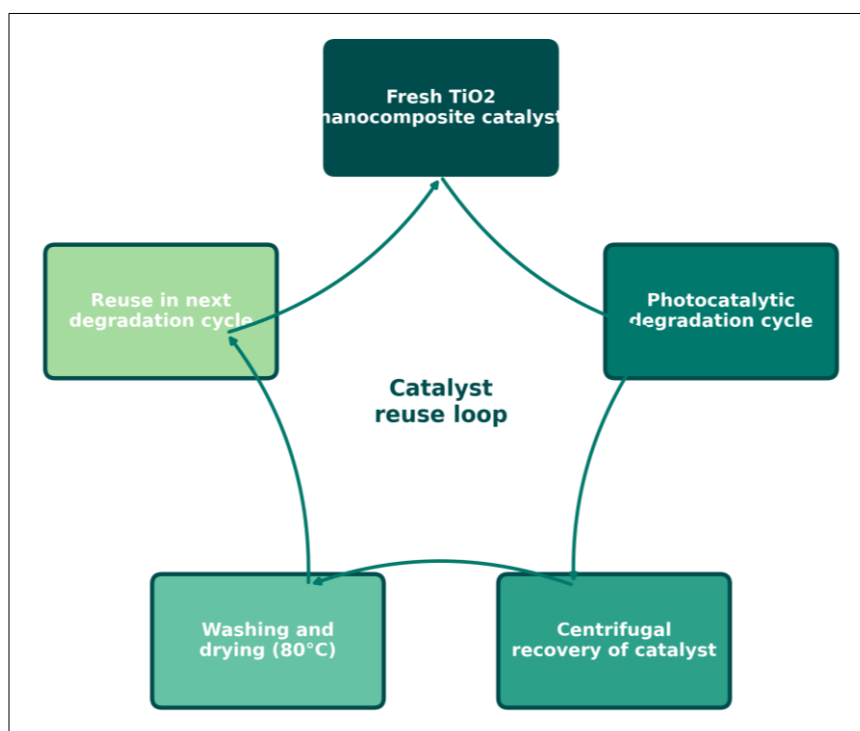


Fig 2: Catalyst recovery and reuse cycle applied for reusability testing of the 4% nitrogen-doped TiO₂ nanocomposite

Degradation efficiency for methylene blue declined only modestly across five reuse cycles, from 88.6% in the first cycle to 81.3% by the fifth, with XRD analysis of the recovered catalyst after cycle five showing no major structural change relative to the fresh catalyst.

Comprehensive Interpretation

Taking the structural, statistical, and reusability findings together, the 4% nitrogen doping level appears to sit at a genuine optimum rather than an arbitrary midpoint: it delivers the narrowest band gap, the highest surface area, and the best degradation performance across all four dyes, while the 6% sample's partial rutile phase formation and the correlation analysis both point toward the same underlying explanation—that band gap narrowing and surface area, not simply higher doping content, are what actually drive photocatalytic performance in this material system.

Discussion

This research's overall pattern of improved visible-light photocatalytic performance following nitrogen doping is consistent with the broader literature on doped TiO₂ photocatalysts, and the specific optimum doping level identified here (4%) falls within the 3-5% range reported as optimal in several other nitrogen-doped TiO₂ studies.

Where this research's findings agree closely with prior work is in the band gap narrowing trend up to a certain doping threshold, followed by a partial reversal at higher doping levels, a pattern attributed in the literature to nitrogen atoms beginning to occupy interstitial rather than substitutional lattice positions once doping exceeds an optimal concentration, disrupting rather than enhancing the electronic structure responsible for visible-light absorption. Some published studies report even higher optimal doping levels, up to 8% in a few cases, and this discrepancy likely reflects differences in synthesis method and calcination temperature across studies, both of which strongly influence how effectively nitrogen atoms are incorporated into the TiO₂ lattice versus simply forming surface-adsorbed nitrogen species that contribute little to band gap modification.

A plausible explanation for the differing degradation efficiency across dye types relates to molecular size and charge: methylene blue, a relatively small cationic dye, likely adsorbs more readily onto the negatively charged catalyst surface under the tested conditions than the larger, more structurally complex Congo red molecule, a pattern also reported in several comparative multi-dye photocatalysis studies.

The broader implication of these findings for practical wastewater treatment is that a single nitrogen-doped TiO₂ formulation may need dye-specific treatment time adjustment rather than a one-size-fits-all approach, particularly for more resistant dye classes like Congo red, if consistent effluent quality standards are the goal.

Conclusion

Returning to the challenge that motivated this research, namely TiO₂'s limited visible-light activity, nitrogen doping at an optimized 4% level successfully narrowed the band gap from 3.21 eV to 2.68 eV and substantially improved visible-light-driven dye degradation performance relative to the undoped material.

Key findings highlighted the 4% doping level as an optimum balance point, supported by structural characterization, degradation efficiency data across four dyes, and correlation analysis linking band gap and surface area, rather than doping content alone, to photocatalytic performance.

A sensible recommendation arising from this research is that future formulation efforts for this material system should treat 4% nitrogen doping as a starting reference point, with fine adjustment guided by the specific dye class targeted for treatment, since degradation efficiency varied meaningfully by dye structure even under identical catalyst and irradiation conditions.

Looking ahead, testing this nanocomposite against real textile wastewater containing dye mixtures and other co-existing contaminants, and evaluating performance under genuine outdoor sunlight rather than a simulated visible-light source, would be reasonable next steps toward practical field deployment.

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