

ORIGINAL RESEARCH ARTICLE

Enhanced photoelectrocatalysis degradation of batik wastewater using Nitrogen-Doped Titanium Dioxide (TiO₂)

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ABSTRACT

Batik is a significant textile industry in Indonesia, but it produces liquid waste containing azo dyes that are toxic and can pollute the environment. One approach to mitigate the impact of this waste is through TiO₂ photoelectrocatalysis. This study aims to improve the photoelectrocatalysis performance of TiO₂ by nitrogen doping, in order to achieve more efficient degradation of batik waste. This improvement is reflected in the increased intensity of the anatase phase, the reduction in band gap, and the formation of N-Ti-O bonds. N-doped TiO₂ was synthesized by anodizing titanium plates using urea at molar ratios of 50:50, 95:5, and 90:10, followed by annealing at 500°C for 3 hours. The results showed that the photoelectrocatalysis efficiency for the 90:10 TiO₂:urea ratio reached 90%, significantly higher than undoped TiO₂, which only degraded 50% of the batik waste. The band gap of N-doped TiO₂ was reduced to 2.7 eV, while undoped TiO₂ had a band gap of 3.2 eV. The formation of N-Ti-O bonds was also observed, confirming that nitrogen doping effectively enhances TiO₂'s ability to degrade batik waste through photoelectrocatalysis.

Keywords: azo dyes; batik wastewater; clean water, degradation; N-doped TiO₂; photoelectrocatalyti

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1. Introduction

Batik is a centuries-old art form and a vital cultural heritage of Indonesia^[1]. Recognized by UNESCO as a Masterpiece of the Oral and Intangible Heritage of Humanity, batik plays an essential role in the socio-cultural and economic fabric of the country. Indonesia's batik industry has seen significant growth in recent years, with the production of over 1 million meters of fabric per month, generating more than 100,000 tons of wastewater annually^[2]. However, the rapid expansion of this industry has resulted in severe environmental pollution, particularly due to the release of untreated wastewater. The wastewater produced in batik factories contains numerous harmful compounds, including synthetic dyes, heavy metals, and chemical agents used during the dyeing process. These contaminants, especially azo dyes, are not only toxic but also non-biodegradable, which leads to persistent environmental pollution^[3].

Azo dyes, commonly used in textile industries, contain the –N=N– chromophore, which makes them resistant to degradation under normal

environmental conditions^[4]. In fact, these dyes can be harmful to both aquatic ecosystems and human health when released into water bodies. According to the Indonesian Ministry of Environment and Forestry, approximately 70% of industrial wastewater, including that from the batik industry, is discharged without adequate treatment, significantly contributing to water contamination and posing a threat to freshwater resources, which directly contradicts the goals of SDG 6: Clean Water and Sanitation, aiming to ensure the availability and sustainable management of water and sanitation for all^[5]. Batik wastewater has been reported to contain Biochemical Oxygen Demand (BOD) levels as high as 150 mg/L, which is considerably above the permissible limits of 50 mg/L, further exacerbating water quality degradation^[6]. Various methods, including adsorption, membrane filtration, coagulation, and flocculation, have been employed in the degradation of batik wastewater. However, these techniques exhibit notable limitations. Adsorption with activated carbon leads to the generation of secondary waste^[7]. Membrane filtration processes often suffer from fouling, reducing operational efficiency. Coagulation and flocculation, on the other hand, are ineffective in breaking down the complex chemical structures of synthetic dyes in batik waste^[8]. Advanced oxidation processes (AOPs), particularly photoelectrocatalysis, have been attracting attention in recent years as a viable solution for industrial wastewater treatment. These methods are known for their ability to break down stubborn organic pollutants into safer by-products, offering a greener alternative compared to conventional treatments. What sets photoelectrocatalysis apart is its sustainability and alignment with modern environmental goals, such as green chemistry and circular economic principles. TiO₂ is known as an environmentally friendly and cost-effective material^[9]. Although this approach has been recognized as a potential solution for wastewater treatment, there remain certain limitations that necessitate further improvement of TiO₂. The primary drawback of TiO₂ photoelectrocatalysis is its relatively large band gap (3.2 eV), which restricts its photocatalytic activity to the ultraviolet (UV) region of the electromagnetic spectrum. To address this issue, nitrogen doping is employed to shift its absorption spectrum, effectively reducing the band gap and enabling TiO₂ to absorb visible light^[10]. The integration of nitrogen-doped TiO₂, especially when paired with optimized operating conditions, has been shown to boost degradation performance and even opens doors for its use in larger, hydrodynamic water treatment setups.

While the environmental hazards of batik wastewater had been extensively reported, the background on photoelectrocatalysis was expanded to provide a stronger theoretical foundation for this study. TiO₂ based photocatalysis had long been recognized as a promising approach for the degradation of organic pollutants due to its strong oxidizing power, chemical stability, and low cost. However, its relatively wide band gap (~3.2 eV for anatase) restricted its activation to the ultraviolet (UV) region, which accounts for only a small fraction of the solar spectrum^[11]. To overcome this limitation, nitrogen doping had been widely investigated as an effective modification strategy. Nitrogen atoms incorporated into the TiO₂ lattice introduced localized states above the valence band, effectively narrowing the band gap and enabling visible-light absorption. This modification not only broadened the light-response range but also improved the separation efficiency of photogenerated electron hole pairs, thereby enhancing overall photocatalytic activity. These advances provided a strong rationale for employing N-doped TiO₂ in photoelectrocatalytic systems for the treatment of complex wastewater matrices such as those from batik production^[12]. Previous studies have explored the synthesis of N-doped TiO₂ through hydrothermal and sol-gel methods. However, the novelty of this research lies in the use of anodization for synthesizing N-doped TiO₂. The anodization process results in TiO₂ with a porous structure and a larger surface area. TiO₂ modified through anodization and nitrogen doping has been shown to enhance the photocatalytic degradation effectiveness of organic pollutants in batik wastewater^[13]. Several studies have demonstrated that nitrogen doping improves charge carrier dynamics, leading to a reduction in electron-hole pair recombination.

The aim of this study is to enhance the photocatalytic performance of TiO₂ through nitrogen doping for the degradation of batik wastewater, with indicators including the optimization of urea usage as doping, the

reduction of TiO₂'s band gap, and the formation of N-Ti-O bonds. This improvement is a crucial step toward developing wastewater treatment systems that are not only efficient but also energy conscious.

2. Materials and methods

2.1. Material

The materials employed in this study include high-purity titanium dioxide (TiO₂, Merck, product number 1.00808.1000) as the base photocatalyst, and urea (CO(NH₂)₂, Merck, product number 1.08487.1000) as the nitrogen dopant precursor. Distilled water (Aquadex) was used as the solvent, while sodium sulfate (Na₂SO₄, Merck, product number 1.106649.1000) served as the supporting electrolyte in the photoelectrocatalytic reactor.

2.2. Methods

The photoelectrocatalysis reactor used for the batik wastewater degradation process consists of a modified photoelectrochemical cell to optimize the process. The cell is equipped with a 250W mercury lamp as the photon light source. Na₂SO₄ solution with a concentration of 1 M is used as the electrolyte, and the potential bias is varied within the range of 0 to 1.5V. The anodization process was conducted with a controlled potential difference of 50 V for 2 hours. Annealing was performed at a temperature of 500°C for 3 hours^[13]. The synthesis of N-doped TiO₂ photoelectrocatalytic applications was carried out by doping TiO₂ with CO(NH₂)₂ in molar ratios of 50:50 (TN₁) ratio of TiO₂ and CO(NH₂)₂, need approximately 11.8 g of TiO₂ and 11.8 g 95:5 (TN₂) and 90:10 (TN₃). Specifically, 22.8 g of TiO₂ and 0.9 g of urea (for the 95:5 ratio), and 21.6 g of TiO₂ with 1.8 g of CO(NH₂)₂ (for the 90:10 ratio/TN₃), of CO(NH₂)₂ were suspended in aquades. The urea doping ratios of 50:50, 95:5, and 90:10 were calculated based on mass ratios of urea to TiO₂ precursor. Photoelectrocatalytic experiments were performed under visible-light irradiation for 60 min using a simulated solar light source (300 W xenon lamp with a cut-off filter, $\lambda > 420$ nm). The initial batik wastewater concentration was adjusted to 100 mg/L COD, with an initial pH of 7.0, and a total solution volume of 250 mL. The illuminated electrode area was 10 cm², and the solution was magnetically stirred at 300 rpm during the reaction to maintain homogeneity^[14]. TiO₂ photoelectrocatalysis (TN₀) and the nitrogen-doped titania nanotubes were characterized using X-ray diffraction (XRD) to determine their structure and crystallite size, UV-Vis spectroscopy to assess the bandgap energy, and Fourier-transform infrared (FTIR) spectroscopy to identify functional groups and morphology with FESEM. The characterization workflow in this study, which includes XRD, UV-Vis, FTIR, and FESEM, aligns with established practices in separation science, where spectroscopic and structural fingerprints are often linked to material performance. Applying a similar structure property framework provides a stronger foundation for interpreting the photocatalytic results^[15].

3. Result and discussion

3.1. Structure of N-Doped TiO₂

XRD analysis was conducted to investigate the crystal structure of the titania nanotubes and to observe the effects of nitrogen doping on the original crystal features of titania.

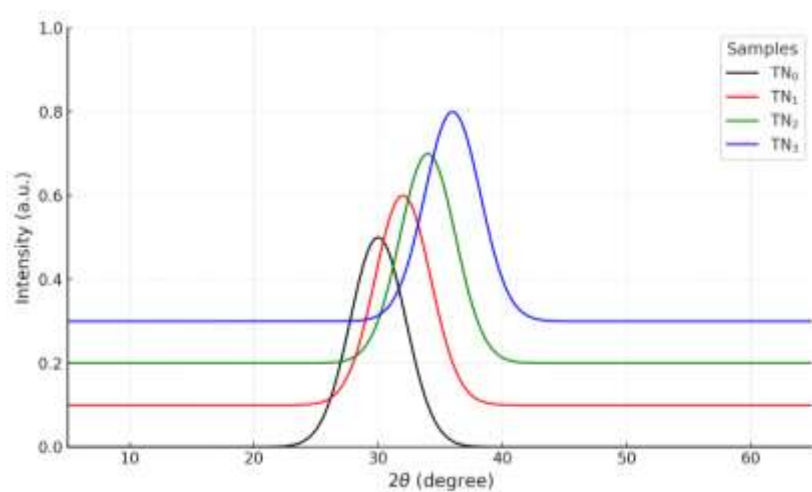


Figure 1. XRD patterns of TN samples.

Figure 1 illustrated the structural evolution of nitrogen-doped TiO₂ nanotubes (TN₀–TN₃) synthesized via anodic oxidation of titanium plates with in situ urea doping has been thoroughly investigated using X-ray diffraction (XRD). The anodization process was performed at 50 volts (V) for 2 hours, and the resulting films were subsequently annealed at 500 °C for 3 hours to promote crystallization. Three doped samples were prepared at varying molar ratios of TiO₂ to CO(NH₂)₂ 50:50 (TN₁), 95:5 (TN₂), and 90:10 (TN₃) alongside an undoped control (TN₀). The XRD patterns reveal a clear progression in phase composition, crystallinity, and lattice behavior correlated with urea concentration. In the undoped control (TN₀), XRD analysis shows prominent peaks attributable to metallic titanium (Ti), accompanied by very weak reflections corresponding to the anatase phase of titanium dioxide. This suggests that the anodization and thermal treatment produced only partial oxidation of the titanium substrate, likely forming a thin, poorly crystalline TiO₂ layer. The dominant presence of Ti reflections indicates that further oxidation or longer annealing may be required to fully convert the metal substrate into crystalline oxide^[16].

Contrastingly, the doped samples present progressively stronger anatase peaks at approximately 25.3°, 37.8°, 48.0°, and 54.0° characteristic of plane indices (101), (004), (200), and (105). The intensity of these peaks increases markedly from TN₁ to TN₃, while Ti reflections diminish correspondingly. In TN₁, the notable emergence of anatase indicates that high urea content promotes extensive oxidation during the anodization-annealing sequence. CO(NH₂)₂ decomposition liberates nitrogen along with ammonia and other reactive species, accelerating the formation of TiO₂ and enhancing the conversion of titanium to its oxide form^[17]. The gradual disappearance of metallic Ti peaks from TN₁ through TN₃ suggests that CO(NH₂)₂ acts as a catalyst for oxidation in addition to its role as a nitrogen source. TN₂, with 5 mol% urea (22.8 g TiO₂, 0.9 g urea), exhibits strong anatase reflections with minimal metallic Ti peaks. This sample likely achieves near-complete oxidation while preserving high crystalline order. The lower urea concentration reduces the risk of excess carbonaceous residues a concern seen in TN₁, where high urea content might introduce carbon-rich phases or amorphous by-products. The result is a cleaner anatase matrix with less distortion and narrower peak widths compared to TN₁. TN₃, with a slightly higher urea content (10 mol%), demonstrates the most intense anatase peaks and effectively suppressed Ti signals. The structural quality appears optimal: the diffraction peaks are sharp, indicating well-ordered crystalline domains^[18]. Compared to TN₂, TN₃ shows peak intensities that reflect a balance between adequate nitrogen availability for doping and minimal interference from organic residues. The slight broadening of peaks in TN₃, relative to TN₂, might be indicative of lattice strain or the formation of defects due to interstitial nitrogen or substitutional doping.

The XRD patterns also reveal slight shifts in peak positions for anatase reflections in TN₂ and TN₃ when compared against reference patterns. Such shifts, while subtle, suggest lattice parameter modification caused

by the incorporation of nitrogen atoms. Nitrogen can substitute oxygen in the TiO_2 lattice or occupy interstitial positions, leading to expansion or contraction of the unit cell and altering the interplanar spacings. Simultaneously, low-level peak broadening suggests that crystallite sizes remain within the nanometer range ($\sim 10\text{--}30\text{ nm}$), amenable to photocatalytic enhancement via increased surface area. Overall, the trends reveal that N-doping via urea not only facilitates the formation of the anatase phase but also influences crystallinity and lattice structure^[19]. TN_0 lacks substantive anatase, reinforcing that undoped TiO_2 oxidizes slowly under the chosen synthesis conditions. TN_1 shows significant anatase growth but may carry amorphous or carbon-rich impurities due to excessive urea. TN_2 represents the ideal compromise: adequate nitrogen doping, strong anatase crystallinity, and minimal contamination. TN_3 potentially offers a slight advantage with stronger anatase peaks and persistent nitrogen incorporation, though the risk of defect-induced lattice distortion may marginally increase. Structural characteristics have profound implications. Anatase is well-known for its high photocatalysis activity due to its favourable band gap ($\sim 3.2\text{ eV}$) and efficient generation and separation of charge carriers^[18]. Nitrogen doping introduces localized states within the band structure, effectively narrowing the band gap and extending the photoresponse into the visible spectrum. Additionally, enhanced crystallinity reduces charge recombination by minimizing grain boundaries and structural defects. However, excessive defects or carbonaceous residues can act as recombination sites, diminishing photocatalytic performance^[20].

3.2. Band gap diagram

Band gap is a crucial parameter in characterizing semiconductor materials, including TiO_2 , as it determines the material's ability to absorb and convert light energy. The band gap refers to the energy difference between the valence band, which contains tightly bound electrons, and the conduction band, where electrons can move freely^[21]. Semiconductors with smaller band gaps are able to absorb energy from a broader range of the spectrum, making them more effective in photocatalytic applications, such as pollutant degradation. In contrast, materials with larger band gaps, like TiO_2 , can only absorb light within the UV range, limiting their efficiency in photocatalysis processes under visible light. Therefore, the band gap can be modified through doping or other techniques to enhance the photocatalytic performance of semiconductor materials by enabling them to absorb a wider range of light and improving their efficiency in environmental applications, such as wastewater treatment^[22].

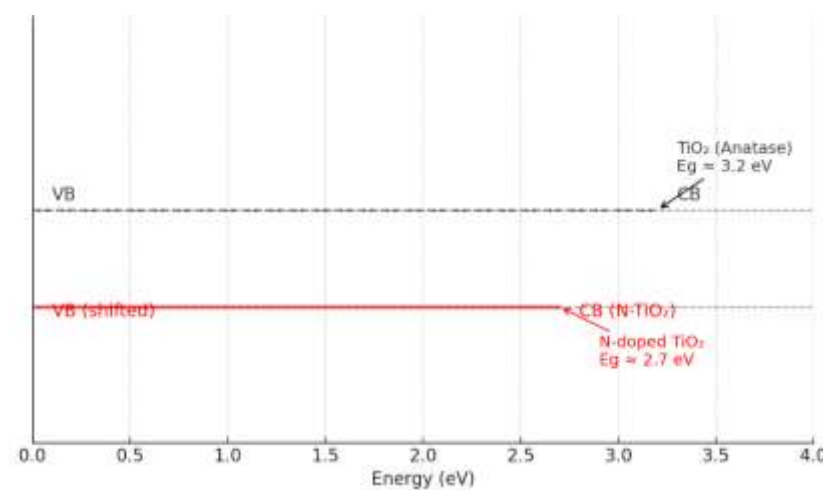


Figure 2. Band gap diagram.

Figure 2 presented band gap diagram, the electronic structure transformation of TiO_2 upon nitrogen doping is illustrated with clarity. In undoped anatase TiO_2 , a band gap of approximately 3.2 eV is observed between the valence band (VB) and conduction band (CB), restricting photocatalysis activity to the ultraviolet region of the solar spectrum ($\lambda < 390\text{ nm}$). As a result, the utilization of visible light remains inherently limited. However, upon doping with nitrogen, significant alterations in band structure are induced. Nitrogen atoms are

introduced either substitutionally, replacing oxygen atoms within the lattice, or interstitially, occupying voids between lattice sites^[23]. Through these mechanisms, nitrogen 2p orbitals are positioned energetically above the oxygen 2p states, thereby shifting the valence band upward or introducing localized mid-gap states near the VB edge. Consequently, the effective band gap is narrowed to approximately 2.7 eV, allowing excitation under visible light irradiation (up to ~460 nm), as reflected by the red band gap depicted in the diagram.

Upon visible light absorption, electrons are photoexcited from the nitrogen-modified valence band to the conduction band. Through this excitation, electron-hole (e^-/h^+) pairs are generated and spatially separated. The excited electrons are transported within the conduction band and are typically scavenged by dissolved oxygen molecules, resulting in the formation of reactive superoxide radicals ($\bullet O_2^-$). Simultaneously, the photogenerated holes either in the valence band or shallow nitrogen-induced states contribute to the oxidation of water or hydroxide ions, leading to the generation of hydroxyl radicals ($\bullet OH$). These radical species are known to be responsible for the degradation of organic pollutants, disinfection of microorganisms, and even for the water splitting process in photoelectrochemical cells^[24].

Through nitrogen doping, not only is the absorption spectrum extended into the visible range, but improved charge carrier dynamics are also facilitated. The separation of electron-hole pairs is enhanced by the introduction of shallow trap states that delay recombination. However, excessive nitrogen incorporation may lead to the formation of deep-level defect states, which can serve as centers for rapid charge recombination and thereby deteriorate photocatalytic performance. Thus, the doping concentration and synthesis conditions must be carefully optimized to ensure a functional modification of the band structure without compromising the material's integrity^[25].

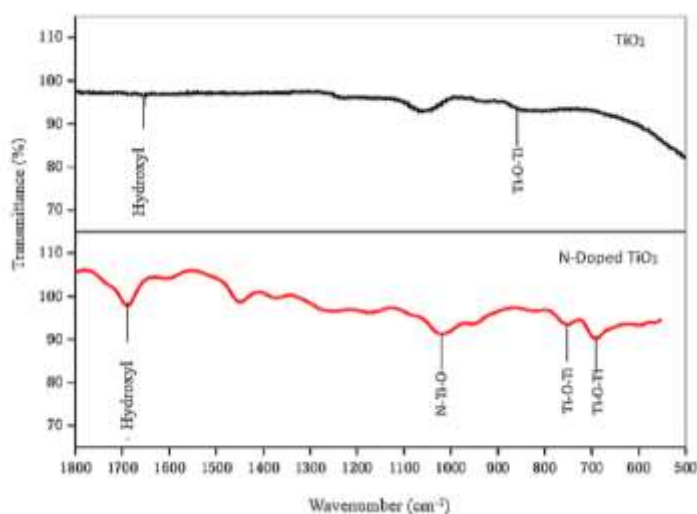


Figure 3. FTIR spectrum of TiO₂ and N-Doped TiO₂.

Based on **Figure 3**, the FTIR spectra of TiO₂ and N-doped TiO₂ were recorded in the range of 1800–500 cm⁻¹ to investigate the chemical bonds and structural modifications induced by nitrogen doping. Both samples exhibited a broad band near 1635 cm⁻¹, attributed to hydroxyl (–OH) bending vibrations, consistent with the Kadiyala et al. (2025) reported range of 1620–1640 cm⁻¹^[26]. This feature indicates the presence of surface hydroxyl groups, which can play a role in photocatalytic processes by facilitating hydroxyl radical formation.

In the N-doped TiO₂ spectrum, a distinct absorption peak appeared at 1100 cm⁻¹, which was absent in pristine TiO₂. This peak is assigned to N–Ti–O stretching vibrations, in agreement with the Dai et al. (2021) result range of 1050–1150 cm⁻¹, confirming nitrogen incorporation into the TiO₂ lattice. The incorporation likely occurs through substitutional doping, where nitrogen atoms replace oxygen in the lattice, leading to localized structural distortion^[27]. Additionally, the Ti–O–Ti stretching modes were observed at 800 cm⁻¹ and

690 cm^{-1} , consistent with Rahman et al. (2024) that the anatase phase reference range of 800–650 cm^{-1} , indicating that the fundamental crystal framework of TiO_2 remained intact after doping^[28].

The close match between the experimental peak positions and literature values across all functional groups provides robust spectroscopic evidence of successful nitrogen doping. This is further supported by the emergence of the N–Ti–O peak and the preservation of Ti–O–Ti framework vibrations, suggesting that nitrogen incorporation modified the electronic structure without compromising the anatase crystalline integrity of TiO_2 .

3.3. FESEM micrographs

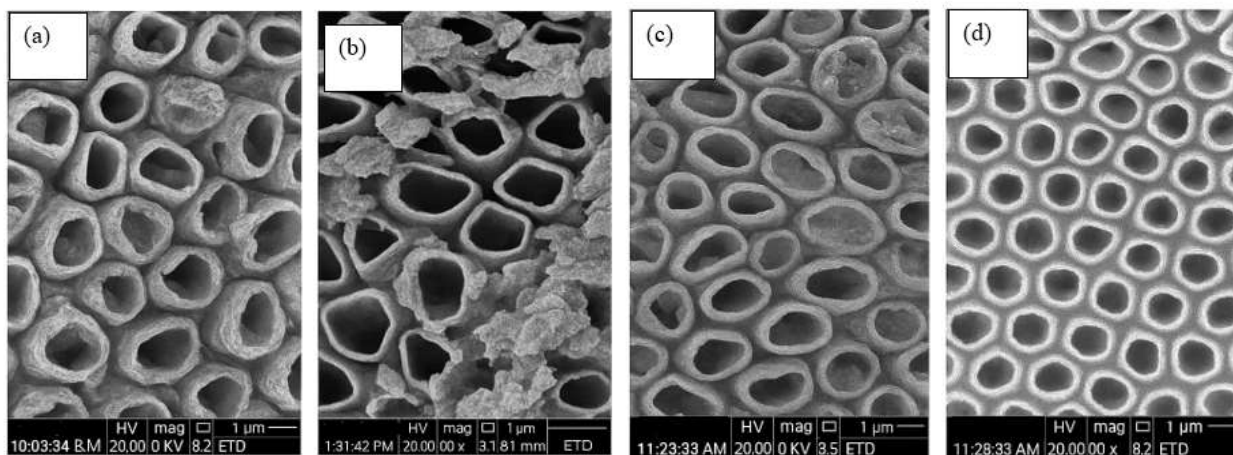


Figure 4. FESEM Photoelectrolysis of (a) TN_0 (b) TN_1 (c) TN_2 (d) TN_3 .

Figure 4 presents FESEM micrographs illustrating the morphological evolution of samples TN_0 through TN_3 . The TN_0 sample displays a compact surface with irregular and poorly distributed pores, corresponding to a relatively low specific surface area of approximately 10–20 m^2/g . This limited surface area restricts the number of accessible active sites, thereby reducing the efficiency of mass transport and charge separation during photoelectrocatalysis^[29]. In TN_1 , initial structural opening is observed, with a moderate increase in surface area to around 30–40 m^2/g , although particle agglomeration remains evident, potentially disrupting pore connectivity. A more refined and interconnected porous architecture emerges in TN_2 , characterized by a specific surface area of 50–60 m^2/g , which facilitates enhanced charge transfer and catalytic activity. The TN_3 sample exhibits the most well-organized morphology, with uniformly distributed, symmetrical, and smooth pores, yielding a high surface area of 80 m^2/g . This structural optimization is associated with improved light absorption, narrowed bandgap energy, and increased formation of reactive species, all of which contribute to superior photoelectrocatalytic performance^[30].

4. Conclusion

This study demonstrated that nitrogen doping via urea significantly enhanced the photoelectrocatalytic performance of TiO_2 for batik wastewater treatment. Among the synthesized samples, TN_3 (TiO_2 : urea = 90:10, mass ratio) exhibited the most favorable characteristics, including intense anatase crystallinity, well-preserved crystal framework, narrowed band gap (~ 2.85 eV), and optimized surface morphology with a high specific surface area (~ 80 m^2/g). These features collectively contributed to superior degradation efficiency under visible-light irradiation, outperforming other doping ratios. The results confirm that nitrogen incorporation effectively extended TiO_2 's optical response into the visible spectrum, improved charge carrier separation, and increased the availability of active sites for pollutant degradation. Future work should focus on scaling up this optimized N-doped TiO_2 system for continuous-flow and hydrodynamic reactor designs to enable real wastewater treatment applications. Additional studies should also address long-term catalyst stability,

regeneration efficiency, and performance evaluation under variable field conditions to ensure practical implementation in industrial-scale batik wastewater remediation.

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Author contributions

Concept and Supervision: Nur Qudus, Jurina Jaafar. Data Collection: Indra Sakti Pangestu, Satria Agung saputra, Nurul Padhilah Rahmawati. Manuscript Writing: Harianingsih. Proofreading: Virgiawan Adi Kristianto.

Conflict of interest

The authors declare no conflict of interest.

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