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**Peningkatan Degradasi Amoniak Menggunakan Titania Nanotube yang
Didoping Nitrogen sebagai Fotoanoda Pada Proses Fotoelektrokatalisis**

Tim Penelitian:

Dr. Tiur Elysabeth, ST., MT (Ketua)

Dr. Arifina Febriasari, S.Si., M.Sc

Euis Uswatun Hasanah, ST., MT

**PROGRAM STUDI TEKNIK KIMIA
FAKULTAS TEKNIK
UNIVERSITAS SERANG RAYA**

HALAMAN PENGESAHAN

1. **Judul Penelitian** : **Peningkatan Degradasi Amoniak Menggunakan Titania Nanotube yang Didoping Nitrogen sebagai Fotoanoda Pada Proses Fotoelektrokatalisis**
2. **Ketua**
Nama Lengkap & Gelar : Dr. Tiur Elysabeth, ST., MT
NIDN : 0403128502
Fakultas/Program Studi : Teknik / Teknik Kimia
Jabatan Fungsional/Gol. : Lektor /Penata III C
E-mail/ No. Telp. : tiurelysabeth@unsera.ac.id / 087809348097
3. **Jangka Waktu** : Maret – Juli / Tahun 2025
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Ketua Penelitian



Dr. Tiur Elysabeth, ST., MT
NIDN. 0403128502

Serang, 01 Agustus 2025

Mengetahui,

Ketua Lembaga Penelitian dan Pengabdian Masyarakat



Dr. Ing. Farid Wajdi, M.Sc
NIDN. 0419097206

IDENTITAS TIM PENELITIAN

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Peningkatan Degradasi Amoniak Menggunakan Titania Nanotube yang Didoping Nitrogen sebagai Fotoanoda Pada Proses Fotoelektrokatalisis

Ketua Tim Penelitian:

Nama Lengkap & Gelar : Dr. Tiur Elysabeth, ST., MT
NIDN : 0403128502
Bidang Ilmu : Teknik Kimia
Unit Kerja/Fakultas/Prodi : Teknik / Teknik Kimia
Instansi : Universitas Serang Raya

Anggota Tim Penelitian:

No	Nama	Bidang Ilmu	Status Dosen/Mahasiswa	NIM/NIDN
1	Dr. Arifina Febriasari, S.Si., M.Sc	Teknik Kimia	Dosen	0425028504
2	Euis Uswatun Hasanah, ST., MT	Teknik Kimia	Dosen	0420129002

Enhanced Ammonia Degradation Using N Doped Titania Nanotubes as Photoanode: Photoelectrocatalytic Approach

Tiur Elysabeth^{1,a}, Arifina Febriasari¹, Euis Uswatun Hasanah¹

¹ Department of Chemical Engineering, Faculty of Engineering, Universitas Serang Raya, Serang 42162, Indonesia

^{a)}Corresponding author: tiurelysabeth@unsera.ac.id

Abstract. The application of nitrogen-doped titania nanotube arrays (N-TiNTAs) as photoanodes for the photoelectrocatalytic elimination of ammonia has been thoroughly investigated. These photoanodes were fabricated using a straightforward one-step anodization procedure, where titanium foil was anodized in an electrolyte solution composed of urea (as the nitrogen donor), ammonium fluoride, distilled water, and glycerol, maintained at a constant voltage of 50 V for two hours. The fabricated nanotube arrays were then subjected to thermal annealing at 500 °C for three hours under a continuous flow of nitrogen gas at 60 mL/min. Structural examination through FESEM revealed the presence of highly organized nanotubular formations. XRD analysis demonstrated that the anatase phase predominates under these annealing conditions. In addition, UV-Vis DRS measurements indicated that the optical band gap of the N-TiNTAs is narrower than that of the undoped TiO₂ nanotubes, implying improved light harvesting. Under optimal experimental conditions, an ammonia removal efficiency as high as 61.41% was achieved, highlighting the effectiveness of N-TiNTAs as promising photoanodes for advanced wastewater treatment technologies.

INTRODUCTION

The rapid expansion of the industrial sector across various fields has led to significant environmental challenges. One of the notable consequences is ammonia pollution. The presence of ammonia in the environment contributes to eutrophication, resulting in uncontrolled growth of aquatic plants and disruption of ecological balance [1]. In industrial settings, acute exposure to high ammonia levels can result in severe injuries, while chronic exposure is associated with various pulmonary symptoms [2]. Ammonia emissions, primarily from farming and animal husbandry, contribute to chronic lung diseases, inflammation of airways, and irritation of eyes, sinuses, and skin. Additionally, ammonia plays a role in forming secondary particulate matter, further impacting human health and the environment [3].

Photocatalysis is considered one of the simplest and most environmentally friendly techniques for pollutant degradation. However, its effectiveness is often hindered by the high rate of electron-hole recombination. This limitation can be addressed by combining photocatalysis with electrochemical processes, forming a method known as photoelectrocatalytic. Titanium dioxide nanotube arrays have shown promising potential as photoanodes in photoelectrocatalytic (PEC) processes for water treatment and hydrogen generation. These nanostructures offer large surface areas and efficient electron transport pathways, enhancing photocatalytic activity [4, 5]. The structural parameters of TiO₂ nanotubes, such as tube length and morphology, significantly influence their PEC performance [4]. PEC processes demonstrate superior degradation efficiency compared to photocatalysis or electrolysis alone, as they effectively reduce electron-hole pair recombination [5]. The PEC activity of TiO₂ nanotube arrays can be further improved by optimizing electrolyte composition, pH, and the presence of organic additives. These findings highlight the potential of TiO₂ nanotube-based photoelectrocatalysis for environmental applications.

Nitrogen doping is an effective method to enhance the photoelectrochemical performance of TiO₂ nanotube arrays by shifting their absorbance to larger wavelengths [6]. Various techniques have been employed for N-doping,

including immersion in urea solution followed by annealing [7], electrochemical doping using amine solutions [8], and ammonia treatment at high temperatures [9]. These methods successfully introduce nitrogen atoms into the TiO_2 structure without affecting its morphology, resulting in narrower band gaps and improved visible light responsiveness. The photoconversion efficiency of N- TiO_2 can increase by up to 19% compared to pristine TiO_2 [7]. The thickness of the nanotube layers also plays a crucial role in determining the magnitude of photoresponse under both UV and visible light irradiation [9]. Overall, N-doping of TiO_2 nanotube offers a simple, cost-effective, and environmentally friendly approach to enhance their photoelectrochemical properties.

The present study aims to enhance the photoelectrocatalytic degradation of ammonia through the use of nitrogen-doped titania nanotube arrays. A comparative evaluation will be conducted between undoped and doped titania nanotubes to determine their relative degradation efficiencies. Furthermore, the study will analyze and contrast the effectiveness of photocatalytic and photoelectrocatalytic processes under the same conditions.

EXPERIMENTAL

Synthesis of Nitrogen-Doped Titania Nanotube Arrays (N-TiNTAs)

The titanium foil ($3.0\text{ cm} \times 2.0\text{ cm}$) was initially subjected to surface refinement through mechanical polishing with sandpaper, followed by chemical etching in a ternary solution comprising hydrofluoric acid, nitric acid, and distilled water in a volumetric ratio of 1:3:6 for 2 minutes. Post-treatment, the foil was thoroughly rinsed with distilled water and dried under ambient conditions. The formation of amorphous nitrogen-doped TiO_2 nanotube arrays (N-TiNTAs) was subsequently achieved via a one-step anodic oxidation technique, employing a 60 mL electrolyte composed of glycerol, 0.5 wt% ammonium fluoride, 25 wt% distilled water, and 0.2 wt% urea as the nitrogen source. Anodization was conducted at a constant applied potential of 50 V for a duration of 2 hours, using a two-electrode configuration powered by a direct current (DC) supply, wherein the titanium foil functioned as the working electrode (anode) and platinum foil as the counter electrode (cathode). Throughout the anodization process, continuous magnetic stirring was employed to ensure electrolyte homogeneity and process consistency.

Characterization of N-TiNTAs

The morphological characteristics of the synthesized N- TiO_2 were investigated utilizing Field Emission Scanning Electron Microscopy (FESEM, JEOL JIB-4610F). Optical bandgap energy was evaluated by means of UV-Visible Diffuse Reflectance Spectroscopy (UV-DRS, Agilent Technologies Cary 60) within the wavelength range of 300–800 nm, and the corresponding bandgap values were derived using the Kubelka–Munk transformation. The phase composition and crystalline structure were characterized via X-ray Diffraction (XRD, Shimadzu 7000 Maxima-X) employing $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$), operated at an accelerating voltage of 40 kV and a current of 30 mA. Diffraction patterns were recorded over a 2θ range of 10° to 80° , with a scanning speed of 2° per minute.

Photoelectrocatalytic Degradation of Ammonia

Photoelectrocatalytic degradation experiments were performed in a photoelectrochemical (PEC) system, utilizing a 250 mL Pyrex reactor equipped with quartz windows, a Nafion membrane, and a magnetic stirrer to ensure solution homogeneity. Illumination was provided by a mercury lamp, with the entire setup housed within a reflective enclosure to optimize light distribution. A platinum plate was employed as the counter electrode. Ammonia concentration was quantitatively monitored at 30-minute intervals using a UV-Visible spectrophotometer (Thermo Scientific Genesys 10).

RESULTS AND DISCUSSION

Effect of nitrogen doping on titania nanotube arrays properties

Figure 1 displays the FESEM micrographs of unmodified TiO₂ and nitrogen-doped TiO₂ (N-TiNTAs) samples prepared with varying amounts of urea as the nitrogen precursor. As reported in our previous study, nitrogen doping does not significantly alter the nanotube structure, although a surface layer presumably composed of nitrogen species was observed to accumulate [10]. The formation of nanotube arrays on the titanium substrate is governed by a competitive mechanism between the growth of the oxide layer and its chemical dissolution [11].

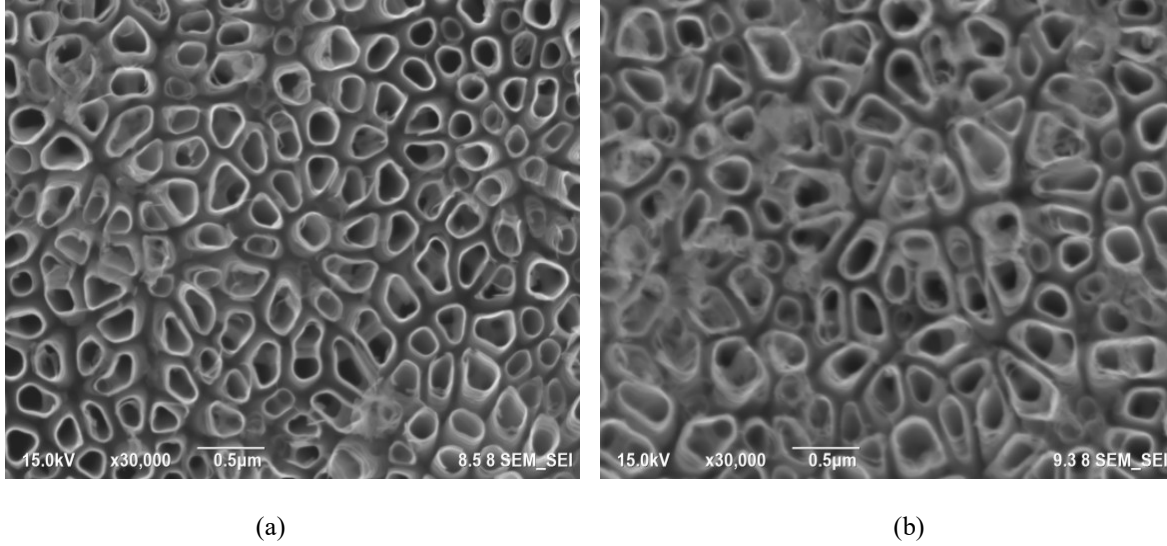


FIGURE 1. FESEM top image of (a) TiNTAs, (b) N-TiNTAs

X-ray diffraction (XRD) analysis was employed to investigate the crystal structure of titania nanotubes and to assess the influence of nitrogen incorporation on their original crystalline characteristics. As depicted in Figure 2, the XRD pattern of N-TiNTAs samples annealed at 500 °C reveals six prominent peaks located at 2θ values of 25.3°, 37.9°, 48.4°, 54.04°, 70.65°, and 76.20°, which correspond to the (101), (004), (200), (105), (220), and (215) planes of anatase-phase TiO₂, consistent with JCPDS card No. 21-1272 [12, 13]. Although nitrogen atoms are incorporated into the TiO₂ nanotube framework, their presence does not produce distinct diffraction signals, likely due to their uniform and minimal distribution within the lattice [14, 15]. Nitrogen doping influences the crystallite size, increasing it from 27.06 nm in pristine TiO₂ to 37.32 nm in N-TiNTAs. This size enhancement is attributed to the shift in diffraction peaks toward lower angles, which suggests the presence of lattice distortion and strain induced by nitrogen incorporation. Recent work by Ocampo-Gaspar et al. (2025) demonstrated that substitutional N-doping of TiO₂ nanoparticles (≈1 %) increased the average crystallite size from ~13.3 nm to ~15.2 nm, accompanied by a shift in the (101) and (200) diffraction peaks toward higher 2θ values evidence of lattice distortion induced by nitrogen incorporation [16]. Other studies similarly report broadening of XRD peaks and variations in crystallite size depending on doping levels, consistent with the presence of internal strain in the TiO₂ lattice [17]. The Debye–Scherrer equation was utilized to determine the crystallite size [18].

$$L = \frac{0.9 \lambda}{(\beta \cos \theta)} \quad (\text{Equation 1})$$

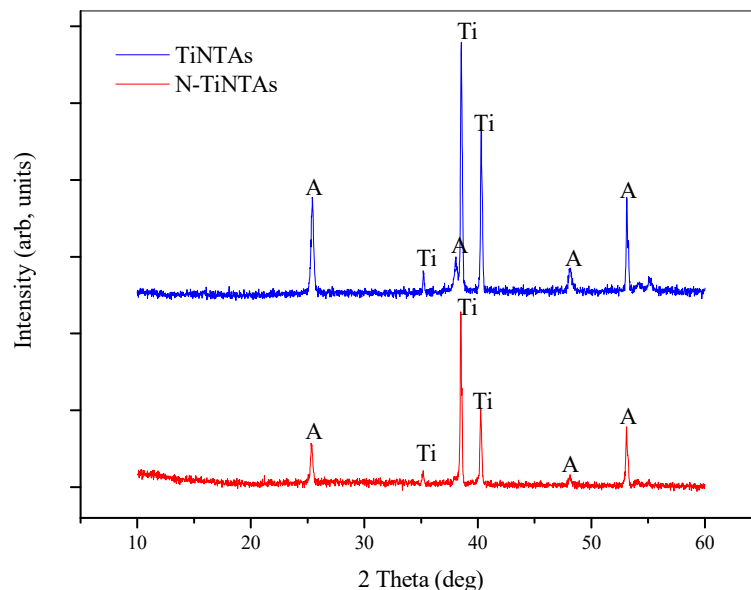


FIGURE 2. XRD patterns of titania nanotube arrays

UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) was employed to evaluate the optical absorption behavior of the samples within the 300–800 nm wavelength range. As illustrated in Figure 3, the introduction of nitrogen and nickel dopants influences the light absorption properties, with N-doped samples exhibiting a noticeable red shift in absorption. The bandgap energies of the photocatalysts were estimated using the Kubelka–Munk function in combination with Tauc plot analysis [19], and the calculated values are summarized in Table 1. The undoped TiO_2 nanotube displays a bandgap of 3.17 eV, which is marginally lower than the standard anatase value of 3.20 eV. This slight narrowing may result from incidental nitrogen incorporation originating from ammonium fluoride during the anodization process. A more significant reduction in bandgap is observed for N-TiNTAs where nitrogen is intentionally introduced through urea addition. Previous studies have attributed this bandgap narrowing to the formation of N–Ti–O bonds, which cause an upward shift in the valence band, thereby reducing the energy gap [20].

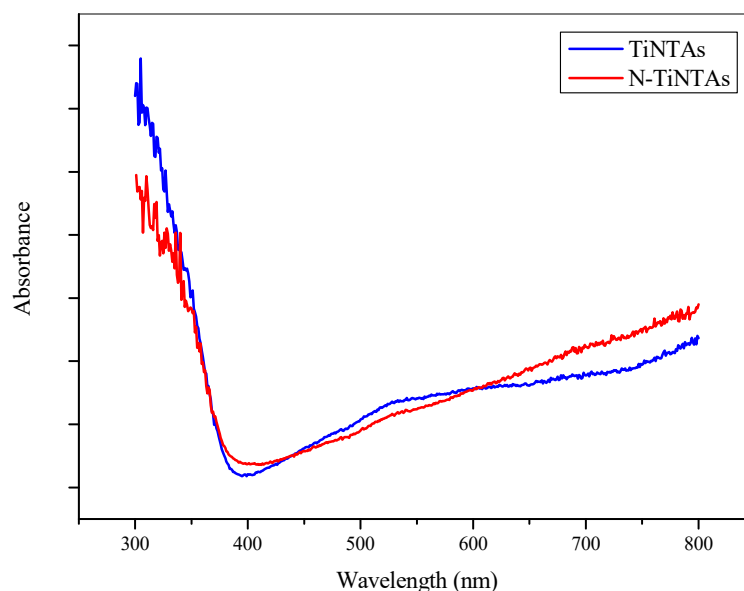


FIGURE 3. UV-DRS reflectance spectrum of the photocatalyst

TABLE 1. Bandgap energy of titania nanotube arrays

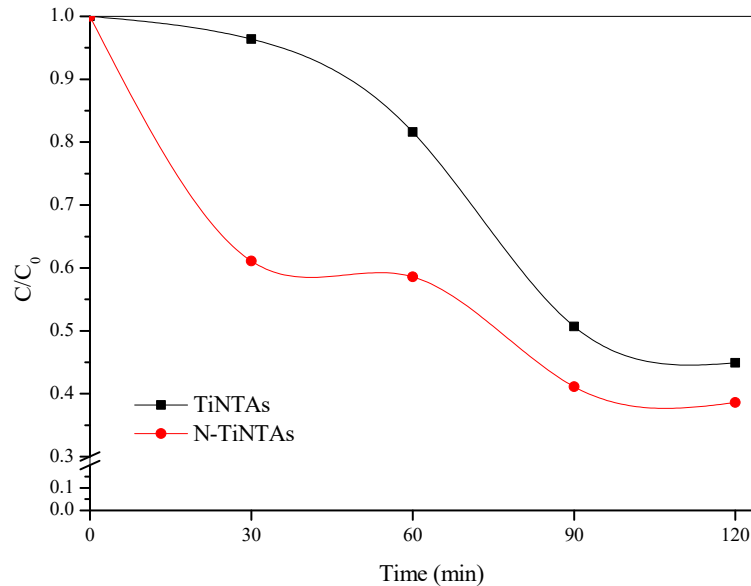
Sample	EG (eV)
TiNTAs	3.17
N-TiNTAs	2.89

Ammonia degradation performance test

The ammonia degradation experiment was conducted in a photoelectrochemical system comprising two electrodes: a photoanode based on titania nanotubes and a platinum plate serving as the cathode. The initial ammonia concentration was set at 500 mg/L, and the system was irradiated using a mercury lamp for 120 minutes. This section evaluates the efficiency of the photoelectrocatalytic degradation of ammonia using two types of photoanodes: undoped titania nanotubes (TiNTAs) and nitrogen-doped titania nanotubes (N-TiNTAs). Additionally, a comparison is made between the photocatalytic and photoelectrocatalytic performances using the same photoanodes.

Figure 4 illustrates the photoelectrocatalytic performance of TiNTAs and N-TiNTAs in degrading ammonia. The data reveal that N-TiNTAs demonstrate superior degradation capability compared to TiNTAs. This enhanced activity is attributed to the narrower bandgap of N-TiNTAs, which leads to improved photocurrent generation under both UV and visible light. The increase in photocurrent facilitates the excitation of electrons from the valence band to the conduction band. These excited electrons are transferred to the cathode, thereby minimizing electron-hole recombination. The remaining holes in the valence band are then available to produce hydroxyl radicals ($\bullet\text{OH}$), which are crucial for the oxidative degradation of ammonia [21, 22]

Conversely, the trend is reversed under purely photocatalytic conditions as depicted in Figure 5, where TiNTAs outperform N-TiNTAs. Although nitrogen doping effectively narrows the bandgap and enhances visible-light absorption, it also increases the likelihood of electron recombination with holes. This recombination reduces the availability of holes to form hydroxyl radicals, thereby diminishing the photocatalytic degradation efficiency of ammonia.

**FIGURE 4.** Photoelectrocatalytic degradation of NH_3 using undoped and doped titania nanotubes

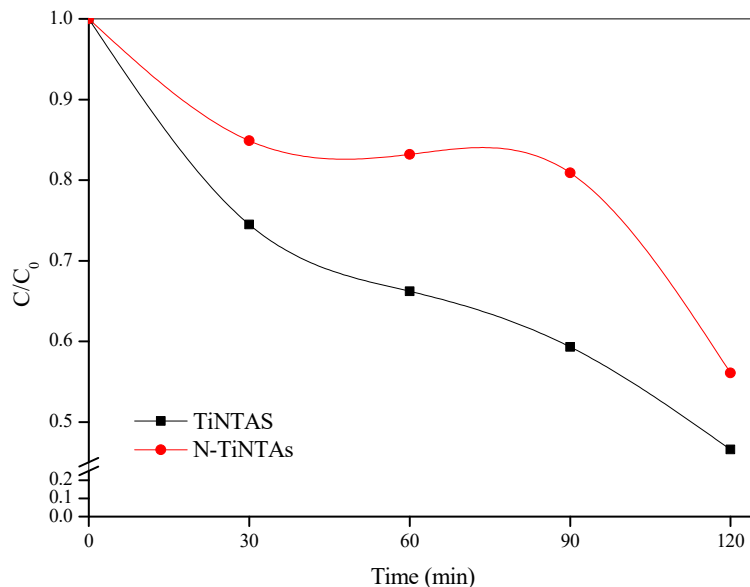


FIGURE 5. Photocatalytic degradation of NH₃ using undoped and doped titania nanotubes

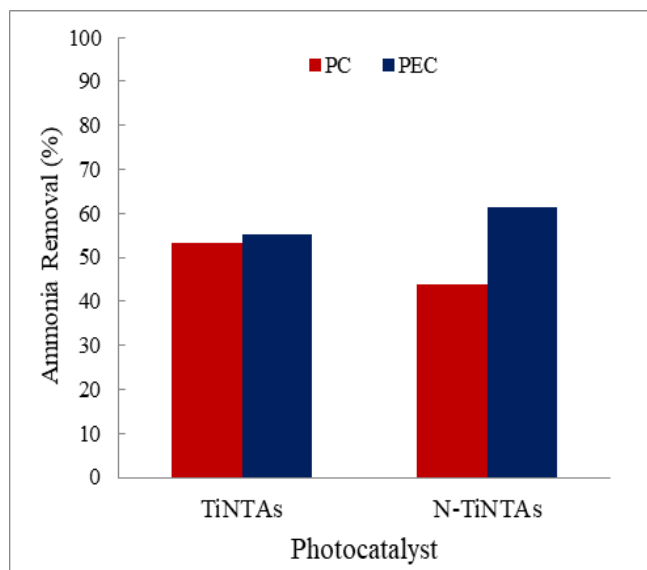
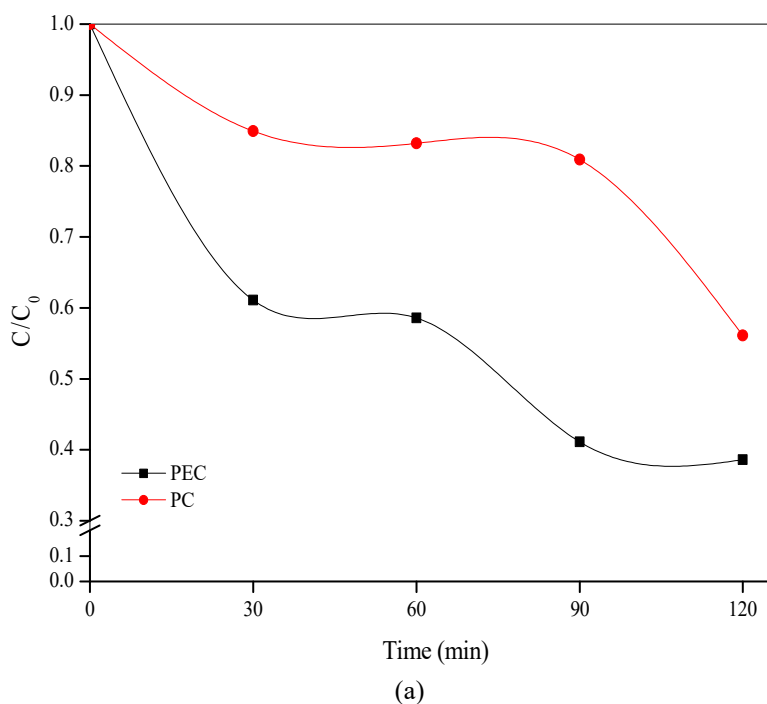


FIGURE 6. Photocatalytic and photoelectrocatalytic degradation of ammonia over TiNTAs and N-TiNTAs: (a) relative concentration of ammonia and (b) ammonia removal

Photocatalytic (PC) and photoelectrocatalytic (PEC) degradation of ammonia were conducted in the absence of a supporting electrolyte. As illustrated in Figure 6(b), variations in the relative concentration and ammonia removal indicate that PEC treatment using TiNTAs achieved a removal efficiency of up to 55.11%, which is approximately 2% higher than that of the PC process. The PEC process also demonstrated improved ammonia removal for the N-

TiNTAs photoanode compared to its PC counterpart. These findings suggest that PEC offers superior degradation efficiency for both types of photoanodes, likely due to a synergistic effect involved in the PEC mechanism. In contrast, the PC process is limited by a high rate of electron-hole recombination, which hampers overall efficiency. This limitation can be mitigated by applying a PEC approach, which enhances charge carrier separation and utilization, thereby improving the degradation performance [23-25]

Summary

In this study, nitrogen-doped titania nanotube arrays were successfully synthesized through a one-step anodization method combined with in-situ nitrogen doping using urea as a nitrogen precursor. The anodized samples were subsequently annealed under nitrogen atmosphere to ensure effective incorporation of nitrogen into the TiO₂ lattice. Optical analysis confirmed a significant bandgap narrowing as a result of nitrogen doping, which enhanced the light absorption properties of the material. When applied as a photoanode in the photoelectrocatalytic degradation of ammonia, the N-TiNTAs demonstrated superior performance, achieving a high removal efficiency of 61.41%. These findings highlight the potential of the synthesized N-TiNTAs as a promising material for efficient photoelectrocatalytic treatment of ammonia-containing wastewater.

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