Effect of urea loading on the anodic synthesis of titania nanotube arrays photoanode to enhance photoelectrochemical performance

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Abstract. The development of efficient photoanode to improve the photoelectrochemical performance under UV light was investigated. The nitrogen-doped titania nanotube array was prepared by one step anodic oxidation of titanium foil in a solution of electrolyte-containing urea as nitrogen precursor at 50 V for 2h. During the process, the urea was added to the electrolyte solution with different concentrations, 0.1%, 0.2%, and 0.4% based on the weight of electrolyte that containing 25% water, 0.5% ammonium fluoride, and glycerol. The synthesis was followed by annealing at 500°C for 3h under 60ml/min of N2 gas to induce the crystalline phase. SEM analysis showed that titania nanotube was successfully synthesized with average diameter is 72 - 153 nm. Refer to XRD analysis titania nanotube mostly have anatase phase with the crystallite size of 27-37 nm depending on loading of urea. Bandgap energy was determined by UV-DRS analysis and showed that nitrogen-doped titania nanotube arrays have smaller bandgap energy. The photoelectrochemical responses of titania nanotube before and after nitrogen doping were examined by linear sweep voltammetry method. Photocurrent density measurements showed better activity on nitrogen-doped titania nanotube. Nitrogen-doped titania nanotube caused the flatband potential shifted to a negative value and the smaller space charge layer, resulting in the higher photocurrent density and photoconversion efficiency.

Keywords: Photoelectrochemical, Urea loading, Photoanode, Titania nanotube

1. Introduction
Anodization is one of an interesting method for synthesizing titania nanotube. This method is due to the unique structure of the titania nanotubes formed. Besides, a large surface area, better adsorption capacity, and unidirectional charge transfer [1] also make the synthesis of titania nanotubes with this method more widely used for recent years. Highly ordered titania nanotube arrays (TiNTAs) possess excellent photocatalytic properties and high photoconversion efficiency [2]. Because of these attractive features, TiNTAs are often used in various applications, including photocatalysts [3-6], solar cell system [7, 8], and photoanodes in various photoelectrocatalytic process [9-11]. However, the use of titania
nanotube still has disadvantages, including large bandgap energy and a high rate of electron-hole recombination. These two significant factors lead to low quantum yields, and titania nanotube could be active in UV light region.

One of the most popular methods of shift the absorbance of TiNTAs to larger wavelength and simultaneously photoelectrochemical performance is modified TiNTAs by doping nonmetal atoms. Several methods for doping nonmetal atoms into TiNTAs structure have been investigated by many researchers. Among the many types of nonmetal dopants that were studied, nitrogen is the most effective because of oxygen and nitrogen has a similar chemical, structural, electronegativity, coordination number, and ionic radii [12]. The hybridization of O 2p and N 2p orbitals forms the new energy level above the valence band, thus narrowing the bandgap energy and increasing the activity of TiNTAs under visible light [13]. If nitrogen-doped titania nanotube arrays (N-TiNTAs) are irradiated under UV light, the nitrogen atom can act as an electron trapper, thus prevent electron-hole recombination [14]. Nitrogen doping can shift the flatband potential in a more negative direction [15] and increase the photocurrent response under both visible and UV light [10]. The application of nitrogen dopants to titania nanotubes arrays has been carried out in various methods including chemical deposition, ion implantation, one step anodization of titania plate using electrolyte-containing nitrogen precursors, and annealing with ammonia gas at high and low temperatures[3]. The process of doping nitrogen in situ during the anodization process is a popular method because it can produce N doped titania nanotube arrays directly at low temperatures, thereby reducing production costs [3].

Herein, we present one-step anodization to synthesis nitrogen-doped titania nanotube arrays (N-TiNTAs). The titanium foil was anodized using an electrolyte solution containing urea as a nitrogen precursor at potential 50V for 2h and followed by annealing process under 60 ml/min N₂ gas flow at 500°C for 3h. The studies concerning the morphology, structure, and shifting of the diffuse reflectance spectrum of TiNTAs before and after doped by nitrogen. The photoelectrochemical properties were examined using linear sweep voltammetry method to obtain the changes of photocurrent density, flatband potential, space charge layer, and photoconversion efficiency of TiNTAs. The present research is related to our previous work [16].

2. Experimental

2.1. Material

Titanium foils with a purity of 99.6% and sandpaper 1500 grits were applied for mechanical polished. HNO₃ (Merck, 65%), HF (Merck, 40%), and aquadest were applied for chemical polished. The electrolyte solution was containing glycerol (Brataco), 0.5% wt NH₄F (Merck, 98%), and 25%wt aquadest. Urea (Merck, P.A) was applied as a precursor of nitrogen and N₂ for annealing gas. Na₂SO₄ 1M was used as an electrolyte solution in the photoelectrochemical test.

2.2. Synthesis of nitrogen-doped titania nanotube (N-TNTAs)

Mechanically polished of the Ti foil (3.0 cm x 2.0 cm) with sandpapers, then it was chemically polished in the mix solution of hydrofluoric acid, nitric acid and water (1: 3: 6) for 2 min. Then, Ti foil was rinsed with aquadest and dried at ambient temperature. The nitrogen-doped titania nanotube array was synthesized by anodic oxidation of titanium foil in 60 ml electrolyte solution that containing glycerol, 0.5 wt% ammonium fluoride, 25 wt% aquadest and loading of urea (0.1 wt%, 0.2 wt%, and 0.4 wt%). This method was conducted at a potential of 50 V for 2 h by using a DC power supply with magnetically stirring and used the two-electrode system, Ti foil as anode and Pt foil as a cathode. After that, the sample was rinsed with aquadest and followed by annealing process at a temperature of 500
° C for 3 hours under 60ml/min N₂ gas to induce the crystalline phase. After that, it was naturally cooled to the room temperature.

2.3. Characterization of undoped and nitrogen-doped titania nanotube

The TiNTAs and N-TiNTAs morphology analysis were determined by Scanning Electron Microscope, SEM (ZEISS) using accelerating voltage 20 kV. The crystal structure of TNTAs was observed by Shimadzu X-ray Diffractometer (XRD) 7000 Maxima-X type with the scan rate at 2° min⁻¹ over the scan range 10-80° and it was operated at 40 kV, and 30 mA with the source of X-ray radiation was Cu Nía (λ=0.15406 nm). The size of crystallite was estimated from FWHM (full width at half maximum) by Debye-Scherrer equation. The shifting of the diffuse reflectance spectrum was determined by UV diffuse reflectance spectroscopy (UV-DRS) using Spectrophotometer Shimadzu UV 2450 type in a wavelength range of 200-800 nm.

2.4. Determination of photoelectrochemical properties

The photoelectrochemical properties were examined using a photoelectrochemical cell with three-electrode. TiNTAs and N-TiNTAs were used as a working electrode, a platinum foil as the counter electrode, and Ag/AgCl as a reference electrode in saturated KCl. The photoelectrochemical cell consists of a cylindrical vessel which was completed by 11 Watt UV Blacklight and Na₂SO₄ 1M as a solution of electrolyte. The photoelectrochemical performance was measured using a scanning potentiostat (eDAQ, version 9.1). Measurement of photocurrent density was conducted by linear sweep voltammetry method with potentiodynamic scan from -1.0 V to 1.0 V at a scan rate of 25 mV s⁻¹.

![Figure 1. Scheme of the photoelectrochemical cell](image-url)

3. Results and discussion

3.1. Morphology, crystallography, and optical properties of nitrogen-doped titania nanotube arrays

The structures of nanotube arrays on the surface on titanium substrates depends on competition reaction of oxidation layer formation and chemical dissolution [17]. The SEM characterization was carried out to prove the morphology of titania remains in the
nanotube form, and it does not change even though urea was added as a nitrogen precursor. The morphology of nitrogen-doped TiNTAs can be compared with undoped TiNTAs as presented in Fig. 2. As shown in the figure, there is no change in morphology. It shows that the nanotubular structures can sustain from the impact of doping and thermal treatment, even the surface of N-TiNTAs is covered by a layer that is predicted to be the amount of nitrogen that has accumulated on the surface area. The mean size inner diameter for TiNTAs is 96 – 160 nm and for N-TiNTAs is 72 – 153 nm. The inner diameter of N-TiNTAs is smaller than TiNTAs.

The effect of nitrogen-doped on TiNTAs crystallography is shown in Fig. 3. The figure showed that TiNTAs and N-TiNTAs have 100% anatase phase. The undoped TiNTAs and N-TiNTAs structures show identical patterns. This structure is due to the amount of N atom entering the matrix was too small, and the atoms were dispersed evenly. Thus it did not affect the crystal structure formation. The similar results obtained by Luo et al. [18]. However, the urea concentration affected the crystallite size. The crystallite size for TiNTAs is 27.06 nm, N-TiNTAs$^1$ (0.1% urea) is 33.05 nm, N-TiNTAs$^2$ (0.2% urea) is 37.32 nm, and N-TiNTAs$^3$ (0.4% urea) is 36.89 nm. Nitrogen doping level has a significant effect on the growth of titanium oxide particle size during the doping process. It is due to the shifting of diffraction peak to smaller angles, which are related to distortion and strain in the crystal structure due to the incorporation of nitrogen atoms [19]. Debye-Scherrer equations could be used for calculating the crystallite size, as follow [20]:

$$L = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where L is crystallite size (nm), $\lambda$ is a wavelength of X-ray radiation (nm), $\beta$ is full width at half maximum (rad), and $\theta$ is diffraction angle (degree).

The nitrogen doping effect on the light absorption of TiNTAs is shown in Fig. 4. In the picture, the diffuse reflectance spectrum of N-TiNTAs shifted to a higher wavelength. It

![Figure 2. SEM images of (a) TNTAs, (b) N-TNTAs$^1$ (0.1% urea), (c) N-TNTAs$^2$ (0.2%urea) and (d) N-TNTAs$^3$ (0.4%urea)](image)
showed that nitrogen atoms could enter the matrix of TiNTAs and formed N-Ti-O bond. It resulted in an increase in energy level on the valence band and narrowing the bandgap energy [13]. Diffuse reflectance spectrum data could be converted according to Kubelka Munk function where $F(R) = (1-R)^{2}/2R$, $R =$ reflectance and $F(R)$ proportional to the absorption coefficient. From the data of UV diffuse reflectance spectrum, bandgap energy of TiNTAs, N-TiNTAs$^1$ (0.1% urea), N-TiNTAs$^2$ (0.2% urea), and N-TiNTAs$^3$ (0.4% urea) can be calculated to be 3.12, 3.08, 2.84, and 3.04 eV, as reported in our previous report [16].

**Figure 3.** XRD patterns of (a) TiNTAs, (b) N-TiNTAs$^1$ (0.1% urea), (c) N-TiNTAs$^2$ (0.2% urea) and (d) N-TiNTAs$^3$ (0.4% urea)

**Figure 4.** UV-DRS reflectance spectrum of the TiNTAs and N-TiNTAs
3.2. Photoelectrochemical Measurement

Study of the photoelectrochemical properties of titania nanotube arrays synthesized with nitrogen doping can be seen from the photocurrent density relationship to the bias potential measured using the linear sweep voltammetry method at a scan rate of 20 mV/s of -1.0 to 1.0 V (vs. Ag/AgCl). The photocurrent density increased with increasing bias potential and subsequently shows a stable photocurrent density, which curves shape according to an n-type semiconductor. Figure 5 shows that nitrogen doping significantly affected the TiNTAs electrode. Photocurrent density increased with increasing urea content as a nitrogen precursor in TiNTAs. These results implied that nitrogen doping could improve photoelectrochemical performance. Maximum photocurrent density was obtained under the condition of N-TiNTAs² with 0.2% urea. However, photocurrent density decreases at N-TiNTAs³ with 0.4%. It is predicted because of the higher concentration of urea, the larger size of the molecule; thus, the diffusion rate was lower. The low diffusion rate caused the decreasing in the number of N entered the TiNTAs matrix; thus it accumulated on the surface area as impurities and affected the light irradiation process.

One factor that influences the process of charge carrier is the space charge layer which generated at the semiconductor – electrolyte interface. The space charge layer could be calculated using the equation below [21]:

\[ d_{sc} = \sqrt{\frac{\varepsilon_0 \varepsilon \left(U - U_{fb}\right)}{q N_D}} \]  

Where \( \varepsilon \) is material dielectric constant, \( \varepsilon_0 \) is vacuum dielectric constant (8.85 x 10^{-12} F/m), U is a bias potential, \( U_{fb} \) is flatband potential, q is electron charge (1.602 x 10^{-19} C), and \( N_D \) is donor density. The parameters used for the calculation are the value of \( \varepsilon \) and \( N_D \) obtained from literature 85 and 6 x 10^{19} cm^{-3}, respectively. Flatband potential derived from potential value where the photocurrent signal was first observed on a voltammogram, theoretically it is proportional to semiconductor flatband potential. Table 1 shows that the addition of 0.2% urea to titania nanotube arrays has the smallest space charge layer. The lower space charge layer improved the carrier charge on the interface. Thus electron collecting process in the external circuit increased that indicated by increasing photocurrent density.

| Urea concentration (%) | Flatband potential, \( U_{fb} \) (V) | Steady-state potential, U (V) | Space charge layer, \( d_{sc} \) (nm) |
|------------------------|--------------------------------------|-------------------------------|-----------------------------------|
| 0                      | -0.788                               | -0.324                        | 8.524                             |
| 0.1                    | -0.888                               | -0.426                        | 8.506                             |
| 0.2                    | -0.906                               | -0.468                        | 8.282                             |
| 0.4                    | -0.840                               | -0.044                        | 11.165                            |

Photoconversion efficiency of titania nanotube arrays states the ability of light energy to chemical energy conversion, in this case, is the formation of hydrogen gas. Photoconversion efficiency was calculated through the following equation [22]:

\[ \eta(\%) = \frac{J_P \left[ \left( E_{rev}^0 - E_{app} \right) / I_{light} \right]}{x100} \]  

Where \( \eta \) is photoconversion efficiency, \( J_P \) is photocurrent density (mA/cm²), \( E_{rev}^0 \) is standard potential for water splitting (1.23V/NHE), \( E_{app} \) is the applied potential (vs. Ag/AgCl), and \( I_{light} \) is light intensity. Photoconversion efficiency vs. the applied potential graph is shown in Fig. 6. The N-TiNTAs² (0.2% urea) showed the maximum photoconversion efficiencies (7.21%) at -0.612V vs Ag/AgCl.
Figure 5. Photocurrent density vs potential in electrolyte solution 1M Na$_2$SO$_4$ used UV black light 11W for titania nanotube with urea concentration variation (a) TiNTAs, (b) N-TiNTAs$^1$ (0.1% urea), (c) N-TiNTAs$^2$ (0.2% urea), and (d) N-TiNTAs$^3$ (0.4% urea).

Figure 6. Photoconversion efficiency vs. for titania nanotube with urea concentration variation.
4. Conclusion
In summary, the nitrogen-doped titania nanotube arrays were synthesized by one step anodic oxidation method. The morphology was observed by SEM, and the results showed that N-TiNTAs were successful with inner diameter is 72 - 153 nm. XRD analysis showed the titania nanotube mostly have anatase phase with the crystallite size of 27-37 nm depending on the loading of urea. UV-DRS result showed that the bandgap energy decreased on N-TiNTAs with 0.2% urea addition. Photocurrent density measurements showed better activity on N-TiNTAs. Maximum photocurrent density was obtained under the condition of N-TiNTAs with 0.2% urea. However, photocurrent density decreases at N-TiNTAs with 0.4%. The N-TiNTAs (0.2% urea) showed the maximum efficiencies of 7.21% at -0.612V vs. Ag/AgCl and the smallest space charge layer.

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References
1. Lee K, Mazare A, Schmuki P 2014 Chemical Reviews 114 9385-454. doi:10.1021/cr500061m.
2. Smith YR, Ray RS, Carlson K, Sarma B, Misra M 2013 Materials 6 2892-957 PubMed PMID: doi:10.3390/ma6072892.
3. Mazierski P, Nischk M, Gołkowska M, Lisowski W, Gazda M, Winiarski MJ, et al. 2016 Applied Catalysis B: Environmental 196 77-88. https://doi.org/10.1016/j.apcatb.2016.05.006.
4. Ratnawati, Gunlazuardi J, Dewi EL, Slamet 2014 International Journal of Hydrogen Energy 39 16927-35. https://doi.org/10.1016/j.ijhydene.2014.07.178.
5. Xu S, Du AJ, Liu J, Ng J, Sun DD 2011 International Journal of Hydrogen Energy 36 6560-8. https://doi.org/10.1016/j.ijhydene.2011.02.103.
6. Zhang X, Wang L, Liu C, Ding Y, Zhang S, Zeng Y, et al. 2016 Journal of Hazardous Materials 313 244-52. https://doi.org/10.1016/j.jhazmat.2016.03.094.
7. Sarkar A, Singh AK, Sarkar D, Khan GG, Mandal K 2015 ACS Sustainable Chemistry & Engineering 3 2254-63. doi:10.1021/acssuschemeng.5b00519.
8. Subramanian A, Wang H-W 2012 Applied Surface Science 258 6479-84. https://doi.org/10.1016/j.apsusc.2012.03.064.
9. Cho IS, Choi J, Zhang K, Kim SJ, Jeong MJ, Cai L, et al. 2015 Nano Letters 15 5709-15. 10.1021/acs.nanolett.5b01406.
10. Georgieva J, Valova E, Armyanov S, Tatchev D, Sotiropoulos S, Avramova I, et al. 2017 Applied Surface Science 413 284-91. https://doi.org/10.1016/j.apsusc.2017.04.055.
11. Zhang L, Cao H, Pen Q, Wu L, Hou G, Tang Y, et al. 2018 Electrochimica Acta 283 1507-13. https://doi.org/10.1016/j.electacta.2018.07.072.
12. Chen X, Burda C 2008 Journal of the American Chemical Society 130 5018-9. doi:10.1021/ja711023z.
13. Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y 2001 science 293 269-71.
14. Asahi R, Morikawa T, Irie H, Ohwaki T 2014 *Chemical Reviews* **114** 9824-52. doi:10.1021/cr5000738.
15. Peighambardoust NS, Khameneh Asl S, Mohammadpour R, Asl SK 2018 *Electrochimica Acta* **270** 245-55. https://doi.org/10.1016/j.electacta.2018.03.091.
16. Elysabeth T, Slamet, Sri Redjeki A 2019 *IOP Conference Series: Materials Science and Engineering* **509** 012144. 10.1088/1757-899x/509/1/012144.
17. Liang H-c, Li X-z 2009 *Journal of Hazardous Materials* **162** 1415-22. https://doi.org/10.1016/j.jhazmat.2008.06.033.
18. Luo N, Jiang Z, Shi H, Cao F, Xiao T, Edwards PP 2009 *International Journal of Hydrogen Energy* **34** 125-9. https://doi.org/10.1016/j.ijhydene.2008.09.097.
19. Boningari T, Inturi SNR, Suidan M, Smirniotis PG 2018 *Chemical Engineering Journal* **350** 324-34. https://doi.org/10.1016/j.cej.2018.05.122.
20. Wu H, Zhang Z 2011 *International Journal of Hydrogen Energy* **36** 13481-7. https://doi.org/10.1016/j.ijhydene.2011.08.014.
21. Zhu W, Liu X, Liu H, Tong D, Yang J, Peng J 2010 *Journal of the American Chemical Society* **132** 12619-26. doi:10.1021/ja1025112.
22. Parkinson B 1984 *Accounts of Chemical Research* **17** 431-7. doi:10.1021/ar00108a004.