Photo-electro-catalytic performance of highly ordered nitrogen doped TiO$_2$ nanotubes array photoanode

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Abstract. Highly ordered nitrogen doped TiO$_2$ nanotubes arrays (N-TNTAs) were synthesized via a one step anodization method at 40 V for 1 hour, in the electrolyte containing ammonium fluoride (NH$_4$F), water and triethylamine solution, followed calcination under N$_2$ atmosphere at 450°C for 3 h. The obtained samples were characterized by means of FE-SEM image showed that the N-TNTs are in a highly ordered array, having inner diameters, wall thickness, tube length of 65 nm, 30 nm and 900 nm, respectively, The X-ray diffraction (XRD) patterns of N-TNTAs and undoped TiO$_2$ nanotubes arrays (TNTAs) are identical consists of anatase phase, which suggests that the doping of N does not affect the crystalline structure. X-ray photoelectron spectroscopy (XPS), revealed that N atom was incorporated into the lattice of a TiO$_2$ nanotube array film. The infrared spectra, showed a new peak at 1240 cm$^{-1}$ may indicate the incorporation of N into the lattice of TiO$_2$ through substituting O atoms, in the form of ~N-Ti-O~. A red shift of the absorption edge toward the visible region of N-TNTAs are observed by diffuse reflectance spectroscopy (DRS), which is corresponding to a band gap of 2.8 eV. The photo-electro-catalytic (PEC) degradation efficiency toward methylene blue solution under visible light illumination of the N-TNTAs electrode was 89%, in which the rate constant of N-TNTAs electrode was 8 times better compared to that the undoped TNTAs photo-electrode.

1. Introduction

Titanium dioxide (TiO$_2$) based electrode have been great attention to be promising in photoelectrochemical applications to degrade various organic pollutants, such as dyes, aromatic compound and pesticides, under UV light irradiation [1,2]. Using the TiO$_2$ photo-electrode have many advantages, chemical stability, high efficiency, non toxicity and low cost [3]. In contrast to nanostructure, highly ordered TiO$_2$nanotubes arrays (TNTAs) not only have large surface to volume ratios and adsorptive capacity, but also have good photocatalytic activity, because of its nanotubes array structure, which enhances the electron transfer, promotes ion diffusion in the TNTAs electrode and electrolyte interface [4]. Upon the TNTAs surface irradiated with UV light, the electrons are excited from valence band to the conduction band, generating the photoelectron-hole. The positive hole can react with the water molecule produce the hydroxyl radicals. The positive hole and radical hydroxyl are powerful oxidants for degradation the organic compounds adsorbed onto the TNTAs electrode surface. However, one of the disadvantages of TiO$_2$ is wide band (3.0-3.2 eV) can absorb only the UV light, which limits the application of TNTAs electrode in organic pollutant degradation to utilize visible light. Another problem the application of TiO$_2$ photocatalyst is low efficiency of photocatalytic degradation, because high recombination rate of the photoelectron and hole during the photocatalytic process [5].

Many researchers have been attempt to extend the absorption range of TiO$_2$ to visible light region by non metal doping such as N, B and S into TiO$_2$ lattice [6-9]. Among the non metal, N doping is one most promising to increase the efficiency for solar energy utilization.
Some studies shown that N doped TiO$_2$ would increase its visible light photo-response. Asahi et al. [6] prepared N-doped TiO$_2$ with good photocatalytic activity under visible light irradiation. The N dopants incorporated into TiO$_2$ lattice by annealing under NH$_3$ or N$_2$ atmosphere. Substitution of O by N atoms into to TiO$_2$ lattice is more effective due to the comparable atom radii and electronegativity [10]. In this case, the oxygen vacancies can be formed by mixing N (2p) and O (2p) atomic orbitals which decrease the band gap energy of TiO$_2$ [11]. In recent years, various methods were developed to preparation of the N-doped TiO$_2$ nanotubes arrays (N-TNTAs) film, such as sputtering, hydrothermal, chemical vapour deposition and electrochemical oxidation. The common methods were electrochemical oxidation, which is anodizing of titanium foil in glycerol electrolyte containing NH$_4$Cl solution, followed calcination can be used to achieve TiO$_2$ nanotubes arrays [12]. The electrochemical oxidation is a simple method and convenient approach to achieve a uniform of TiO$_2$ nanotubes array film on titanium substrate.

Recently, the TiO$_2$ nanotube array has been applied as electrode in photo-electrochemical system for degradation of organic pollutants [13]. The photo-electro-catalytic degradation efficiency could be further improved by applying a bias potential across the photo-electrode. The bias potential applied to photo-anode would enhance photoelectron transfer from photo-anode to counter electrode results in the improved separation of photoelectron and hole pairs [14].

In the present work, a simple method with one-step anodization was used to synthesize the N-TNTAs electrode from titanium foils using ethylene glycol electrolyte and NH$_4$F containing of triethylamine (C$_6$H$_{15}$N) followed calcination process under N$_2$ atmosphere at 450°C for 3 h. We have studied the effects of N doping on the properties of the TNTAs, including crystal structure and optical properties. The effects of N doping on the photo-electrochemical properties are investigated. Preliminary photocatalytic activity is examined using photo-electro-catalytic (PEC) method for degradation of methylene blue solution under visible light illumination.

2. Experiment

2.1. Synthesis of TNTAs and N-TNTAs
Titanium (Ti) foils (purity 99.6%, 0.3 mm thickness) was purchased from Baoji Jinsheng Metal Material Co. Prior to anodization, the Ti foils (1.5 cm x 3.0 cm), were first mechanically polished with sand papers 1200 grits and then degreased by sonication in acetone, ethanol, deionized water for 10 min, respectively and finally dried in nitrogen stream. The anodization was carried out in a two-electrode configuration, where Ti foil was used as an anode and stainless steel foil as a cathode. The distance between the anode and the cathode was 1.5 cm. The electrolyte consisted of NH$_4$F (0.3 wt%) in ethylene glycol and deionized water (2.0 wt%) and placed in a quartz semi-silinder reactor [15-16]. The anodization potential was controlled at 40 V for 1 h using a DC power supply [16]. After anodization process, the obtained sample rinsed with deionized water and dried in nitrogen stream. For preparation of N-doped TiO$_2$ (N-TNTAs), similar process was performed in the electrolyte consisting of triethylamine 1.5 mol.L$^{-1}$. The crystallization of the N-TNTAs was carried out by thermal annealing in a furnace at 450°C for 3 h with a heating rate of 5.0°C min$^{-1}$, held for 3 h under N$_2$ atmosphere [17] and cooled naturally to room temperature. This simple method comprises simultaneously N doping and fabrication of TiO$_2$ nanotubes.

2.2. Characterization of the TNTAs and N-TNTAs electrode
The morphology of the N-TNTAs was characterized by field emission scanning electron microscope (FESEM-FEI-Inspect F50) with accelerating voltage of 20 kV. The crystal structures of the N-TNTAs and TNTAs were analyzed by X-ray diffraction (XRD-PHILIPS PW 1710) using Cu K$\alpha$ as radiation source in the range 10-80°(20). The elemental composition and chemical states were examined by X-ray photoelectron spectroscopy (XPS, K-alpha Thermo Scientific) using a monochromatic Al K$\alpha$ radiation source (15 mA, 14 kV). The functional groups present in the N-TNTAs and TNTAs were determined by FTIR analysis (Shimadzu IR Prastige-21) over a wavenumber range of 400-4000 cm$^{-1}$. The UV-visible diffuse reflectance spectroscopy (DRS) analysis was used to calculate the band gap
energy of the photocatalysts using spectrophotometer (Shimadzu 2450) with software UV Probe (DRS-8000 Shimadzu).

2.3. Photocurrent and Photo-electro-catalytic activity measurements

The photoelectrochemical properties were performed in a semi-cylindrical quartz reactor (3.0 cm x 4.0 cm) using a three-electrode with a N-TNTAs or TNTAs film (with effective area 1.5 cm x 1.5 cm) as the working electrode, an Ag/AgCl electrode as the reference, and a platinum foil as the counter electrode in 0.1 mol L$^{-1}$ KOH as the electrolyte. The photo-anode was exposed to the visible light through a window. A 50 W Hollolite lamp (Philip, China) was used as the light source (dominant wavelength 425 nm, contain UV light a portion of ~10%), which provided an irradiation intensity of 3.7 mW cm$^{-2}$ was used as the visible light source. The light meters were used (Krisbow KW 06-288) was used to measure the intensity of the incident visible light. A scanning potentiostat (eDAQ, version 9.1) was used to perform a potentiodynamic scan form -1.0 to 1.0 V at a rate of 10 mV S$^{-1}$ and measure the generated photocurrent. The photocurrent density was also measured at a fixed bias potential 0.5 V, with a light pulse of 1 min 40 S, using multi pulse amperometry method under visible light irradiation.

The photo-electro-catalytic (PEC) activities of N-TNTAs or TNTAs as photo-anode, were evaluated by analyzing PEC degradation of methylene blue (MB) in aqueous solution as a model organic pollutants under following condition: vigorous stirring, 0.1 M KOH solution as electrolyte and pH 5.5. The MB solution with an initial concentration of 10 mg L$^{-1}$ and the reaction solution was 30 mL. Prior to PEC degradation, the electrode was soaked in MB solution with a concentration of 10 mg L$^{-1}$ in the dark for 30 min to establish the adsorption-desorption equilibrium. During the PEC reaction, the concentration of MB was determined at a time interval of every 10 min by measuring the absorbance using a UV-visible spectrophotometer (Shimadzu 2450) at wavelength 655 nm. The reaction solution (~2.0 mL) was quickly withdrawn at a given reaction intervals, and was quickly returned to the reactor after being analyzed. The Photocatalytic (PC) degradation of MB was examined also using the same of the functional electrodes without applying an external bias potential.

3. Results and discussion

3.1. Characterization of the electrode

The FESEM images of N-TNTAs shown in Fig.1. As shown in Fig.1, the morphology of the N-TNTAs are open at the top, with inner diameter and wall thickness average 65 nm, and 30 nm, respectively.

**Figure 1.** FESEM top view image and cross section (inset picture) of N-TNTAs

**Figure 2.** XRD patterns of the (a) TNTAs and (b) N-TNTAs
The cross-sectional image of the N-TNTAs sample shown the well-aligned nanotube arrays are vertical to the substrate, with height are approximated to 900 nm. There are clearly observed that the morphology of the N-TNTs on surface are homogeneously have highly ordered tubes shape.

The XRD patterns of TNTAs and N-TNTAs are compared in Fig.2. The crystal structures of TNTAs and N-TNTAs after annealing at 450°C for 3 h gave peaks the diffraction of the field (101), (004), (200), (204), which correspond predominantly to anatase TiO$_2$ (JCPDS card No.21-1272). It can be observed that the XRD patterns of both samples are identical, which may be implied that the N incorporated to TiO$_2$ lattice does not significantly affect the TNTAs crystalline structure. The Ti peaks from substrate characteristic are observed for the TNTAs and N-TNTAs, which suggests that synthesis of nanotubes TiO$_2$ on the surface of Ti substrate was successfully.

**Figure 3.** High-resolution XPS spectra of N 1s (A), Ti 2p (B), O 1s (C), and C 1s (D) of the TNTAs and N-TNTAs electrode

The XPS spectra of N 1s, Ti 2p, and O 1s TNTAs and N-TNTAs after annealed at 450°C under N$_2$ atmosphere are presented in Fig. 3. Figure 3.A. shows that N 1s peak of N-TNTAs observed at 400.6 eV, whereas no appearing distinct peak at the same binding energy for TNTAs. The N 1s peak localized around at 406 eV could be assigned to indicate the presence of N incorporated in TiO$_2$ lattice formed N-Ti-O linkages, which is consistent with many researchers [7,18,19]. The amount of N atomic introduced to the TiO$_2$ nanotubes arrays approximate 1.58 at.%. The electronegativity of N doped into TiO$_2$ lattice is lower than O element, leading to reducing of electron density on the N [18]. This indicates that annealing process indeed leads to substitution of N atoms for O sites in TiO$_2$ lattice. It shows that oxygen vacancies would be formed in TiO$_2$ surface and the impurity energy level was intruded between band gap of TiO$_2$. The Ti 2p spectra are presented in Fig.3.B. Compares the Ti 2p$_{3/2}$ peak of N-TNTAs and TNTAs it was found that downshift to approximately 0.3 eV.

The red shift binding energy may be implied a higher electron density [20] and might be attributed to the presence of Ti$^{3+}$ centre in N-TNTAs [21]. This further testifies that N atomic is incorporated into the lattice and substitutes for oxygen [18]. Figure 3.C. shows O 1s spectra of
TNTAs and N-TNTAs photocatalysts. The peak O 1s for N-TNTAs appears around 530.2 eV and 531.6 eV, indicate the presence of two states of oxygen, formed Ti-O-Ti and N-Ti-O linkages, respectively [18]. According to the N 1s region of N-TNTAs (Fig.3.A), suggests that the peak at 400.6 eV, should be attributed to the reduced nitrogen of N-Ti–O. Also significant changes upon N incorporation to TiO₂ lattice, the O1s peak at 530.8 comes from Ti-O-Ti linkages in TNTAs and a shift to 530.2 eV which is observed for N-TNTAs. These results suggest that the N atomic were successfully introduced to TiO₂ lattice. Figure 3.D. shows the C 1s spectra for TNTAs and N-TNTAs. The C atomic may be incorporated to TiO₂ lattice as residual from electrolyte during anodization process, which consistent with the published value of the C 1s peak for N-doped TiO₂ [7,22].

![Figure 4. FTIR spectra of N-TNTAs-amorphous (a), TNTAs (b), and N-TNTAs (c)](image)

![Figure 5. DRS UV-Visble reflectance spectra of TiO₂ P-25 (a), TNTAs (b), and N-TNTAs (c)](image)

To verify the incorporation of N and C elements in the TiO₂ lattice, FTIR analysis was performed. The functional groups that present in the obtained samples of TNTAs and N-TNTAs are studied by characteristic FTIR spectra as shown in Fig.4. During the anodization process, the C₆H₅N molecules as the nitrogen source were adsorbed on the surface of TiO₂ amorphous. Before calcination the peak at 1580 cm⁻¹ could be assigned to the surface adsorbed of N-O (Fig.4.a). After calcination at 450°C under N₂ atmosphere, the peak at 1580 cm⁻¹ was not appearance, but the new peak around 1460 cm⁻¹ is attributed to N-Ti-O stretching vibration, as shown in Fig.4.c. Compared to FTIR spectrum of TNTAs, the peak around 1460 cm⁻¹ is not observed. These results may be indicated that the incorporation of N atomic into TiO₂ lattice, cause shift the absorption band of O-Ti-O stretching to low wavenumber. Furthermore, a small peak at around 1100 cm⁻¹ assigned to Ti-O-C stretching. It may be indicated that C atomic was incorporated to TiO₂ lattice. These results are also evidenced by XPS spectra analysis of C 1s core levels for N-TNTAs and TNTAs. The peaks observed at 410 and 805 cm⁻¹ correspond to the Ti-O-Ti stretching vibrations of crystalline TiO₂ [22]. The strong absorption band at around 2500-3600 cm⁻¹ is ascribed to the associated hydroxyls groups from either water molecules. In addition, after calcined at 450°C in N₂ atmosphere for 3 h, a small peak at around 3240 cm⁻¹ which is assigned as O-H stretching of the hydroxyl group to Ti atoms for TNTAs and all the N-TNTAs was observed.

Figure 4 shows the diffuse UV-Vis reflectance spectra of the standard TiO₂ P 25 (curve a), TNTAs (curve b), and N-TNTAs (curve c). The band gap energy (Eg) of the photocatalysts are determined by applying Kubelka-Munk function F(R) [12] as follow:

\[ F(R) = \frac{1}{(1-R)^2} = \frac{K}{(h\nu - Eg)} \]

where \( F(R) \) is reflectance, \( h\nu \) is the photon energy and \( K \) is the constant characteristic of TiO₂. A plot of F(R) versus \( h\nu \) should show a linear region just above the optical absorption edge [12,27]. Using the Tauc plot, the band gap energies for all samples are resulted. The band gap of N-TNTAs (2.8 eV; 420 nm), decrease from 3.19 eV (380 nm), is caused by incorporating N atomic to form N-Ti-O bonds [12]. The band gap of the N-TNTAs is lower than all photocatalysts. These results consistence with FTIR and XPS analysis. Since all photocatalysts undergoe reducing the band gap
compared to TiO$_2$-P25 (3.22 eV), they might ascribe the extended photo-response to visible light region and could be activated by visible light as well.

3.2. Photoelectrochemical properties

The photocurrent response measurements were performed under visible light illumination to investigate the behavior of the transfer carriers. It can provide useful information of the photocatalytic process.

It is known that inter-band electron transition is a companied by relaxation and recombination in TiO$_2$, and consequently, only part of the photons absorbed by TiO$_2$ can contribute to generation of a photocurrent [8]. Therefore, it is necessary to take into account the photocurrent density-potential applied of the TNTAs and N-TNTAs photo-anode under visible light illumination. Figure 6 shows that the photocurrent density of TNTAs and N-TNTAs electrode in the dark and visible light irradiation. The photocurrent density of N-TNTAs and TNTAs photo-anode under darkness are negligible.

In visible light irradiation for the N-TNTAs, the photocurrent density is significantly higher than that of TNTAs at all bias potential, which is about 10 times than the TNTAs. The high photocurrent conversion efficiency may be contributed to improve the optical absorption capability caused by the N-doping [21]. The absorption shoulder up to visible region may have important roles in enhanced visible light photocurrent conversion efficiency of the N-TNTAs. For the undoped TNTAs electrode, no significant photocurrent density over the bias potential range because the energy of visible light illumination is smaller than the band gap energy of TNTAs. This result can be ascribed to N atoms incorporated in TiO$_2$ lattice which are able to narrow the band gap [6], promote the excitation of photoelectron-hole pairs by visible light [19]. It can be observed also from Fig.6, the zero-current potential ($E_{-\text{zcp}}$) for the N-TNTAs and TNTAs were -0.91 and -0.76 V, versus Ag/AgCl, respectively. The negative shift of 0.15 V for the N-TNTAs compared to that the TNTAs can be ascribed to the N-doping need a lower potential (less energy) to extract the photoinduced electrons to external circuit, exhibited fast light response due to efficient charge transfer. Increasing bias potential applied lead to increase the generated photocurrent density then reach a relatively steady state within a certain range of potential (fixed potential 0.2 V). The photo-anode shift in photocurrent density is attributed to decrease in recombination on the surface of N-TNTAs, which could be determined by the surface structure.

The photoelectron-hole separation and electrode transfer interface, the photocurrent response of N-TNTAs electrode is evaluated by amperometric $I$-$t$ curves, which were collected with visible light on or off cycles, at a fixed bias potential 0.2 V. As shown in Fig.7.the experiment run for 180 s firstly, then illuminating time was taken for 20 s each time. The photocurrent responds with the turn-on and turn-off the visible light quickly. When the visible light illumination is turn on, the photocurrent of
TNTAs quickly increases to 0.13 mA.cm$^{-2}$ and remains constant until the irradiation is turned off while rapidly drop to the background photocurrent of steady state density (0.06 mA.cm$^{-2}$). The photocurrent arises from the photoelectron-hole separation in the surface of N-TNTAs, and the charge transfer process is very rapidly. For the N-TNTAs photo-anode, possess higher photocurrent than TNTAs. We can see in Fig.7, the photocurrent density of N-TNTAs showed is higher than TNTAs. Based on these results, the N-doping caused increased the oxygen vacancies and narrow band gap [6], indicating that broadening visible light region and hindering recombination of photoelectron-hole. The photocatalytic activity of TiO$_2$ usually depend on the transfer rate of surface charge carriers from the bulk to the surface and recombination rate of photogenerated electrons and holes, a faster photogenerated electrons and holes transfer leading to higher photocatalytic activity of TiO$_2$ [23-26].

3.3. Photo-electro-catalytic performance of N-TNTAs electrode

In the photoelectrochemical system, the MB may undergo decomposition driven by direct electrolysis (EC), photocatalysis (PC) and synergic photo-electro-catalysis (PEC).

![Figure 8](image.png)

Figure 8.(A). Concentration of MB and (B) degradation efficiency (%) under different conditions: (a) PC under visible light; (b) direct EC at bias of 0.2 V in the dark; (c) PEC N-TNTAs under visible light and 0.2 V bias potential; and (d) PEC TNTAs under visible light and 0.2 V bias potential.

The EC, PC and PEC degradation of MB solution using N-TNTAs and TNTAs electrode was present in Fig.8. As shown in Fig.8.A that within 240 minutes, the EC process was obviously slower than PC and PEC process. The resulting concentration-reaction time curves show noticeable differences in the removal MB concentration among experiment. In order to quantitatively describe MB degradation in this work, can be applied by the Langmuir-Hinshelwood (L-H) equation, which is usually used to characterize the PC and PEC degradation process of organic compounds, as following the first order reaction [14,27]:

$$\ln \frac{C_0}{C_t} = -kt$$

where $C_0$ is the initial concentration, $C_t$ is the concentration of MB at the reaction time (t) and $k$ is the rate constant (min$^{-1}$).

The degradation efficiency (%) under different conditions PC, EC and PEC reaction time for 240 min was shown in Fig.8.B. When no external potential was applied, the visible light illumination resulted 42 % of the MB was removed by photocatalysis on N-TNTAs electrode after 240 min (curve a). When the N-TNTAs is used as the photo-anode (0.2 V) without visible illumination, degradation of MB exhibited slow rate constant 1.0x10$^{-3}$ min$^{-1}$ (curve b) from electrolysis process. In contrast, when the N-TNTAs photo-anode apply external bias potential 0.2 V under visible illumination for 240 minutes, the MB was degraded about 89% and a much greater rate constant of 8.5x10$^{-3}$ min was observed (curve c). Using the TNTAs as photo-anode (0.2 V) under visible light illumination only small the MB was degraded with a rate constant of about 1x10$^{-3}$ min (curve d). The rate constant of N-TNTAs electrode was 8 times better compared to that the un-doped TNTAs electrode. These results
were corresponding to the enhanced photocurrent density as given in Fig.6. Accordingly, there should be a synergistic effect between the electricity and radiation energy. The photocatalytic activity of TiO$_2$ usually depends on the charge transport ability [27,28] and a faster photoelectron leading to a higher photocatalytic activity [24].

![Graph showing comparison of photocurrent density-time profile for MB in KOH (10 mgL$^{-1}$) PEC degradation obtained from N-TNTAs and TNTAs electrode (bias potential 0.2 V).]

Figure 9. Comparison of photocurrent density-time profile for MB in KOH (10 mgL$^{-1}$) PEC degradation obtained from N-TNTAs and TNTAs electrode (bias potential 0.2 V).

The typical photocurrent density versus time profiles obtained during of PEC degradation of MB with initial concentration of 10 mgL$^{-1}$ in KOH solution under given condition were shown in Fig.9. The photocurrent density observed for N-TNTAs electrode is found much higher than TNTAs electrode. This result is consistent with the enhanced the LSV response, given in Fig.6, and improved the PEC activity given in Fig.8. of the N-TNTAs electrode. The photoelectron-hole could either recombine with electrons or react with OH$^-$ ions or H$_2$O oxidizing them to form OH$^-$ radicals. The OH$^-$ radicals, are responsible for the decomposition of MB molecules. The photoelectron could reduce the adsorbed MB or react with O$_2$ adsorbed on the electrode surface or dissolved in water to form superoxide radical anion O$_2$$^\cdot$-, which can be transformed to OH$^-$ radicals by further reactions [22]. The result is definitely consistent with the photocatalytic properties which can be attributed to the N atoms doped in TiO$_2$ can narrow the band gap, promote the excitation of electron-hole pairs by visible light and enhance the visible light photo-response [29]. The obviously enhanced rate constant in the PEC process can be attributed to the suppression of recombination between the photogenerated electron and hole pairs by external electric field and the special highly ordered nanotube array is favorable for the transport of the photogenerated electrons. In addition, such nanotube structures also show improved mechanical stability, since the TiO$_2$ is directly attached to the tube walls and there are more supporting points in the nanotube structure. The effect photo-stability of the electrode for the PEC degradation of MB was evaluated, there is no apparent deactivation of the N-TNTAs photocatalysts are observed after five cycles. This clearly shows that the photocatalysts are stable during the PEC process.

4. Conclusion

The highly ordered N-doped TiO$_2$ nanotube arrays (N-TNTAs) were applied as an photo-anode in the PEC degradation of MB aqueous solution, which the efficiency was degrade 89% compared with undoped TiO$_2$ electrode only 12%. Under visible light illumination, the N-TNTAs photo-anode showed higher photocurrent density and photo-electro-catalytic activity for degradation of MB solution than TNTAs electrode. The rate constant of N-TNTAs electrode about 8.5x10$^{-3}$ min was 8 times better compared to that the TNTAs electrode. This improved the PEC performance can be attributed to the increased visible light absorption, the improved photoelectron-hole separation by external bias potential applied. These results suggest that the highly effective N-TNTAs electrode, with strong mechanical stability and superior transport of photoelectron and hole pairs, may serve well as a promising photo-electro-catalyst and may provide an easy and efficient route to remove pollutant organic such as methylene blue from wastewater.
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