



# Development of titania nanotube arrays: The roles of water content and annealing atmosphere



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## HIGHLIGHTS

- Water content of 25 v%, annealing with 20% H<sub>2</sub> produced highest photocurrent of TNTAs.
- Vertically oriented, long with optimal wall thickness of TNTAs increase photocurrent.
- Annealing with H<sub>2</sub>/Ar plays an effective role in reducing the band gap.

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## ABSTRACT

The effect of water content in the electrolyte solution during annealing process in the synthesis and modification of titania nanotube arrays (TNTAs) by anodic oxidation process has been investigated. Variations in annealing technique that leading to some specific properties of the TNTAs produced have been examined. Doped-TNTAs were obtained by the in-situ anodic oxidation method in glycerol containing fluoride solution followed by annealing to induce crystallization. FESEM and SEM results indicated that TNTAs with inner diameters of 49–80 nm, wall thicknesses from 28 to 42 nm and lengths from 1407 to 1570 nm were synthesized. At water content of 25 v% in the electrolyte solution, self-organized with vertical, ordered of TNTAs with relatively uniform diameter was observed. Suitable morphology of TNTAs such as well developed tubes, vertically oriented, highly ordered, long with optimal diameter and wall thickness of TNTAs could suppress recombination of electrons–holes and, therefore, increase photoelectrochemical properties. Annealing with H<sub>2</sub>/Ar is found to be efficient for introducing dopant C and N into the lattice of TNTAs to form Ti–O–C and N–Ti–O (FTIR analysis). Therefore, the reducing band gap can be obtained (UV–Vis DRS analysis). Annealing under H<sub>2</sub>/Ar of as-synt TNTAs with water content of 25 v% in the electrolyte solution produced anatase phase (XRD analysis) and showed optimal condition in producing the highest photocurrent density.

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## 1. Introduction

TiO<sub>2</sub> is one of the most promising photocatalysts and has attracted much attention due to its advantages such as non-toxicity, stability, environmental harmlessness and low cost [1–6]. Activation of this photocatalyst needs photon energy, which can be provided by solar light at ambient condition instead of thermal energy. This photocatalyst has many applications such as being a

photocatalyst in H<sub>2</sub> production [1,3], pollutant degradation [3–8], dye-sensitized solar cells (DSSC) [3,9] and even in sanitation and cancer therapy [10]. However, TiO<sub>2</sub> has several drawbacks such as photoinduced electron–hole recombination [1,2], visible light inactivity (band gap of TiO<sub>2</sub>: 3.2 eV for anatase, 3.0 eV for rutile) [1–9] and limited surface area [1,11,12]. Consequently, its utilization efficiency especially in solar light is still poor as the UV portion accounts for only about 5% while visible light accounts for about 45% in solar spectra [2,4,5,8,13]. Hence, some modification strategies need to be examined to reduce those drawbacks of TiO<sub>2</sub> such as morphology modifications (to increase the surface area), addition of non-metal doping (to extend the photo-responsiveness to the visible light) or metal doping (to minimize recombination of

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electron–hole) and coupling with other semiconductors such as CdS [11].

Many attempts to alleviate those drawbacks have been studied, and one of them is synthesizing TiO<sub>2</sub> by anodic oxidation of titanium metal in order to get morphology of TiO<sub>2</sub> nanotube arrays that have larger surface area compared to the randomly distributes and shape nanoparticles [3,11,12]. TiO<sub>2</sub> synthesized by the anodic oxidation process (TNTAs) exhibit better properties than TiO<sub>2</sub> in a randomly distributes and shape nanoparticles system as morphology of TNTAs enhances photon absorption, effectively increases the surface area and provides excellent electron–hole separation properties [11,12]. Accordingly, the morphology of the TNTAs can improve performance in its photoactivity. Formation of TNTAs in organic electrolyte such as glycerol with high viscosity result in a low growth rate of nanotube since the tube growth rate is a diffusion-controlled process [11,14]. However, extending anodization time resulted in the increasing the tube length. Magnetically stirring during the anodization process can be used to enhance the mass transfer of the ions inside the solution and therefore increase the growth rate. The smooth wall that improves properties of TNTAs is another interesting result of anodization in glycerol electrolyte solution [11]. Furthermore, decreasing the viscosity by adding the various water content into glycerol electrolyte solution plays an important role in determining the optimum growth rate, dimension and the morphology of TNTAs. As a result, the specific properties that improve the characteristics of TNTAs caused by variation in water content during anodization can be obtained.

Doping TiO<sub>2</sub> with non-metal such as C [4,6,8], N [1,3–6,13], B [2,8], I [5] and co-doping with N+S [3], C+N [4,6], C+B [8] and N+I [5] has been demonstrated to reduce the band gap, thus improving its photocatalytic activity under visible light. Non-metal (for example N) incorporated into TiO<sub>2</sub> lattice can create new valence bands through the mixing of N 2p states with O 2p states without affecting the conduction band level [4]. Many researchers performed non-metal doped-TiO<sub>2</sub> in a two-step fabrication approach, and the preparation process was relatively complex [1,3–6,8]. On the other hand, when TNTAs synthesized in organic electrolyte such as glycerol (14 vol% H<sub>2</sub>O + 0.14 M NH<sub>4</sub>F), may lead to the adsorption of this organic molecules on the TNTAs during anodic oxidation process. Annealing this as synthesized TNTAs at 450 °C for 1 h result in the incorporation of carbon element in the lattice of TNTAs (as carbon doping), since the organic molecules possibly decomposed thermally [14]. The nitrogen doped TNTAs have also been prepared by two-step in situ anodization process with ethylene glycol containing NH<sub>4</sub>F solution as reported by Wu and co-worker [15]. They reported that nitrogen incorporation in the TNTAs was supplied by the NH<sub>4</sub>F and it was retained by annealing in dry nitrogen environment at 450 °C for 1 h. Moreover, the simple method by in-situ doping or one pot reaction resulted in better quality nanotubes than the post-treatment method as reported by Milad and co workers [16]. They studied in situ carbon doping to TNTAs with polyvinyl alcohol containing NaF as electrolyte solution and followed by annealing in air at 500 °C for 3 h. To summarize, annealing techniques were performed to produce crystalline phase and may also lead to the incorporation of dopants that already available in the electrolyte solution along the anodic oxidation process (in-situ doping). Furthermore, variation of annealing atmosphere play important role in the incorporating dopants in the lattice of TNTAs. In order to get TNTAs with specific properties (well morphology with the longer tube length at precise thickness, low band gap value with anatase crystal structure and high photoelectrochemical properties) that enhance the photocatalytic activity of the TNTAs, arrangement of water content on the specific technological variations in annealing technique is very crucial. However, to the best of our knowledge, the studies on the roles of

water content and variation of annealing atmosphere in the synthesis and modification of TNTAs by in-situ doping still remain substantially missing.

In this study, we investigated the significance effects of water content in the glycerol electrolyte solution and the variations in the process annealing technique that improve the specific characteristic and photoelectrochemical properties of doped-TNTAs via in-situ anodization.

## 2. Materials and methods

### 2.1. Fabrication of TNTAs

Titanium foils (from Baoji Jinsheng Metal Material Co., 99.6% purity, 0.3 mm thickness) were used as a substance for the growth of TNTAs. Prior to anodization, the Ti sheets (3 cm × 2 cm) were first mechanically polished with a 1500 cc sandpaper in order to obtain an appropriate brittle and flat surface. Subsequently, Ti samples were degreased in a mixture of HF, HNO<sub>3</sub> and H<sub>2</sub>O with a volume ratio of 1:3:6 for 2 min, rinsed in deionized water and dried under air. TNTAs were obtained by the anodic oxidation process which performed in a two electrode configuration with a Ti foil as an anode and a platinum, Pt (3 cm × 1.5 cm, thickness 1 mm) as a cathode at room temperature. The distance between the two electrodes was kept at 3.5 cm in all experiments. This distance is selected by considering the reactor size and morphology of TNTAs to be produced [17]. A direct current power supply (Escord 6030SD) was utilized to control the voltage at 30 V for 2 h. This equipment also measured the current generated as a function of time. A mixed electrolyte solution (60 ml) of glycerol (from Brataco) containing 0.5 wt.% NH<sub>4</sub>F (Merck, 98%) with different water content (5, 10, 25 and 50 v%) were used as the electrolyte solutions and non-metal doping source in the anodization process. The selection of constant parameters such as annealing temperature [18,19], voltage [12,20–22], amount of NH<sub>4</sub>F [11,12,22,23] and time [11,12] is based on the optimal condition as suggested by some previous studies. To homogenize the electrolyte solution in order to get TNTAs with uniform size [24] and to enhance the mobility of the ions inside the solution [19], magnetically stirring with acceleration of 150 rpm was performed along with the anodization. As-synthesized TNTAs were properly washed in distilled water and subsequently dried under air atmosphere (denoted as as-synt TNTAs). To study the effect of mode annealing, the as-synt TNTAs were then annealed in a furnace to convert the amorphous phase to the anatase phase using air (denoted as A-TNTAs) and using 20% hydrogen in an argon atmosphere (denoted as H<sub>2</sub>-TNTAs) at 500 °C with the rate of 150 ml s<sup>-1</sup>. The temperature of the furnace was raised to 500 °C with a heating rate of 9.2 °C min<sup>-1</sup>, held for 3 h and cooled naturally to room temperature. TNTAs produced by anodic oxidation with 10 and 25 v% water content in the electrolyte solution were denoted as TNTAs-10 and TNTAs-25, respectively.

### 2.2. Characterization

The morphology of TNTAs was characterized using scanning electron microscopy (SEM) JEOL-6390A and field emission scanning electron microscopy (FESEM) FEI-Inspect F50 with accelerating voltage of 20 kV. The elemental analysis of the TNTAs was determined by the energy-dispersive X-ray spectroscopy (EDS) attached to the SEM (at 20 kV). FTIR analysis (Shimadzu IR Prastige-21) was performed to determine the functional groups present in the TNTAs. The FTIR spectra of the photocatalysts were taken over a wavenumber range of 400–4000 cm<sup>-1</sup>. A UV–Vis Spectroscopy (DRS) analysis was used to calculate the energy band gap of the TNTAs samples using spectrophotometer Shimadzu 2450 type. The

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