MATERIALS PHYSICS AND MECHANICS RESEARCH ARTICLE

Submitted: February28, 2025 **Revised: July22, 2025** **Accepted:October23, 2025**

Fabrication and characterization of zinc nitrate doped TiO_2 nanotubes for dye-sensitized solar cells

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ABSTRACT

Zinc-doped titanium dioxide nanotubes were successfully synthesized, characterized, and tested as materials for energy conversion in dye-sensitized solar cells. The TiO_2 nanotubes were grown through single-face anodization at a constant direct current voltage of 50 V and room temperature on titanium sheets with a thickness of 0.25 mm and purity of 99.7 %. The electrolyte was composed of ethylene glycol, ammonium fluoride (0.3 % wt. NH_4F), and deionized water (2 % v/v H_2O). The titania nanotubes were doped with Zn using $Zn(NO_3)_2$ as the dopant source. The molar ratios of zinc nitrate were varied from 1, 3, 5, and 7 mM. X-ray diffraction, scanning electron microscopy, and ultraviolet-visible spectroscopy (techniques were employed to characterize the Zn-doped titanium dioxide nanotubes. The samples were then tested in dye-sensitized solar cells, and their photoelectric conversion efficiencies were calculated. As a result, amorphous-TiO_2 structure was transformed into the crystalline anatase phase after annealing. The best performance was observed for the 5 mM zinc nitrate sample, with a photoelectric conversion efficiency of 4.96 % and an energy band gap of 3.18 eV. The findings of this research provide valuable insights for ongoing and future studies in the development of renewable energy.

KEYWORDS

renewable energy • DSSCs • TiO_2 nanotubes

Funding. *The authors would like to greatly thank the following for their support: Thailand Science Research and Innovation Fundamental Fund – FF 2024; the Division of Physics, Faculty of Science, Nakhon Phanom University, Muang District, Nakhon Phanom; and Faculty of Industry and Technology, Rajamangala University of Technology Isan.*

Citation: Samran B, Timah EN, Phatungthane T, Thongpanit P, Kadroon B, Photharin S, Chaiwichian S. Fabrication and characterization of zinc nitrate doped TiO_2 nanotubes for dye-sensitized solar cells. *Materials Physics and Mechanics.* 2025;53(5): 83–89.
http://dx.doi.org/10.18149/MPM.5352025_6

Introduction

It was in 1991, when O'Regan and Gratzel [1–3] made their first dye-sensitized solar cells (DSSCs). Since then, there has been huge growth in research on DSSCs. This huge growth can be accounted for due to the following reasons: they are cheap to produce, easy to fabricate, are a source of renewable energy, are environmentally friendly and have high power conversion efficiency [4–10]. Titanium dioxide or titania (TiO_2) nanotubes can be used in DSSCs to improve the photocatalytic performance and resolve the issue of charge recombination [11–14]. However, one challenge encountered with

titania is the large band gap energy of about 3.2 eV. This large band gap restricts solar energy absorption mostly in the UV region. Many reports suggest that this problem can be solved by doping titania with foreign elements. Examples of elements that have been used as dopant in titania include Fe, N, Cu, and Al [15–19].

A.F.Robledo et al.[6], P.Ramos et al. [20] and A. Javed et al. [21] used ZnO nanostructures in DSSCs. Composite nanofibers of ZnO-TiO_2 in DSSCs was reported by C. Qiqi et al. in 2022 [22]. A 1:2 molar ratio of ZnO-TiO_2 was utilized and obtained photoelectric conversion efficiency (PCE) of 3.66 %. There is great room for improvement on this result by doping titania nanotubes (TNT) using zinc nitrate, $Zn(NO_3)_2$, as a source of the dopant element Zn. This research work reports the fabrication and characterization of Zn-doped TNT for DSSCs. The samples were prepared at the molar ratios of zinc nitrate: 1, 3, 5 and 7 mM. The PCE of each sample will be tested in DSSCs.

Materials and Methods

Direct current (DC) anodization technique was used to develop TNT on titanium sheet from Sigma Aldrich. This process was carried out at a constant voltage supplyof 50 V for 2 h at room temperature. The thickness of the each titanium sheet or foil was 0.25 mm thickness and their purity was 99.7 %. The sheets were polished with abrasive paper and degreased by ultrasonic method in isopropanol, deionized water and ethanol. The electrolyte used for the anodization was composed of the following: ethyleneglycol (EG), ammoniumfluoride (0.3 wt. % NH_4F) and deionized water (2 vol. % D.I. H_2O). The molar concentrations of zinc nitrate was varied sequentially -1, 3, 5 and 7 mM. To ensure that the electrolyte was homogenous, we kept the mixture for 5 h prior to anodization. The array for the anodization consist of two electrodes – a copper electrode and a platinum counter electrode, as seen in Fig. 1. With this set up, the electrolyte can only be in contact with one face of the titanium sheet.

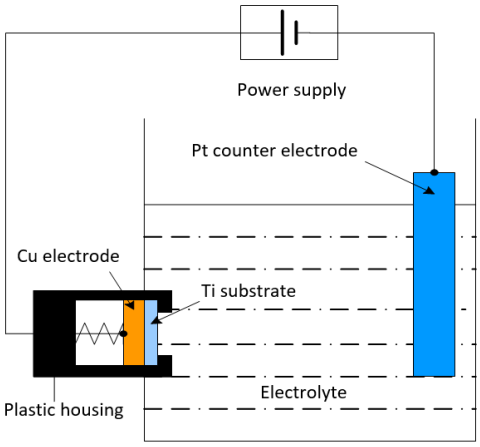

Fig. 1. The schematic diagram of a single-face anodization process

Analysis of the samples was performed before calcination and after anealingin an oven at 450 ºC. The following techniques were used to characterize the samples: X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet-visible

spectroscopy (UV-VIS). After that, the samples were tested in DSSCs. Totest in DSSCs, the titania nanotubes photoelectrodes were immersed for 24 h at room temperature in 0.5 mM solution of N719 dye and acetonitrile/tert-butanol in a 1:1 mixture. To form the counter electrode, platinum solution (H_2PtCl_6) was dropped on a transparent conducting oxide glass (TCO). After heating the TCO at 80 °C for 30 min, the platinium counter electrode was ready. A sandwich assembly of the Pt electrode and the titania nanotube photoelectrode was incorporated into the DSSCs. The current-voltage (IV) characteristic was then analyzed. The following parameters are fundamental in evaluating the photovoltaic properties of the DSSCs: short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (*FF*) and the photoelectric conversion efficiency PCE (η). These parameters are related via the equations that follows [23,24]:

$$FF = \frac{V_m I_m}{V_{OC} I_{SC}}, \quad (1)$$

$$\eta = \frac{V_m I_m}{P_{in}} = \frac{V_{OC} I_{SC} FF}{P_{in}}, \quad (2)$$

where I_m and V_m are the current and voltage, respectively, at the optimal operating point. Their product gives the maximum output power P_m. The power of the incident light is denoted as Pin.

Results and Discussion

XRD analysis

XRD patterns of the zinc-doped titania nanotubes samples before annealing are displayed in Fig. 2. In Fig. 2, we can see the peaks typical to titanium metal. It is also worth noting that the titania were still in the amorphase phase due to the absence of the anatase phase. On the other hand, Fig. 3 displays XRD patterns after calcinating the samples at 450 °C. It is obvious to see the crystalline anatase phase of TiO_2 which are labelled A. The diffraction peaks for the anatase phase occur at the scattering angles of 25.3, 48.8, 54.2, and 55.1°. These results align perfectly with the works of Hailei Li et al. [25], and Shih-Yu Ho et al. [26].

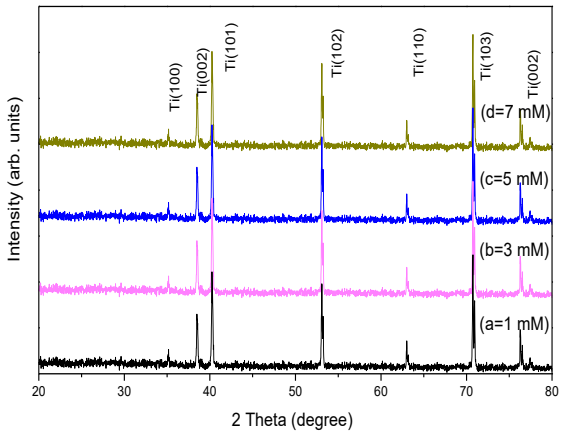

Fig. 2. XRD patterns of Zn-doped TNT before annealing: (a) 1 mM, (b) 3 mM, (c) 5 mM, and (d) 7 mM

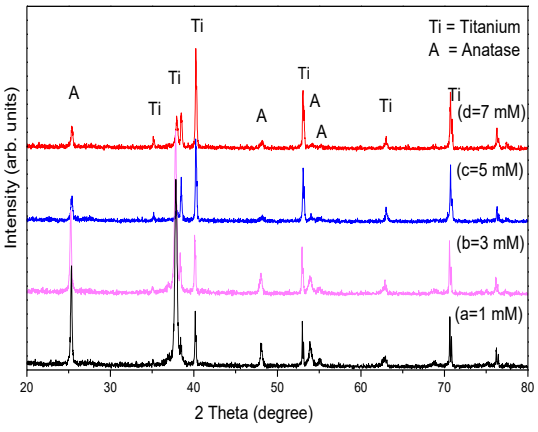

Fig. 3. XRD patterns of Zn-doped TNT after annealing at 450 °C: (a) 1 mM, (b) 3 mM, (c) 5 mM and (d) 7 mM

SEM analysis

The calcinated samples were studied using scanning electron microscopy (SEM). The results presented in Fig. 4 brings to light the changes in the surface morphology of the Zn-doped TNT. The fine structure of the nanotubes gets better with increase in zinc nitrate concentration. However, after 5 mM, the order liness of the nanotube array is heavily disrupted, as seen with the 7 mM sample. A similar result was obtained by X. Chen et al. [27], when varying the concentrations of HCl.

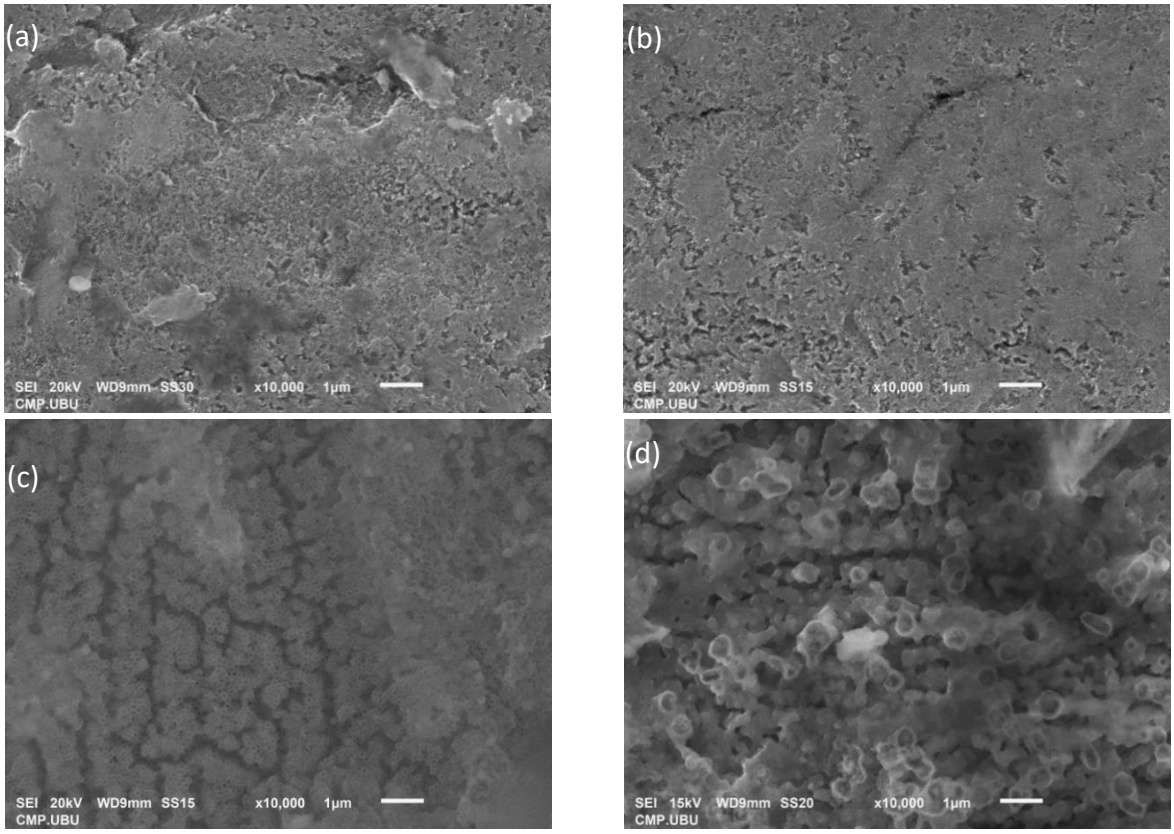

Fig. 4. SEM images of Zn-doped TNT after annealing at 450 ºC: (a) 1 mM, (b) 3 mM, (c) 5 mM and (d) 7 mM

UV-visible spectroscopy analysis

The ultraviolet-visible spectrums of the annealed samples are presented in Fig. 5. The sample with a zinc nitrate concentration of 5 mM had the greatest cut off wavelength (λ_c) of 390 nm. λ_c increased with concentration until 5 mM, and decreased there after at the higher concentration of 7 mM. We can attribute this to the disorderly array of the nanotubes demonstrated in SEM images of Fig. 4(d). A large λ_c implies a smaller energy band gap (E_g), as demonstrated in Table 1 by Eq. (3) [28–30]:

$$E_g = \frac{hc}{\lambda_C} = \frac{1240}{\lambda_C}, \quad (3)$$

where h is the Planck constant (6.626×10^{-34} Js or 4.14×10^{-15} eVs) and c is the speed of light in vacuum (3.00×10^{8} m/s).

Table 1. Energy band gapfrom UV-VIS for different concentrations of Zn-doped TNT after annealing at 450 ºC

Samples	1 mM	3 mM	5 mM	7 mM
λ_c, nm	379	388	390	384
E_g, eV	3.27	3.20	3.18	3.23

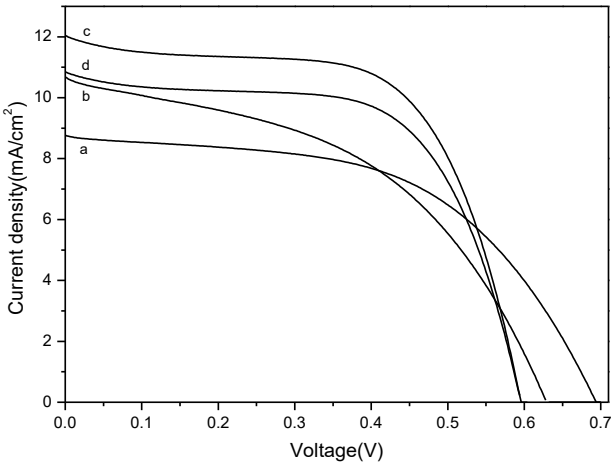

Fig. 5. Current-voltage (IV) characteriztic curves ofZn-doped TNT after annealing at 450 ºC: (a) 1 mM, (b) 3 mM, (c) 5 mM and (d) 7 mM

IV characteristic and photoelectric performance

Figure 5 and Table 2 both reveal that as zinc nitrate concentration increase, the cell efficiency and photocatalytic performance also increase. One explanation to this is that the dopant element Zn serves as charge traps and helps to reduce charge carrierre combination. As more zinc ions replace the titanium ions in the crystal lattice, more charge traps are created. Another reason is that the introduced Zn aid in reducing the band gap energy by forming intermediate energy levels. As a result, the photon absorption of the DSSCs is shifted from the UV region to the Visible light region. This conclusion is supported by the work of Udom T. et al [31]. The 5 mM zinc nitrate sample had the highest PCE of 4.96 %. Because doping reduces the number of trapping states, resulting in a reduction of charge recombination. The efficiency of dye sensitized solar cell of doped Zn-TiO_2 nanotubes obviously declined, which may be due to the formation of recombination centers of photogenerated carriers by the excessive impurity atoms [32]. The cell efficiency at a higher concentration was lower due to a highly distorted and disorganized nanotube array as observed in the SEM images in Fig. 4(d). As a consequence, the charge carrierre combination will be greater, resulting in lower PCE and photocatalytic performance.

Table 2. Photoelectric performance of Zn-doped TNT after annealing at 450 ºC

Samples	J_{sc}, mA/cm^2	V_{oc}, V	*FF*	η, %
1 mM	8.87	0.68	0.53	3.42
3 mM	10.94	0.64	0.49	3.52
5 mM	12.35	0.62	0.64	4.96
7 mM	10.95	0.61	0.62	3.85

Conclusions

Zinc-doped TiO_2 nanotubes were synthesized byDC anodization at 50 V, and their photocatalytic performance were testedin dye-sensitized solar cells (DSSCs). The

electrolyte was composed of ethyleneglycol (EG), ammoniumfluoride (0.3 % wt NH_4F), and deionized water (2 % V H_2O). zinc nitrate was used as the source of the dopant element Zn, and the molar concentrations of zinc nitrate was varied as follows: 1, 3, 5 and 7 mM. The Zn-doped TNT were characterized using several techniques. XRD patterns revealed the transformation of amorphous TiO_2 into the anatase phase after calcination at 450 ºC.The surface morphology and array of the nanotubes were studied using SEM. The nanotubes for the 7 mM sample show highly distorted arrangement. The energy band gaps were determined from the UV-VIS results. The lowest band gap energy of 3.18 eV was obtained for the 5 mM sample. This value can be used to account for the optimal photocatalytic performance of the 5 mM sample when tested in DSSCs. It had the highest PCE of 4.96 %. The results of this research provided significant guidelines for ongoing and future research in the development of sustainable energy.

CRediTauthorshipcontributionstatement

Buagun Samran: conceptualization, data curation, investigation, supervision, writing – review & editing, writing – original draft; **Thanatep Phatungthane**: conceptualization, investigation, supervision, writing – original draft; **Pratya Thongpanit**: conceptualization, investigation, supervision, writing – original draft; **Bhunpawatana Kadroon**: conceptualization, investigation, supervision, writing – original draft; **Saranyoo Chaiwichian**: conceptualization, investigation, supervision, writing – original draft, writing – review & editing.

Conflict of interest

The authors declare that they have no conflict of interest.

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