AIMS Materials Science

AIMS Materials Science, 3(2): 460-469.
DOI: 10.3934/matersci.2016.2.460
Received: 07 March 2016
Accepted: 04 April 2016
Published: 07 April 2016

http://www.aimspress.com/journal/Materials

Research article

The directed preparation of TiO_2 nanotubes film on FTO substrate *via* hydrothermal method for gas sensing application

Pham Van Viet [1,2,*], Le Van Hieu [1], and Cao Minh Thi [2]

[1] Faculty of Materials Science, University of Science, VNU- HCMC, 227 Nguyen Van Cu street, District 5, Ho Chi Minh City, 700000, Vietnam
[2] CM Thi Laboratory - Ho Chi Minh City University of Technology (HUTECH) 475A Dien Bien Phu, Binh Thanh District, Ho Chi Minh City, 700000, Vietnam

* **Correspondence:** Email: pvviet@hcmus.edu.vn.

Abstract: In this research, we directly synthesized TiO_2 nanotubes film on Fluorine doped Tin oxide (FTO) substrate via hydrothermal method from commercial TiO_2 in NaOH solution at 135 °C for 24 hours. The samples were characterized by X-ray diffraction (XRD) pattern, field emission scanning electron microscopy (FESEM) and transmitting electron microscopy (TEM). The average diameter of TiO_2 nanotubes (TNTs) is about 10–12 nm and their length is about a few hundred nanometers. The sensitivity ability of TNTs increases as the gas concentration increases and developing to the highest sensitivity of TNTs is 2.4 at 700 ppm of the ethanol concentration. The same as the gas concentration, the sensitivity of TNTs increases when the temperature increases. Besides, the sensitivity of samples at 250 °C is doubled compared to samples determined at 100 °C.

Keywords: oxides; epitaxial growth; electron microscopy; microporous materials; nanostructures

1. Introduction

Nano-structured materials such as nanocrystals, nanotubes, and nanowires can significantly improve the sensitivity and response time of gas sensors [1]. Because of excellent chemical and physical properties and low manufacturing costs, TiO_2 nanotubes (TNTs) become a promising material for many applications [2]. Recently, there has been an upsurge of interest in doped TNTs coatings with metals, metal oxides and non-metals for the enhanced photocatalytic activity and photochemical water splitting applications, such as Cr, Pt, Mn, Fe, ZnO, WO_3, ZnO and S [3–10].

TNTs fabricated by anodic oxidation of pure Ti surface have been found wide application in electronics. Besides, this anodization process grew nanoporous TiO_2 on the Ti surface, and human osteoblast cell interaction were evaluated on the modified surface [11,12]. In the gas sensing field, there are three general approaches to the synthesis of TNTs on substrate, such as sol-gel synthesis using templates [13], electrochemical anodic oxidation [14,15] and hydrothermal method [16]. Each method has its advantages and drawbacks. For instance, anodization of Ti foil represents one of the simplest methods to obtain highly ordered TNTs. However, Ti foils are not suitable for the fabrication of optoelectronic devices that usually require transparency [17]. In order to this problem, Oomman K. Varghese et al. suggested a somewhat different approach, i.e. Titanium film deposition was carried out on FTO glass substrates and TNTs on FTO was formatted by anodization method [18]. According to Qi Pang et al., TNTs were synthesized by anodization of Ti foil and TNTs were detached and transferred highly ordered TNTs arrays onto FTO glass and two drops of 0.1 M Ti-isopropoxide were subsequently added to the TNTs films to form interconnections between the FTO glass and the TNTs films [19].

Hydrothermal synthesis is highlighted with 99% conversion after 24 hours, easily scales up and recycles NaOH. It is readily synthesized using simple methods with low cost materials [20]. In the previously published research, TNTs were fabricated at powder form and mixed with some solutions. After that, they were pasted on substrates. For example, Liu et al. mixed TNTs powder with the ethanol solution to form a paste. Then, it was coated on an alumina tube bearing a pair of Au electrodes. After they were sintered at 200 °C for 5 hours in the air, a heating wire was inserted into the alumina tube as illustrated [21]. Similarly, Yan Li Wang et al. mixed samples with deionized water to form a paste and the paste was coated on a ceramic tube on which a pair of gold electrodes was previously printed and dried by an infrared light [22].

In this research, we synthesize TNTs on FTO substrate directly by hydrothermal method. Hydrothermal method is suitable approach for preparing TNTs with high crystallinity, controllable phase, large specific surface area and small diameter. After that, we survey the ability of Ethanol gas sensing of TNTs at various concentrations and temperatures.

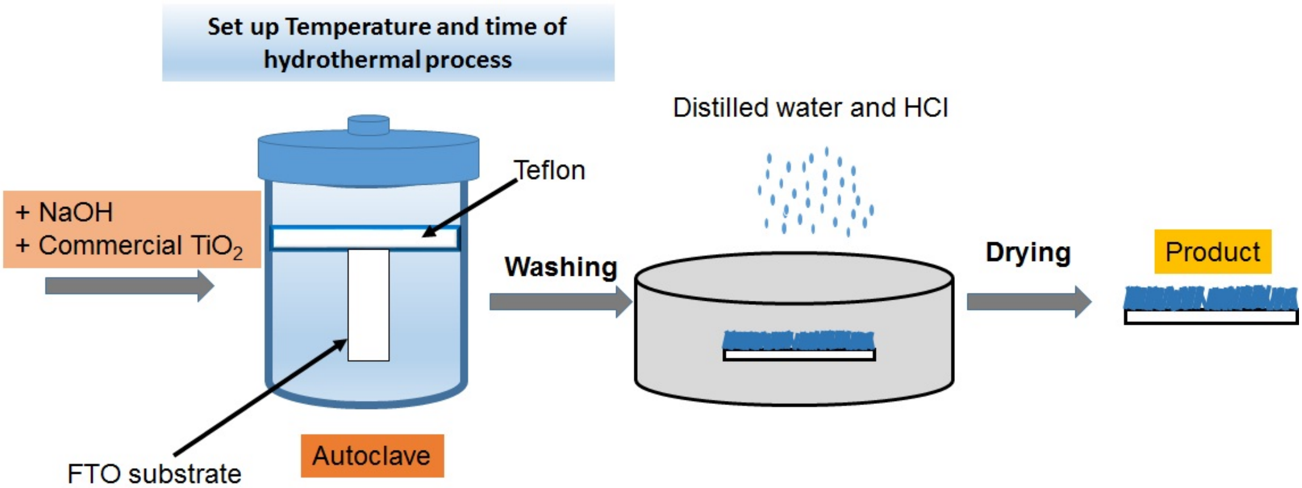
2. Materials and Method

2.1. Reagents

Titanium dioxide powder (commercial powders have several micro meter scale, Merck, Germany, 99.99%), sodium hydroxide powder (NaOH, Merck, Germany, 99.99%), Hydrochloric acid (HCl, China, 99%), Acetone, Ethanol were obtained from Merck and 2 times distilled water used without further purification, FTO substrates Solaronix, Switzerland.

2.2. Preparation of TNTs

Firstly, commercial Titanium dioxide and 93 ml of 10 M NaOH solution were mixed and stirred in an hour. The solution was placed in a PTFE (Teflon)-lined autoclave and heated into 135 °C and kept reactive hydrothermal for 24 hours. FTO substrates are kept perpendicular and submerged in the solution of the Teflon vessel. After the hydrothermal finished, the autoclave was cooled down to room temperature and samples were washed with 0.01 M HCl for over 30 min until the pH reached around 2. After that the samples washed with distilled water until the pH reached around 4. Finally, the samples were dried at 150 °C in an hour. These processes are illustrated on Schematic 1.



Schematic 1. Fabrication process of the TNTs film on FTO substrate via hydrothermal method.

2.3. Sample characterization

The size and morphology of the prepared samples were measured by Field-Emission-gun Scanning Electron Microscopy (FE-SEM, JEOL JSM-7401F) and *Transmission Electron Microscopy* (*TEM,* JEM –1400). The structures of the samples were characterized by X-ray diffraction spectroscopy (XRD, D8–ADVANCE), XRD was performed with Cu-Kα radiation (λ = 1.5418 Å).

Characteristic of gas sensing: Sensitivity of samples (S) was determined from $S = \frac{R_a}{R_g}$ (where R_a is the electrical resistance of the sensor in air, and R_g is the electrical resistance of the sensor in ethanol–air mixed gas) [23,24,25]. Besides, according to Wei-Cheng Tian et al. [24] and Ibrahim A. Al-Homoudi et al. [25], the gas sensors base TiO_2 materials operating at temperatures ranging between 200 and 350 °C. Higher sensor operation temperatures typically led to stronger and faster sensing responses.

3. Results and Discussion

3.1. Morphology and structure of TNTs on FTO substrate

TEM image of TNTs (Figure 1) shows that the surface morphology of samples has the entire nanotubes structure. The average diameter of tubes is about 12 nm and their length is about several hundred nanometers. Besides, our previous publication indicated that the TNTs powder samples which were synthesized by hydrothermal method at 135 °C for 24 hours and were treated by acid and distilled water until the pH reached around 4 have crystallized structure with rutile phase of the (110) peak [16].

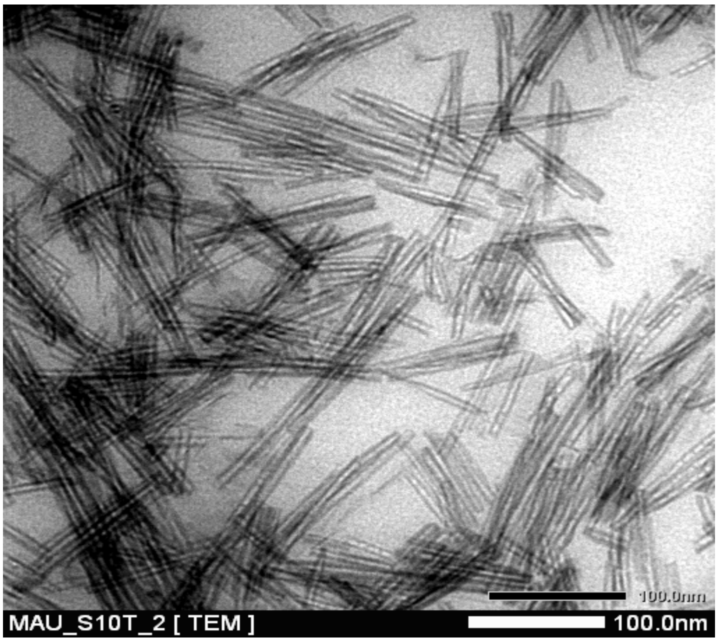


Figure 1. TEM image of TNTs powder synthesized hydrothermal.

Figure 2a is the FE-SEM image of the TNTs coated on FTO substrates (TNTs/FTO). It shows that the morphology of samples has nanowires shape and porous structure. They have diameter from 10 to 25 nm and their length is about a few hundred nanometers. These morphologies are one of suitable parameters for the application of gas sensor [26]. The TEM image shows that the average diameter of TNTs is about 10–12 nm (Figure 2b) and is suitable with results of FE-SEM image (Figure 2a).

Both rutile TiO_2 and FTO have tetragonal structure. Moreover, the lattice matching factor between FTO and rutile TiO_2 is < 2%, a feature that facilitates a linear growth of the rutile phase directly from the substrate [27]. Figure 3 shows XRD patterns of FTO substrate and TNTs/FTO. When TNTs were coated FTO, the intensity of peaks had decreased and the (101) lattice plane disappeared. According to P.Soundarrajan and et al., the (110) crystallographic plane growth of rutile TiO_2 has the most stable surface and the (101) plane will grow at low temperature (120 °C) of the autoclave [28]. In this research, we synthesized TNTs at 135 °C in 24 hours in the autoclave. As a result, the (110) crystallographic plane grow and (101) plane disappeared.

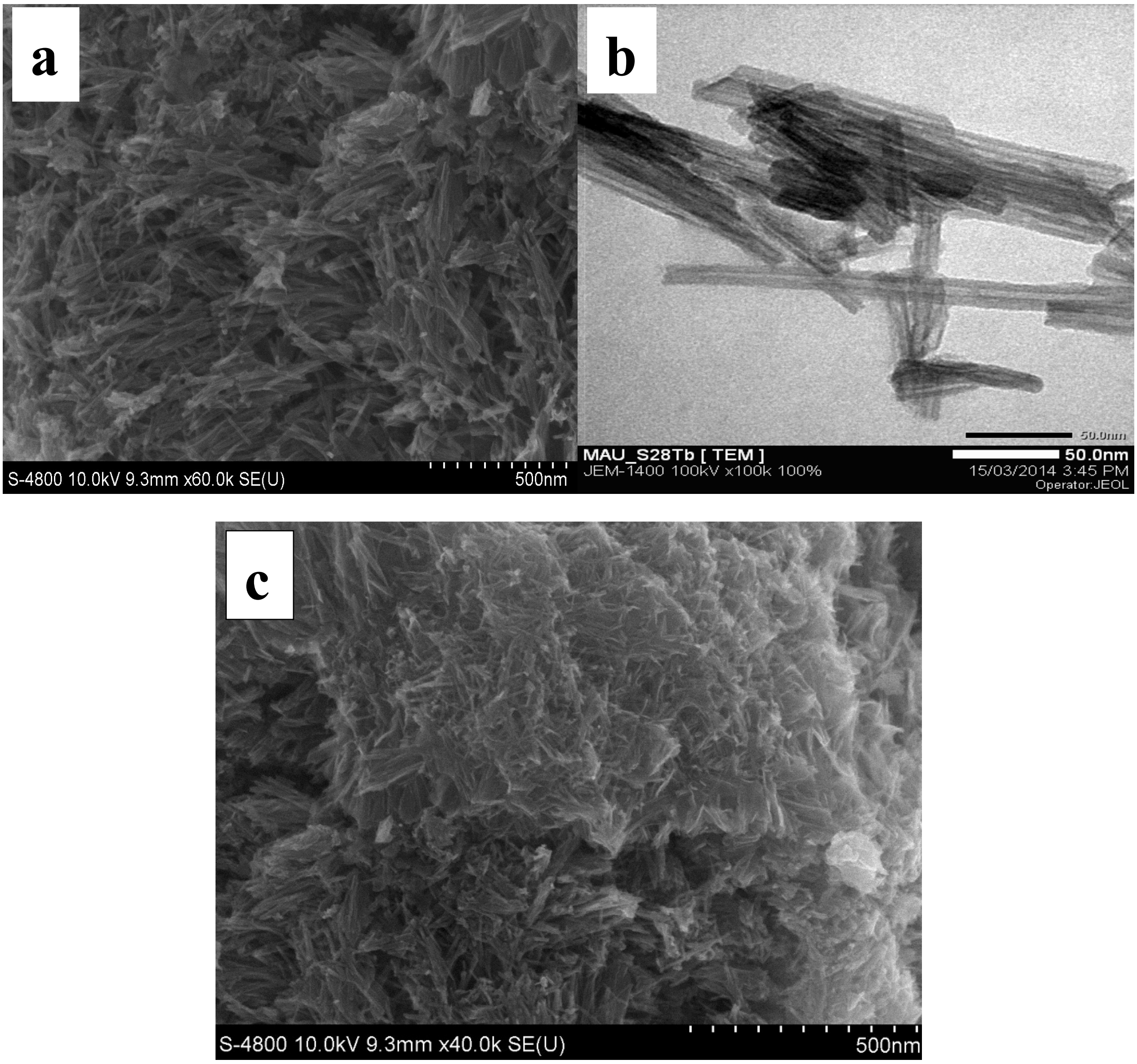


Figure 2. (a) FESEM image of TNTs/TNTs, (b) TEM image of TNTs/TNTs and (c) FESEM image of TNTs/FTO after gas sensing at 250 °C.

3.2. Characteristic of Ethanol gas sensing of TNTs

A model of sensor structure shows as Figure 4. Herein, we coated Ag electrodes by DC Magnetron sputtering method and investigated the ability of gas sensing of TNTs for ethanol gas at various concentrations and temperatures.

According to Sergiu P. Albu et al., the heat treatment of TNTs can also affect the nanotube morphology [29]. Usually, when TNTs extended annealing, they are stable up to 650 °C. However, the tubes start collapsing higher temperatures (> 650 ^{o}C). In an independent research, Odair P. Ferreira et.al. shown that the morphology of nano-tubular will convert to $Na_2Ti_6O_{13}$ nanorods at 600 °C [30,31]. So, the temperature range (from 100 °C to 250 °C) of surveys of gas sensing properties of TNTs will not be effected by the change of TiO_2 morphology. Indeed, the surface morphology of TNTs/FTO is kept stable after survey of gas sensing at 250 °C (Figure 2c).

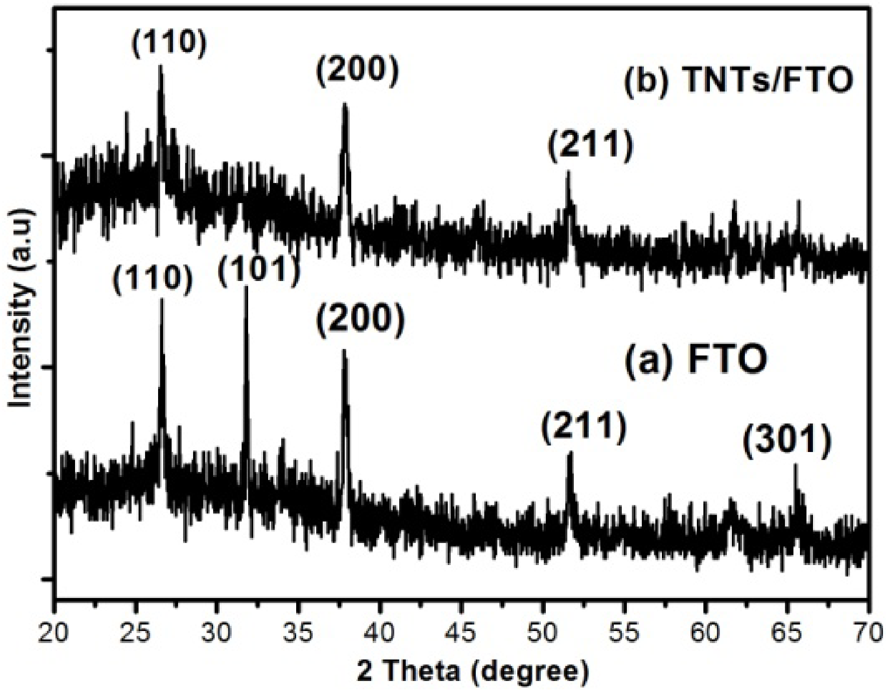


Figure 3. XRD pattern of (a) FTO substrates; (b) TNTs on FTO substrates.

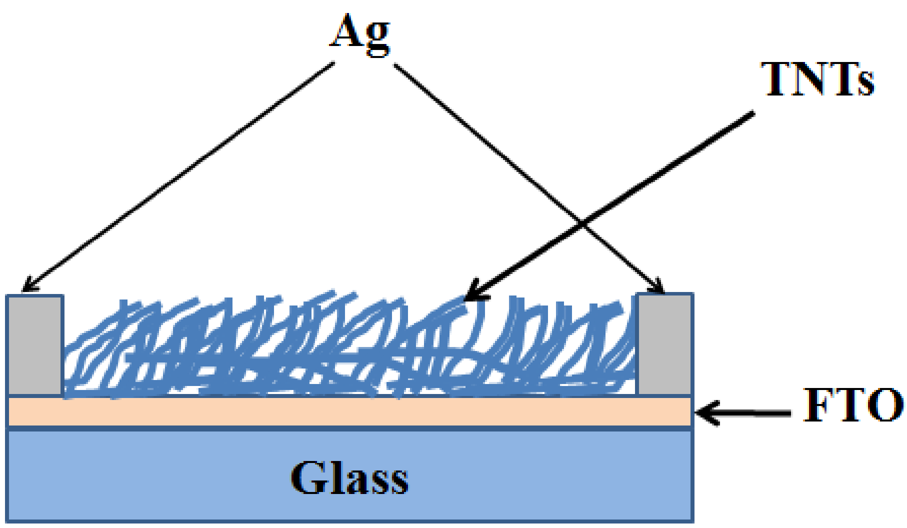


Figure 4. Schematic illustration of the gas sensor.

Figure 5 shows the variation of the sensitivity of sensor for various concentrations of ethanol gas (from 250 to 700 ppm) at 250 °C. In this condition, the sensitivity increases when the concentration of gas increases. The highest sensitivity of TNTs is 2.4 at 700 ppm for the concentration of ethanol gas.

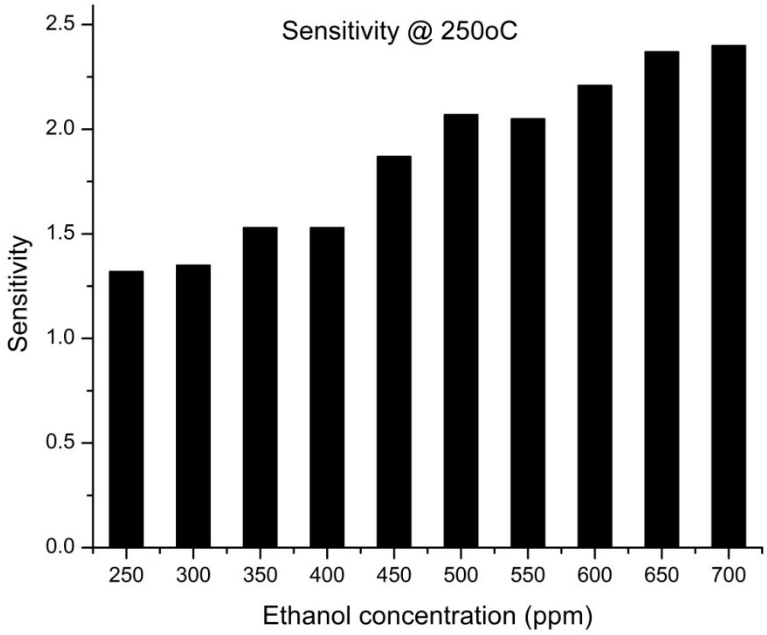


Figure 5. The graph of the sensitivity of TNTs according to various concentrations of ethanol gas at 250 °C.

Figure 6 shows the sensitivity of TNTs according to various temperatures at 500 ppm of the concentration of the ethanol gas. When the temperature increases, the sensitivity of TNTs increases and at 250 °C, the sensitivity is doubled compared to the sample which is determined at 100 °C.

Because the ethanol gas is a reduction gas, so the mechanism of TNTs should follow the surface. Firstly, aqueous ethanol is injected into the chamber and it became gaseous. Then, they diffuse and interact with the absorption oxygen atomic on surface of TNTs and return to electron for material surface. The result leading to the conductivity of the sample increases.

This gas sensing mechanism was reported by Hongsith, et al. [23], Zeng et al. [32] According to these reports, the temperature is higher (250–350 °C), the oxygen molecules are dissociated into oxygen ion atoms with negative electric charges as shown in Eq.(1)

$$\frac{1}{2} O_2 + e^- \rightarrow O^- \quad (1)$$

Then, the oxygen ions on the surface of TNTs are active with the ethanol molecules and give up the electrons from the surface back to the conduction band of the material as shown in Eq.(2)

$$C_2H_5OH + O^- \rightarrow CH_3CHO + H_2O + e^- \quad (2)$$

These cause make the conductivity of materials increase. So the resistance of the sensor decrease.

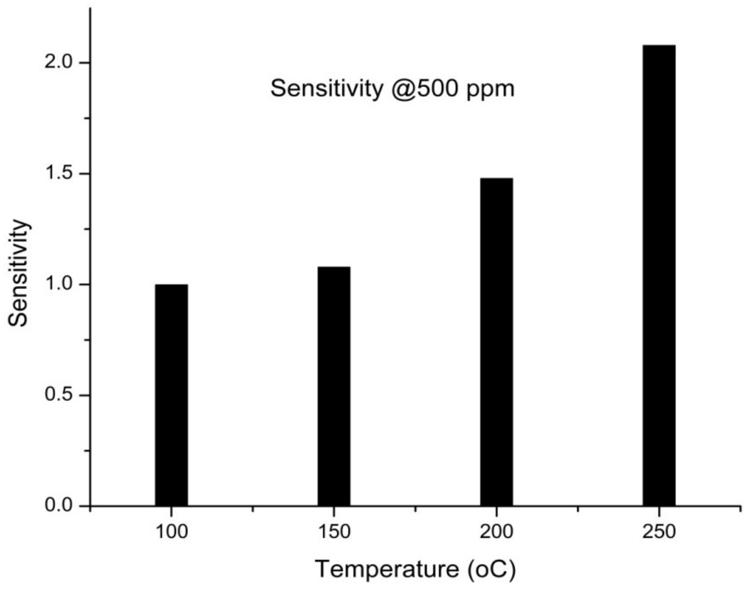


Figure 6. The graph of the sensitivity of TNTs according to various temperatures at 500 ppm of the ethanol gas concentration.

4. Conclusion

We have successfully synthesized TNTs/FTO by a one-step hydrothermal method. Results show that the morphology of samples has nanotubes shape and porous structure. The average diameter of TNTs is about 10–12 nm and their length is about a few hundred nanometers. The sensitivity increases when the gas concentration increases and developing the same temperature of gas sensing.

Acknowledgments

The authors would like to acknowledge to record their gratitude to Administrator Boards of University of Science, Vietnam National University Ho Chi Minh City and Ho Chi Minh City University of Technology (HUTECH) for supporting facilities. This research is funded by Vietnam National University Ho Chi Minh City (VNU-HCM) under grant number C2014-18-14.

Conflict of Interest

Authors declare that there is not conflict of interest.

References

1. Zhai J, Wang L, Wang D, et al. (2011) Enhancement of gas sensing properties of CdS nanowire/ZnO nanosphere composite materials at room temperature by visible-light activation. *ACS Appl Mater Interface* 3: 2253–2258.
2. Zhang X, Zhang J, Jia Y, et al. (2012) TiO2 nanotube array sensor for detecting the SF6 decomposition product SO2. *Sensors* 12: 3302–3313.

3. Momeni MM, Ghayeb Y, Ghonchegi Z (2015) Visible light activity of sulfur-doped TiO2 nanostructure photoelectrodes prepared by single-step electrochemical anodizing process. *J Solid State Electr* 19: 1359–1366.
4. Momeni MM, Ghayeb Y (2015) Fabrication, characterization and photoelectrochemical performance of chromium-sensitized titania nanotubes as efficient photoanodes for solar water splitting. *J Solid State Electr* 20: 683–689.
5. Momeni MM, Ghayeb Y (2015) Photochemical deposition of platinum on titanium dioxide–tungsten trioxide nanocomposites: an efficient photocatalyst under visible light irradiation. *J Mater Sci* 27: 1062–1069.
6. Momeni MM, Ghayeb Y (2015) Visible light-driven photoelectrochemical water splitting on ZnO–TiO2 heterogeneous nanotube photoanodes. *J Appl Electr* 45: 557–566.
7. Momeni MM, Ghayeb Y, Davarzadeh M (2015) Single-step electrochemical anodization for synthesis of hierarchical WO3–TiO2 nanotube arrays on titanium foil as a good photoanode for water splitting with visible light. *J Electroanal Chem* 739: 149–155.
8. Momeni MM, Ghayeb Y (2015) Photoelectrochemical water splitting on chromium-doped titanium dioxide nanotube photoanodes prepared by single-step anodizing. *J Alloy Compd* 637: 393–400.
9. Momeni MM, Hakimian M, Kazempour A (2015) In-situ manganese doping of TiO2 nanostructures via single-step electrochemical anodizing of titanium in an electrolyte containing potassium permanganate: A good visible-light photocatalyst. *Ceram Int* 41: 13692–13701.
10. Momeni MM, Ghayeb Y (2016) Preparation of cobalt coated TiO2 and WO3–TiO2 nanotube films via photo-assisted deposition with enhanced photocatalytic activity under visible light illumination. *Ceram Int* 42: 7014–7022.
11. Crawford G, Chawla N, Das K, et al. (2007) Microstructure and deformation behavior of biocompatible TiO2 nanotubes on titanium substrate. *Acta Biomaterialia* 3: 359–367.
12. Das K, Bose S, Bandyopadhyay A (2009) TiO_2 nanotubes on Ti: Influence of nanoscale morphology on bone cell-materials interaction. *J Biomed Mater Res* 90A: 225–237.
13. Kasuga T, Hiramatsu M, Hoson A, et al. (1998) Formation of Titanium Oxide Nanotube. *Langmuir* 14: 3160–3163.
14. Shokuhfar T, Arumugam GK, Heiden PA, et al. (2009) Direct compressive measurements of individual titanium dioxide nanotubes. *ACS Nano* 3: 3098–3102.
15. Perillo PM, Rodríguez DF (2012) The gas sensing properties at room temperature of TiO2 nanotubes by anodization. Sensor Actuat B Chem 171–172: 639–643.
16. Viet PV, Phan BT, Hieu LV, et al. (2015) The Effect of Acid Treatment and Reactive Temperature on the Formation of TiO_2 Nanotubes. *J Nanosci Nanotechno* 15: 5202–5206.
17. Chu D, Younis A, Li S (2012) Direct growth of TiO2nanotubes on transparent substrates and their resistive switching characteristics. *J Phys D Appl Phys* 45: 355306.
18. Varghese OK, Paulose M, Grimes CA (2009) Long vertically aligned titania nanotubes on transparent conducting oxide for highly efficient solar cells. Nature Nanotechno 4: 592–597.
19. Pang Q, Leng L, Zhao L, et al. (2011) Dye sensitized solar cells using freestanding TiO2 nanotube arrays on FTO substrate as photoanode. *Mater Chem Phys* 125: 612–616.
20. Dmitry V Bavykin FCW (2009) Chapter 1. Introduction and Scope. *RCS Nanosci Nanotechno* 1–19.

21. Liu D, Liu T, Lv C, et al. (2012) Hydrothermal synthesis and gas sensing properties of different titanate nanostructures. *J Mater Sci Mater El* 23: 576–581.
22. Wang YL, Tan S, Wang J, et al. (2011) The gas sensing properties of TiO2 nanotubes synthesized by hydrothermal method. *Chinese Chem Lett* 22: 603–606.
23. Hongsith N, Wongrat E, Kerdcharoen T, et al. (2010) Sensor response formula for sensor based on ZnO nanostructures. *Sensor Actuat B Chem* 144: 67–72.
24. Tian WC, Ho YH, Chen CH, et al. (2013) Sensing performance of precisely ordered TiO2 nanowire gas sensors fabricated by electron-beam lithography. *Sensors* 13: 865–874.
25. Al-Homoudi IA, Thakur JS, Naik R, et al. (2007) Anatase TiO2 films based CO gas sensor: Film thickness, substrate and temperature effects. *Appl Surf Sci* 253: 8607–8614.
26. Yang L, Luo S, Cai Q, et al. (2010) A review on TiO2 nanotube arrays: Fabrication, properties, and sensing applications. *Chinese Sci Bull* 55: 331–338.
27. Liu B, Aydil ES (2009) Growth of oriented single-crystalline rutile TiO(2) nanorods on transparent conducting substrates for dye-sensitized solar cells. *J Am Chem Soc* 131: 3985–3990.
28. Soundarrajan P, Sankarasubramanian K, Sethuraman K, et al. (2014) Controlled (110) and (101) crystallographic plane growth of single crystalline rutile TiO2nanorods by facile low cost chemical methods. *Cryst Eng Comm* 16: 8756.
29. Albu SP, Ghicov A, Aldabergenova S, et al. (2008) Formation of Double-Walled TiO2Nanotubes and Robust Anatase Membranes. *Adv Mater* NA–NA.
30. Odair P, Ferreira AGSF, Filho JM, et al. (2006) Unveiling the Structure and Composition of Titanium Oxide Nanotubes through Ion Exchange Chemical Reactions and Thermal Decomposition Processes. *J Braz Chem Soc* 17: 393–402.
31. Zhou W, Liu H, Boughton RI, et al. (2010) One-dimensional single-crystalline Ti–O based nanostructures: properties, synthesis, modifications and applications. *J Mater Chem* 20: 5993.
32. Zeng W, Liu T, Wang Z (2010) UV Light Activation of TiO2-Doped SnO2 Thick Film for Sensing Ethanol at Room Temperature. *Mater Trans* 51: 243–245.