

Hydrogen sensing properties of doped and undoped TiO₂ nanotubes

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Abstract:

In this work, we fabricated undoped and doped TiO₂ nanotubes for investigating H₂ sensor properties of these structures. Ti foil was anodized in an aqueous HF electrolyte (0.5 wt %) to form TiO₂ nanotube arrays. Carbon doped TiO₂ nanotubes were fabricated by anodization of Ti foil using %0.5 polyvinylalcohol (PVA) in an aqueous HF electrolyte (0.5 wt %). For both doped and undoped TiO₂ nanotubes anodization was performed at a constant potential of 20V and at constant temperature of 20 °C. The two structures were characterized using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), and determined the H₂ sensing properties at 100 °C.

Key words: TiO₂ Nanotubes, Anodization, Carbon, Doped, H₂, Sensor

Introduction

TiO₂ nanotube arrays have been used a wide range of applications in areas such as photoelectrochemical materials, dye-sensitized solar cells [DSSC], hydrogen (H₂) sensors, oxygen (O₂) sensors, bio-sensing and biomedical applications, and catalyst support because of their various properties [1-3]. TiO₂ nanotube arrays firstly were succeeded to fabricate in HF aqueous solution by Grimes et al. After their study, TiO₂ nanotubes were fabricated 22 nm – 76 nm in diameter, 200 nm – 400 nm in length for different voltages. Three methods were used for fabricating TiO₂ nanotubes [4]. First generation: TiO₂ nanotubes, 400-500 nm in length, firstly were fabricated with anodization of Ti for aqueous solution containing F⁻ by Grimes et al. Second generation: The nanotubes, up to 1 mm in length, were synthesized using polar solution such as formaldehyde, ethylene glycol, dimethyl sulfoxide containing F⁻. Third generation: It was clear that there is no need to include F⁻ in the solution for fabricating TiO₂. It was possible to produced the nanotubes using HCl ve H₂O₂ solution. Highly ordered TiO₂ nanotubes were first synthesized using an anodization process by Grimes et al., using hydrofluoric acid (HF) electrolyte [4]. Thereafter, further studies succeeded in controlling and extending the nanotube morphology, the length and pore size, and the wall thickness [1-3]. Many

investigations have been performed for hydrogen gas sensing properties of TiO₂ nanotube arrays at room temperature and the results showed excellent response to hydrogen [1-3, 5-7]. TiO₂ nanotubes were doped with various elements such as carbon, nitrogen, boron, fluorine etc. especially for DSSC applications [1-3]. Bard and coworkers reported fabrication of C-doped TiO₂ nanotubes [9]. Anodized samples were then annealed at 450°C in oxygen for 1 h. To introduce carbon, the nanotube arrays were subsequently annealed at high temperatures (500–800°C) under controlled CO gas flow with no significant morphological changes observed. It was reported that the doping concentration of carbon in the TiO₂ nanotube array could be controlled between 8% and 42% (as determined from the XPS peaks) depending on the CO annealing temperature [9]. Hu et al. incorporated carbon in TiO₂ by annealing as-formed nanotubes in a continuous flow of Ar and acetylene gases, then investigated the photocatalytic activity by evaluating the photodegradation of aqueous methyl blue under sunlight illumination [10]. Hahn et al. performed carbon doping by annealing the TiO₂ nanotubes in N₂ and acetylene gas mixture at 500°C [11]. Xu et al. pursued carbon doping of TiO₂ nanotubes by annealing in air at 500°C for 1 h, and natural gas flame oxidation at 820°C for 18 min, with no significant change found in their quantum efficiency over the visible range [12].

H₂ gas sensing properties of doped TiO₂ nanotube is not investigated yet.

In this study, undoped and carbon doped TiO₂ nanotubes were fabricated and H₂ sensing properties of two structures were investigated depending on carrier gas and temperature.

Experimental Section

Pre-cleaned Ti foil was anodized in an aqueous electrolyte of 0.5 wt% HF using a dc power supply and a platinum foil as cathode in a thermo-stated bath at temperature of 20 °C [6]. Carbon doped TiO₂ nanotubes were fabricated using %0.5 polyvinylalcohol (PVA) in an aqueous HF electrolyte (0.5 wt %) with anodization of Ti foil under the same conditions. All solutions were prepared from reagent grade chemicals and deionized water (18 MΩ). Before the experiments, the solutions were stirred using a magnetic stirrer. After the anodization, the samples were rinsed in deionized water and then dried. All samples were annealed under dry air flow at temperature of 500 °C for 3h. Undoped and C-doped TiO₂ nanotubes were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS).

We prepared sensor devices by contacting the doped and undoped TiO₂ nanotubes with silver paste. For H₂ sensing measurements all samples were tested with concentration range of 100 ppm - 10000 ppm H₂ gas at temperature range of 25 - 200°C.

Result and Discussion

The morphologies of fabricated doped and undoped TiO₂ nanotubes were studied by SEM (Fig 1). Tubular structure is clearly seen from both figures and some part of TiO₂ nanotubes are covered with C (Fig 1b). C, Ti and O peaks are clearly seen from Fig. 2a and Ti2s, Ti2p, O1s and C1s peaks are observed from XPS analysis (Fig 2b).

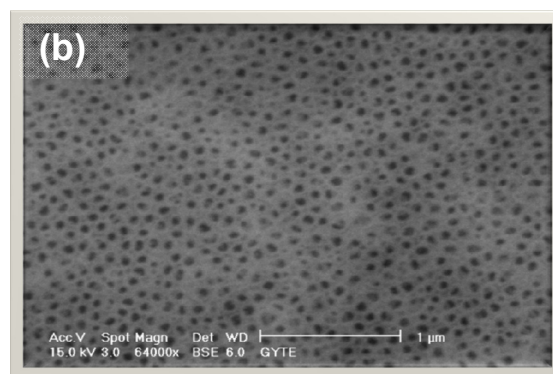
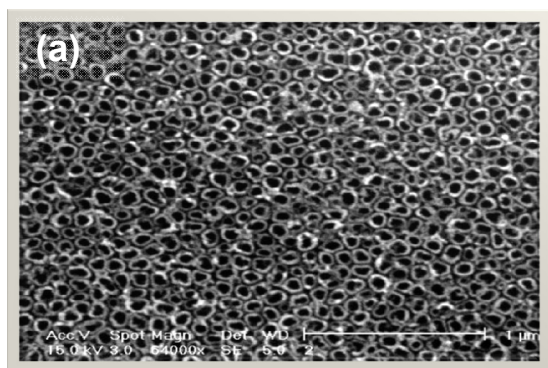


Fig. 1: SEM images of fabricated a) TiO₂ nanotubes [6], b) C-doped TiO₂ nanotubes.

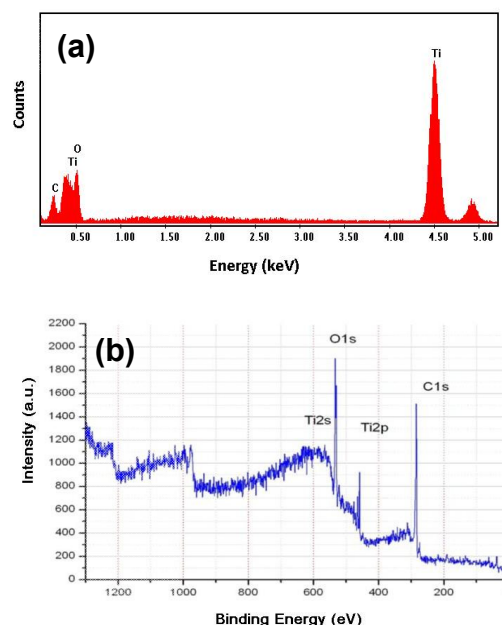


Fig. 2: C-doped TiO₂ nanotubes a) EDX, b) XPS.

Fabricated undoped and C-doped TiO₂ nanotubes were converted into the gas sensor device as shown Fig 3. After fabricating, the bulk nanotubes were pasted on a glass slide using silver paste. Then we contacted from the nanotubes to silver point on the glass with thin cooper wires using silver paste for reducing the pressure on nanotubes. Finally, these devices were placed to gas sensor testing cell.

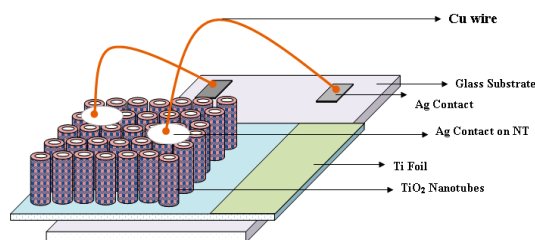


Fig. 3: Sensor Device for Undoped and C-doped TiO₂ nanotubes.

Fig. 4 shows current versus time behaviour of undoped and C-doped TiO_2 nanotubes sensor exposed to 5000 ppm H_2 at 100°C . The conductivity of TiO_2 nanotube is increased with C doping. The exposure to H_2 causes an increase in current of both undoped and C-doped TiO_2 nanotubes. The H_2 sensitivity of undoped was higher than that of C-doped as shown in Fig.4. Effect of temperature and carrier gas will be discussed in detail.

H_2 gas sensing of TiO_2 nanotubes are derived from oxygen vacancies in their structure. The presence of carbon on the surface of the nanotube arrays [9], caused by the adsorption of carbon from PVA-based electrolyte during anodization [14]. Valentin and colleagues [15] described the possible causes for the presence to of carbon atom in the anatase TiO_2 ; 1) the substitution of the oxygen lattice with carbon atom, 2) the replacement of Ti atom with C atom, and 3) the stabilization of an interstitial position by carbonate species. Therefore, the gas sensing mechanism of C- TiO_2 nanotubes is different from undoped TiO_2 nanotubes.

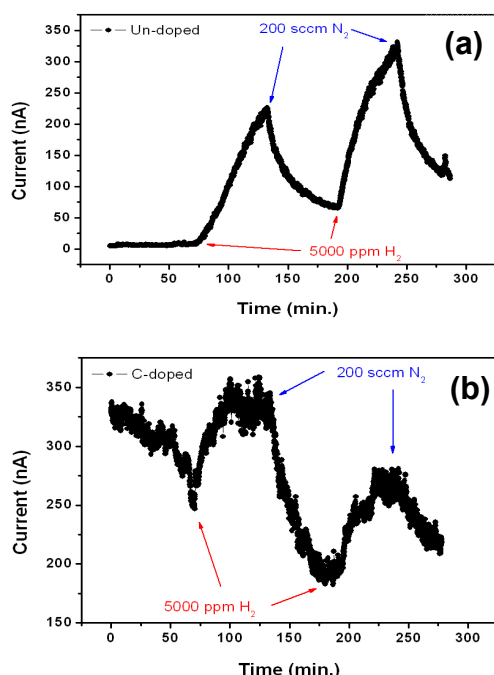


Fig. 4: H_2 sensing properties of undoped (a) and C-doped (b) TiO_2 nanotubes at 100°C .

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References

- [1] C. A. Grimes, G. K. Mor, *TiO₂ Nanotube Arrays: Synthesis, Properties, and Applications*, Springer Science & Business Media, LLC, New York, 2009; DOI: 10.1007/978-1-4419-0068-5
- [2] J.M. Macak, H. Tsuchiya, A. Ghicov, K. Yasuda, R. Hahn, S. Bauer, P. Schmuki, *Current Opinion in Solid State and Materials Science*, 11, 3–18 (2007) DOI: 10.1016/j.cossms.2007.08.004
- [3] G.K. Mor, O.K. Varghese, M. Paulose, K. Shankar, C.A. Grimes, *Sol Energ Mat Sol C* 90, 2011-2075. (2006); DOI: 10.1016/j.solmat.2006.04.007
- [4] Grimes C. A., Mor G. K., *TiO₂ Nanotube Arrays: Synthesis, Properties, and Applications*, Springer Science & Business Media, LLC, New York, (2009).
- [5] D. Gong, C.A. Grimes, O.K. Varghese, W. Hu, R. S. Singh, Z. Chen, E. C. Dickey, *Journal of Materials Research* 16, 3331-3334 (2001)
- [6] O.K. Varghese, D.W. Gong, M. Paulose, K.G. Ong, C.A. Grimes, *Sensors and Actuators B-Chemical* 93 (2003) 338-344; DOI: 10.1016/S0925-4005(03)00222-3
- [7] E. Şennik, Z. Çolak, N. Kılınç, Z. Z. Öztürk, *International Journal of Hydrogen Energy* 35, 4420 (2010)
- [8] G.K. Mor, O.K. Varghese, M. Paulose, K.G. Ong, C.A. Grimes, *Thin Solid Films* 496, 42-48 (2006); DOI: 10.1016/j.tsf.2005.08.190
- [9] Park JH, Kim S, Bard AJ (2006) Novel carbon-doped TiO_2 nanotube arrays with high aspect ratios for efficient solar water splitting. *Nano Lett* 6:24–28
- [10] Hu X, Zhang T, Jin Z, Zhang J, Xu W, Yan J, Zhang J, Zhang L, Wu Y (2008) Fabrication of carbon-modified TiO_2 nanotube arrays and their photocatalytic activity. *Mater Lett* 62:4579–4581
- [11] Hahn R, Ghicov A, Salonen J, Lehto V-P, Schmuki P (2007) Carbon doping of self-organized TiO_2 nanotube layers by thermal acetylene treatment. *Nanotechnol* 18:105604–105608
- [12] Xu C, Shaban YA, Ingler WB, Khan SUM (2007) Nanotube enhanced photoresponse of carbon modified (CM)-n- TiO_2 for efficient water splitting. *Sol Energy Mater Sol Cells* 91:938–943
- [13] Sreekantan S, Saharudin KA, Lockman Z, Tzu TW. Fast-rate formation of TiO_2 nanotube arrays in an organic bath and their application in photocatalysis. *Nanotechnology* 2010;21:365603.
- [14] Valentin CD, Pacchioni G, Selloni A. Theory of carbon doping of titanium dioxide, *Chem Mater* 2005;17:6656-6665.