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Study on the morphology stability of TiO_2 nanotube arrays towards temperature as a potential toxic gas sensor

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Abstract

TiO_2 nanotube arrays were prepared by electrochemical anodization of titanium foil in mixed electrolyte solution of NH_4F, water, and glycerol. The anodized TiO_2 nanotube arrays were calcined at various temperatures and characterized using scanning electron microscope to study the morphology transformation. The results show that at low calcination temperature (300 °C) highly ordered TiO_2 nanotube arrays are observed and remained up to 500 °C. At 700 °C, TiO_2 nanotube arrays are completely destroyed and transformed to irregular shaped particle.

Keywords: TiO_2; nanomaterials; anodization; toxic gas; sensor

1. Introduction

Nanostructured materials are defined as materials that have at least one dimension in the nanoscale size (typically ≤ 100 nm) [1]. Thus, depending on their dimensions they can be classified into a) zero dimension (0-D) nanostructures (e.g. nanoparticles), b) one dimension (1-D) nanostructures (e.g. nanorods, nanowires, nanotubes) c) two dimension (2-D) nanostructures (e.g. thin films), and d) three dimension (3-D) nanostructures materials. These structures can be conceptualized as simple geometrical shape; i.e. dots (0-D), lines (1-D), and squares (2-D). Three dimensional nanostructure materials can be constructed from these low dimensional materials, e.g. an array (3-D) of nanotubes (1-D) [2]. The physical and chemical properties of nanostructured materials are different from those of atoms and bulks materials of the same composition. This is due to the nanometer size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement of electron movements and (iv) reduce

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imperfections, which do not exist in the corresponding bulk materials [3]. For instance, the metallic nanoparticles can be used as an active catalyst, whereby they are inactive in bulk metal. Besides, the superior mechanical properties of carbon nanotubes are well known as normal carbon exhibits weak mechanical properties. Therefore, the uniqueness of the physical and chemical properties of the nanostructured materials constitutes the basis of nanoscience and nanotechnology which can lead to new devices in chemical and biosensor technologies.

Recently, titanium dioxide (TiO_2) nanotubes have been extensively studied because of their non-toxicity, inexpensive, long-term stability against photocorrosion and chemical corrosion [4,5]. This material was explored as a catalyst for production of energy products such as methane and methanol through the photo-reduction of green house gases [6,7]. They are also widely used in electrochemical devices, photovoltaic dye sensitized solar cells and gas sensors application [8,9].

2. Material and Methods

2.1. Preparation

Titanium foil (0.02 mm thick, 99 % purity) with the size 2 cm x 5 cm was washed with acetone and dried at room temperature. Then, a dry titanium foil was used as an anode while the platinum (Pt) electrode served as cathode for anodization process. The anodization process was done at constant applied potential (20 V) for 60 minutes using the electrolyte made from 200 ml glycerol and 2 g ammonium fluoride (NH_4Fl). After anodization the foil was taken out and gently washed with distilled water to remove the occluded ions from the anodize solution. The anodized foil was annealed at 300, 500 and 700 ºC for 1 hour.

2.2. Characterization

The morphology of the samples (as anodized Ti foil, and anodized Ti foil annealed at 300, 500 and 700 ºC for 2 hours, respectively using characterised using scanning electron microscope (JEOL, JSM-6360 LA).

3. Result and Discussion

Fig 1 (a-d) show the SEM of micrograph of as-anodized Ti foil and anodized Ti foil after calcination at 300 °C, 500 °C and 700 °C respectively. TiO_2 nanotube arrays was obtained after anodization of Ti foil at 20 V for 1 hour using fluoride based electrolyte. The diameter of the synthesized TiO_2 arrays are ~45 nm (Fig.1a). The fundamental mechanism formation of TiO_2 nanotubes in fluoride containing electrolytes is the result of three simultaneously occurring processes. First, the field assisted oxidation of Ti metal to form titanium dioxide, second the field assisted dissolution of Ti metal ions in the electrolyte, and lastly the chemical dissolution of TiO_2 due to etching by fluoride ions. Then, the nanotubes of TiO_2 growth up, as a result of a competition between electrochemical oxide formation [Equation 1] and chemical dissolution of TiO_2 due to the action of fluoride ion [Equation 2] [10,11].

$$2Ti + 4H_2O \rightarrow 2TiO_2 + 8H^+ + 8e^- \quad (1)$$
$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O \quad (2)$$

In order to study the stability of nanotubes morphology towards temperature, the samples was calcined at 300, 500 and 700°C for 1 hours. After calcination at 300 °C, uniform and highly ordered TiO_2 nanotube arrays grown on Ti substrate are remained (Fig. 1b). At 500 °C, the nanotube arrays still can be observed. As it can be seen in Fig. 1c, the samples still keep their nanotubes structure. However, at 700 °C, the morphology of calcined sample has a great changes (Fig. 1d). The tubular structures are difficult to observe, otherwise only particles with irregular shape can been seen due to the destruction and coalescence of nanotube structures. From the result obtained, it can be concluded that the nanotubes morphology of TiO_2 are thermally stable up to 500 °C. However, the nanotubes structure collapsed and transformed into irregular particle at 700 °C. This was attributed to high heat energy being applied that would accelerate the crystal growth and TiO_2 phase evolution.

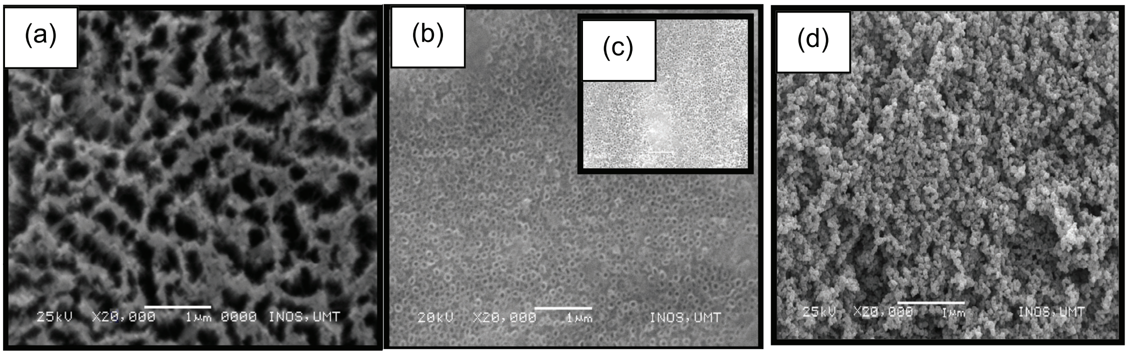

Fig. 1. SEM micrograph of (a) as-anodized Ti foil and calcined anodized Ti foil at (c) 300 °C (d) 500 °C and (e) 700 °C for 1 hour

4. Conclusion

TiO_2 nanotube arrays with the diameters ~45 nm was successfully synthesized using anodization method. The synthesized TiO_2 nanotube arrays thermally stable up to 500°C. However, at 700 °C, nanotubes morphology was transformed to agglomerated particle with irregular shaped.

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