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Structural modulation and band gap optimisation of electrochemically anodised TiO_2 nanotubes

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A R T I C L E I N F O

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A B S T R A C T

This analytical study highlights the effects of dimensional modulations on the characteristic properties of anodically grown Titania nanotubes. Titania nanotubes were grown using electrochemical anodization method employing a two-electrode system. The as-grown nanotubes with different dimensions were characterized in order to study their structural, electrical and optical properties. The investigation reveals that the impact of dimension was pivotal in tuning the band gap of these anodically grown Titania nanotubes which asserts its successful application in various fields. The desired dimensional modulation of the nanotubes was achieved by changing the corresponding anodising voltage. This study also employs a remedial two step anodization technique in addition to the conventional one step method and presents its distinctive edge over the other as established by various characterisation techniques. The comparative variations in the structural and crystallite dimensions of the Titania nanotubes anodised by two different methods were investigated by Field Emission Scanning Electron Microscopy and X-Ray Diffraction spectroscopy respectively, while the band gap tuning ability as well as absorption characteristics were determined by UV-Diffuse Reflectance spectroscopy. Finally, the effective changes in the band gap were corroborated by analysing the field effect dark and photo-conductive nature of the two materials.

1. Introduction

Since the dawn of the nanotechnology era, semiconducting materials (metal oxide) have played an important role in widening its scope of application to various fields [1]. One of the predominant n-type semiconducting materials is Titanium Dioxide (TiO_2). Due to its unique structural, optical and electrical properties [2] it finds applications in varied fields such as gas sensing [3], water splitting [4], solar cells [5] and biomedical applications [6]. Of late, researchers around the globe have been focussing more on the synthesis and growth of nanostructured semiconducting materials [7] as compared to the customary nanoparticles. One dimensional nanostructured materials display strong structural ordering and uniform patterns responsible for enhanced and refined properties in contrast to nanoparticle natured materials. For e.g., it has been proved that successful application of a nanostructured material instead of nanoparticles in Dye Sensitized Solar Cells (DSSC) [8] has efficiently increased the electron mobility and reduced the charge trap states within the electron transport layer due to direct channelling of electron movement across the length of the specific nanostructured material. With these characteristic and defined advantages in mind we have focused this work on the growth and characterisation of nanotube structured TiO_2 synthesized using electrochemical anodization method [9].

The reason behind the selection of tubular structure as well as electrochemical anodization as the synthesis method primarily lies in the simplicity as well as ease of processing [10] through which these defined structured nanotubes are grown on the surface of Titanium foil. Though there are other remedial measures through which Titania nanostructures can be grown, the convenience as well as control over the morphology that can be achieved in growing well defined, orderly arranged tubular structures are hardly feasible with any alternative synthesis processes. Besides the above mentioned distinctive properties, the anodization method also features structural tuning of the dimensions of the nanotube with respect to defined changes in the experimental parameters [11].

Ranging from the applied anodising voltage, anodising time, electrolytic content and pH of the electrolyte, each of these parameters plays an important role in defined tuning of the pore width, pore diameter as well as tubular length of the anodised samples [12].

The pioneering work which initiated research in the field of anodic

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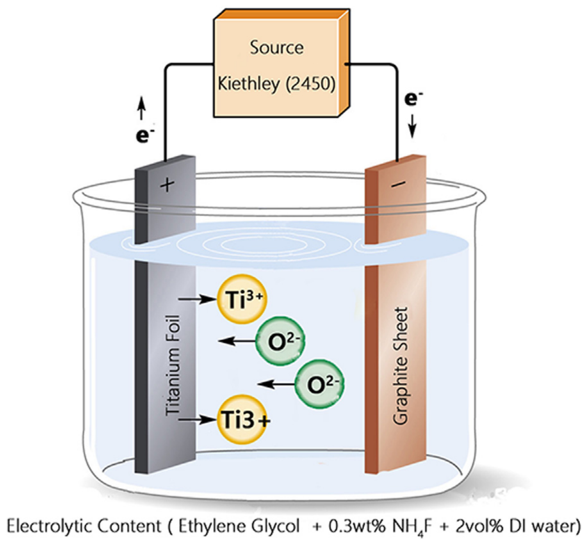

Fig. 1. The schematic diagram of the electrochemical cell employed for the growth of Titania nanotubes.

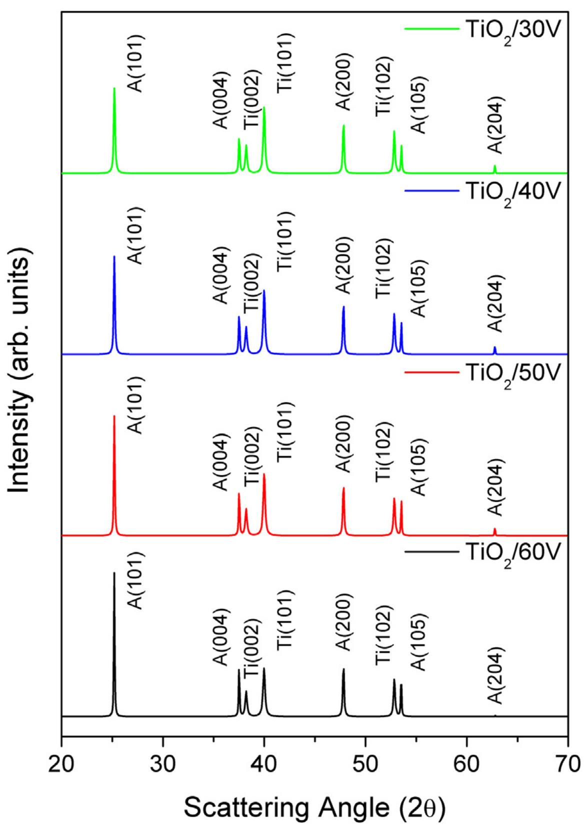

Fig. 2. XRD pattern of Titania nanotubes anodised at various anodising voltage using conventional one step method.

growth of Titania nanotubes was reported by Zwilling et al. [13]. Since then a chain of foundational work has been carried out on this pitch, aimed at intensifying the control over the structural tuning and enhancing their properties in relevance to selective applications. From a transition in electrolytic solvent from aqueous to viscous electrolyte [14] and growth of tubes of length ranging from around 500 nm to the longest of few millimetres [15], the endeavour in the arena of "growth of Titania nanotubes by electrochemical anodization method" has been voluminous.

Apart from the work described above, scientists around the globe

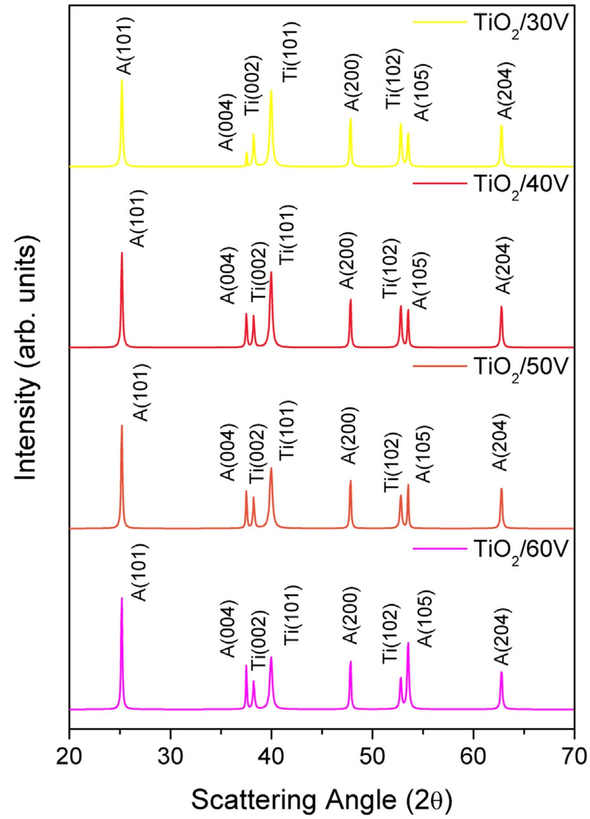

Fig. 3. XRD pattern of Titania nanotubes anodised using two step method at various anodising voltages.

have also ventured into other alternate options which can efficiently enhance the opto-electrical properties as well as increase the surface area of the anodised Titania nanotubes. These remedial measures range from elemental doping of the grown nanotubes to surface treatment of the nanotubes in organic bath post anodization period. To cite a few of the reported works that have been carried out in recent times, doping of nitrogen [16], carbon [17] as well as chromium [18] in the anodised nanotubes with the objective of improving the photocatalytic properties of these materials facilitating their successful application in water-splitting, Lithium ion batteries as well as water cleansing measures in nuclear plants. Besides these approaches, surface treatment of grown Titania nanotubes by titanium tetrachloride ($TiCl_4$) [19] has also been reported as a common measure in DSSC applications, for successful loading of dyes and increasing charge transport properties within the fabricated cell.

One of the remedial facile means through which the characteristic properties as well as structural modulation of the anodised Titania nanotubes can be accomplished is a two-step anodization method [20] in lieu of the accustomed one-step anodization method. This alleviative mean in comparative to other remedial measures doesn't demand an intervention of outside additive agents to assist in the structural and opto-electrical optimisation of the samples. Rather this method necessitates the conventional one-step anodization method to be performed twice so that the eventual outcomes of the anodised nanotubes are greater defined and uniformly distributed. Furthermore, the Titania nanotubes anodised using the two-step method display enhanced adhesion of the grown tubes to the substrate [21] and an advantage of having open ended tubular bottoms attached to the surface [22] which greatly dealt with the prominent problems faced by the conventional tubes grown using one step method. A detailed analysis of the comparative differences between the two methods is done in the results and discussion part.

In the case of optoelectronic devices, one of the most intrinsic