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Archives of Applied Science Research, 2013, 5 (5):28-32  
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## Synthesis and characterization of titania nanotube arrays by electrochemical method for dye sensitized solar cells

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### ABSTRACT

*TiO<sub>2</sub> is known as one of the excellent and demanded materials for its wide applications. In this paper, the growth of TiO<sub>2</sub> nanotube arrays by using simple and inexpensive electrochemical anodizing of a titanium foil is presented. The vertically oriented TiO<sub>2</sub> nanotube arrays were prepared in electrolyte solution of 3 wt % HF (40%) and dimethyl sulfoxide (DMSO) at constant DC voltage of 30 V for 17h. The photoluminescence, crystallinity and surface morphology of prepared nanotube arrays were studied by Spectrometer, XRD and FE-SEM. Room temperature photoluminescence measurement showed a sharp peak at 383 nm corresponding to the band gap energy (3.2 eV) of bulk TiO<sub>2</sub> anatase phase. However, humps at 412 nm and 471 nm are attributed to the free excitations where as at 521 is attributed to the formation of oxygen vacancy at the surface of titania nanotube arrays. XRD measurement revealed the anatase phase of TiO<sub>2</sub> nanotube arrays and found good matching with others reported works. FESEM measurement showed well aligned formation of nanotube arrays of ~80 nm of inner diameter and ~20 nm of wall thickness of TiO<sub>2</sub> nanotubes.*

**Keywords:** TiO<sub>2</sub> nanotube arrays, Photoluminescence, X-ray diffraction, field emission scanning electron microscope.

### INTRODUCTION

Today, an important challenge to our society is the development of efficient devices, intensively for energy conversion and storage. Among all, the energy conversion by dye sensitized solar cells (DSSCs) and energy storage in lithium-ion batteries have brought the enormous attention of researchers. One-dimensional metal-oxide nanostructures have got interest due to their high electron mobility, low carrier recombination rate, high surface-to-volume ratio and excellent surface activity. One of their important applications is in dye sensitized solar cells, as a matter of fact the electron diffusion length in the anodic TiO<sub>2</sub> based DSSCs can be up to 100 μm which is almost four times longer than in case of commercial TiO<sub>2</sub> nanoparticles used in DSSCs. This unique charge transport property has received an intensive research on anodic titania nanotubes for DSSCs. TiO<sub>2</sub> 1D-tubular shape has light scattering effect and enhanced electron charge transport which are the critical issues in photoelectrochemical and photocatalysis applications.

Due to good chemical and electronic properties, TiO<sub>2</sub> is a suitable candidate as active materials in electrochemical devices [1]. Anodic TiO<sub>2</sub> nanotube arrays have received the attention of scientific community due to their ease fabrication with tunable desired properties. In 1953, Keller et al. have described the anodic alumina array as a hexagonally close-packed duplex structure with the combination of a porous and a barrier layer [2]. Further, by using a two-step anodization approach Masuda et al. have presented the optimized degree of self-order in porous alumina [3]. Actually, the research on TiO<sub>2</sub> nanotube arrays is classified into three generations. In first generation, Zwilling et al. have commented the formation of nanoporous anodized titania however, D. Gong et al. have first

reported work on anodized titania nanotubes by using a dilute solution of hydrofluoric (HF) acid as an electrolyte [4-5]. The obtained thickness of anodic layer was limited upto 0.5 $\mu\text{m}$  due to used HF which etched and dissolved most of the growing oxide. In second generation of nanotubes, the rapid rate of titania dissolution was reduced by replacing the HF acid with less aggressive solutions containing fluoride salts and have reported the anodic layer thickness from 2-3 $\mu\text{m}$  [6-9]. However, the use of water yields irregularities (ripples) along the walls of the nanotubes. In third generation of nanotubes, smooth tubes without ripples along the wall were prepared in organic electrolytes which help to reduce the dissolution rate of oxide formation. J. M. Macak et al. have reported the formation of titania nanotubes by using organic electrolyte and found anodic layer thickness about 7 $\mu\text{m}$  [10].

The synthesis of TiO<sub>2</sub> nanotube arrays can be done by using hydrothermal and electrochemical anodization methods [11-12]. The electrochemical anodization synthesis is considered to be the popular one due to its ease process and good controllability on structural properties. Anodic oxidation is one which can be tuned for large area uniform nanotubular arrays on Ti foil with relatively high specific surface. Feng Zhou et al. have reported the synthesis of TiO<sub>2</sub> nanotubes with tunable morphologies by adjusting the reaction conditions during anodization. By changing the process parameters such as reaction temperature, applied voltage and HF concentration either nanoporous TiO<sub>2</sub> nanotubes or free-standing nanotubes were obtained with tunable pore size, length and wall thickness [13]. P. Schmuki et al. have described the anodic growth of self-organized TiO<sub>2</sub> nanotube layers in glycerol/water/ammonium fluoride electrolytes. They found that with the use of these electrolytes, it is possible to grow nanotubes of 20-300 nm with the applied voltage in the range of 2-40V [14]. F. Durstock et al. were successfully fabricated highly ordered TiO<sub>2</sub> nanotubes by using a nanoporous alumina template method. The average external diameter, tube lengths and wall thickness of TiO<sub>2</sub> nanotubes were 295 nm, 6-15  $\mu\text{m}$ , and 21-42 nm respectively. The prepared nanotubes were used as working electrode in dye-sensitized solar cells and achieved power conversion efficiency as high as 3.5% [15]. Jun Wang et al. have studied the effects of electrolyte temperature and anodization potential on the formation of TiO<sub>2</sub> nanotube arrays by using aqueous and nonaqueous electrolytes. In case of aqueous electrolyte, they have found that the anodization potential exerted significant influence on the formation of highly ordered TiO<sub>2</sub> nanotube arrays while little effect from the electrolyte temperature. However, with nonaqueous electrolyte the electrolyte temperature markedly affected the TiO<sub>2</sub> nanotube dimensions [16]. M. Misra et al. have reported the synthesis of Y-branched TiO<sub>2</sub> nanotubes by using a multi-step sonoelectrochemical anodization method. They have observed that a change in anodization temperature ( $\Delta T=10^\circ\text{C}$ ) at a constant applied potential yields a Y-type branched TiO<sub>2</sub> nanotubes with higher photon absorption properties compared the 1D TiO<sub>2</sub> nanotubes [17]. Patrik Schmuki et al. have reported the growth of TiO<sub>2</sub> nanobamboo tubes by using alternating-voltage anodization of Ti in fluoride containing electrolytes. They have found that by a simple variation of the electrochemical conditions, the geometry and surface properties of the nanotube layers can be altered over a wide range. Key to the higher efficiency is the substantial increase in dye loading of the material that can be achieved because of the bamboo rings [18]. Mahendra A. More et al. have reported the aligned TiO<sub>2</sub> nanotubes synthesized by anodization of the Ti foil surface. The tube inner diameter was found to be 60–80 nm with the average wall thickness about 30 nm. A good correlation is found between the photo-enhanced field emission (FE), photoluminescence results and the photoconductivity of the aligned TiO<sub>2</sub> nanotubes array [19].

In this paper, self aligned titania nanotube arrays prepared by electrochemical anodization is studied. In Section 2, the details of synthesis of titania nanotube arrays have been presented. The structural and optical properties of prepared TiO<sub>2</sub> nanostructure are discussed in Section 3. Finally, Section 4 concludes the paper.

## MATERIALS AND METHODS

For anodization, homemade electrochemical setup of two electrodes configuration was used. For synthesis, the commercial available titanium foil (99.9% purity, 0.5 mm thickness, Alfa Aesar) was used as a working electrode and a platinum foil as the counter electrode under constant potential at room temperature. Before the process, titanium foil was degreased in an ultrasonic bath for 10 min. with ethanol and acetone sequentially. The electrolyte solution of 3 wt % HF (40%) and dimethyl sulfoxide (DMSO) was used at constant DC voltage of 30 V for 17h. After synthesis, titanium foil surface is observed to be yellowish in color. Further, as-anodized titanium foil was rinsed in deionized water and used for characterization. The X-ray diffraction measurement is done for phase identification of the as-anodized sample by using XRD (D8 Advance, Bruker AXS). Photoluminescence (PL) spectrum is recorded at excitation wavelength 325 nm by using Photoluminescence Spectrometer (PerkinElmer-LS-55). For surface morphology of titanium foil is measured by using field emission scanning electron microscope (FE-SEM: HITACHI S-4800).

## RESULTS AND DISCUSSION

By using potentiostatic anodization of two electrode configurations, self aligned TiO<sub>2</sub> nanotube arrays were prepared and characterized. Figure 1 shows room-temperature photoluminescence (PL) emission spectra of TiO<sub>2</sub> nanotubes array on titanium foil recorded in the range of 350-600 nm. A sharp PL emission peak can be clearly seen at 383 nm which is corresponding to the band gap energy (3.2 eV) of bulk TiO<sub>2</sub> anatase phase. Two humps were also observed at wavelength 412 nm and 471 nm which may be associated to the free excitations however, a small hump at 521 nm may be due to the formation of oxygen vacancy at the surface of titania nanotube arrays [19, 20].

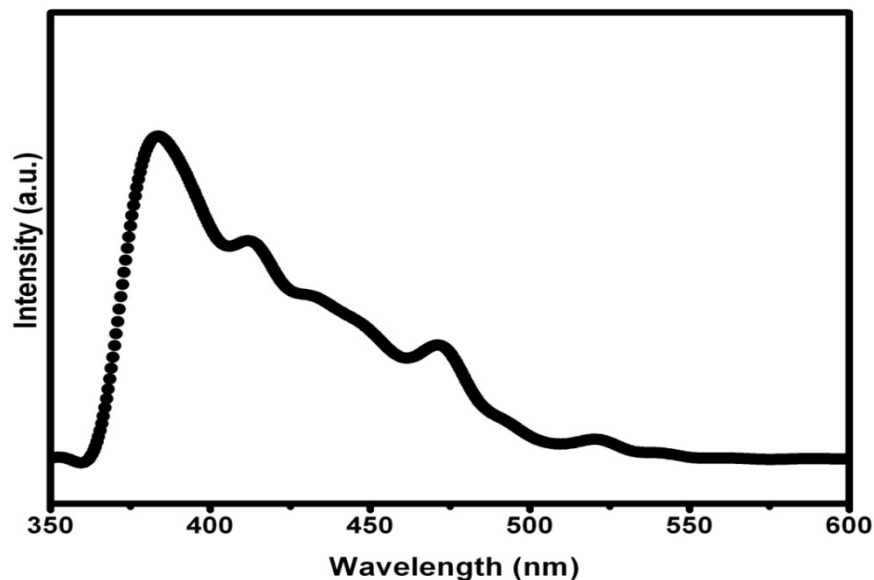


Figure 1. Photoluminescence spectra of anodic TiO<sub>2</sub> nanotube arrays prepared at 30V

Figure 2 shows the x-ray diffraction pattern of TiO<sub>2</sub> nanotube arrays recorded in the range of 20-80 °C. The low intensity peaks at  $2\theta$  value of 25°, 53°, 63° and 74° are corresponding to the anatase phase. It is remarkable that three broad peaks in the XRD pattern confirm the existence of amorphous phase [19, 21]. However, the other peaks at  $2\theta$  value of 38°, 53°, 70° and 76° are related to the titanium substrate itself. The obtained peaks in XRD pattern are consistent with JCPDS Card No. 84-1286.

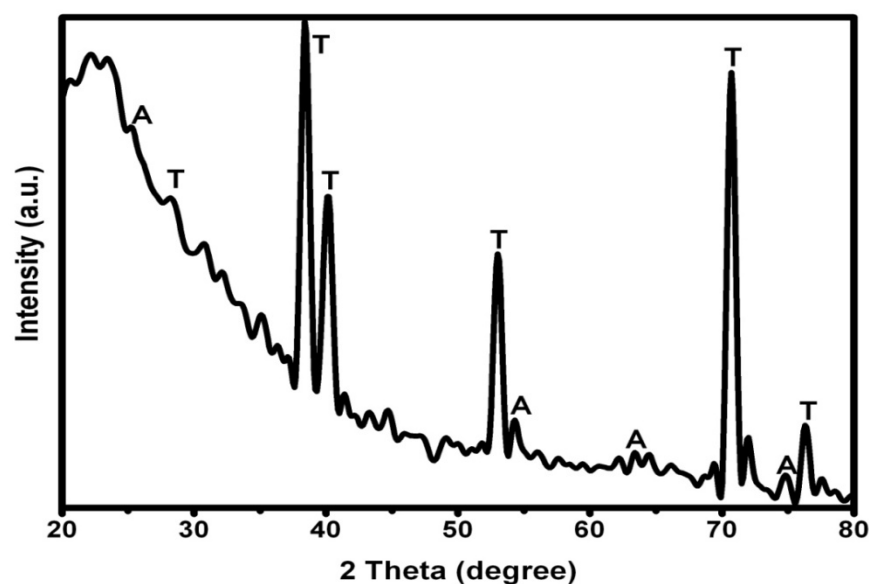


Figure 2. X-ray diffraction pattern of anodic TiO<sub>2</sub> nanotube arrays annealed at 450 °C for 3h

In general, as-prepared TiO<sub>2</sub> nanotube arrays are amorphous in nature which can be converted into anatase or mixture of anatase and rutile after annealing at temperature above 300 °C. A complete conversion to rutile phase has

not been reported so far which is due to the fact that high temperature around 700 °C is required to rutile conversion which results in surface morphology deterioration. Not even high temperature but other parameters are also important such as texture, impurities, feature size etc. To attain the desired properties of TiO<sub>2</sub> nanotube arrays, A. Grimes et al. have reported a approach to prepare crystalline (anatase) nanotube arrays without post annealing through anodization of pre-heated crystalline layer of TiO<sub>2</sub> [22].

Figure 3 shows the typical surface morphology titania nanotube arrays measured by FESEM. As can be seen left side, the prepared nanotube arrays are well aligned. The right side image shows the close up view of aligned TiO<sub>2</sub> nanotube arrays with rough walls. The approximate inner diameter of nanotubes were 80 nm and with wall thickness about 20 nm. Somewhere, regularly spaced rings formed on the side wall can also be observable and are dependent on the anodization condition. In photovoltaic devices, nanotube materials have a significant role because of their effective charge separation due to huge interface, band transport of free carriers for charge transfer mechanism and non-flat morphology which minimizes the reflectance of incident light.

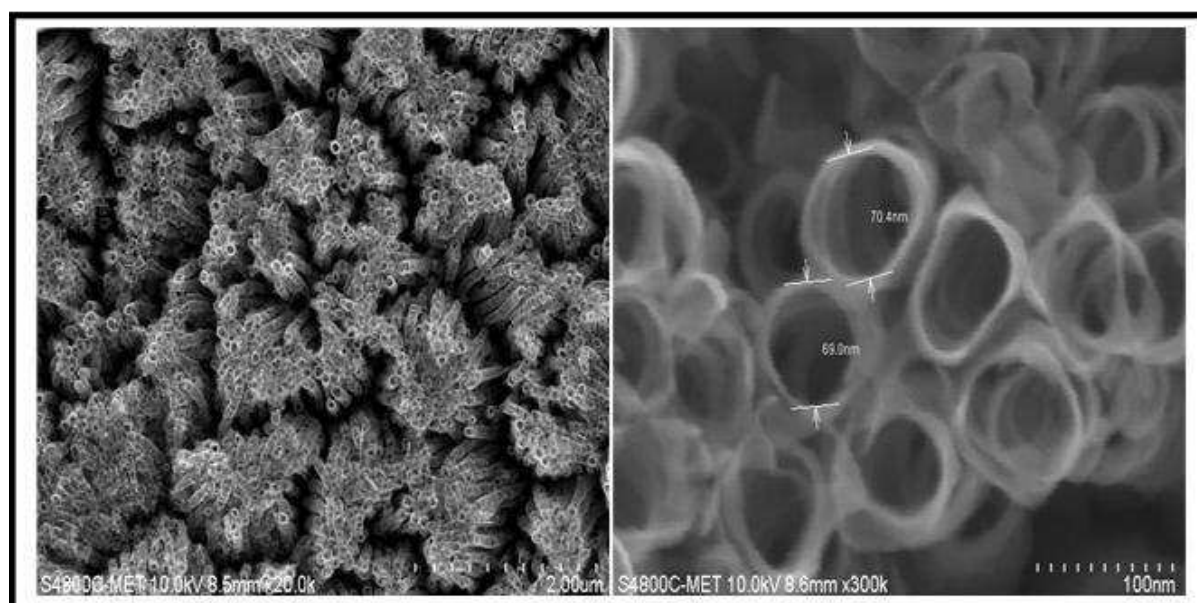


Figure 3. FE-SEM images of anodic TiO<sub>2</sub> nanotube arrays annealed at 450 °C for 3h

### CONCLUSION

By anodic oxidation of TiO<sub>2</sub> foil, nanotube arrays have been prepared and characterized. A sharp PL emission peak at 383 nm corresponds to the band gap energy of bulk TiO<sub>2</sub> anatase phase. In PL spectra, small humps were also observed may be associated to the free excitations and due to the formation of oxygen vacancy at the surface of titania nanotube arrays. By XRD measurement, the anatase phase of TiO<sub>2</sub> nanotube arrays is confirmed at 2θ value of 25°, 53°, 63° and 74° and the obtained peaks in XRD pattern were found to be consistent with JCPDS Card No. 84-1286. By FESEM measurement, well aligned formation of nanotube arrays is confirmed with ~80 nm of inner diameter of nanotubes ~20 nm of wall thickness. Finally, the prepared anatase TiO<sub>2</sub> nanotube arrays are well aligned and hence, suitable for the application in dye sensitized solar cells due to their higher mobility of charge carriers than rutile TiO<sub>2</sub>.

### Acknowledgement

Author is thankful to the INSA, India for the award of INSA Visiting fellowship and express gratitude to Dr. M. A. More (University of Pune, India) for sample measurements.

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