International Journal of Technical Research and Applications e-ISSN: 2320-8163,
www.ijtra.com Special Issue 37 (February, 2016), PP. 16-19

NOVEL HYDROTHERMAL SYNTHESIS OF TITANIA NANORODS WITH DIFFERENT PRECURSORS FOR PHOTOVOLTAIC APPLICATIONS

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Abstract— **We report the novel one-pot hydrothermal synthesis of one dimensional Titanium di-oxide (TiO_2) nanorods directly on conducting indium tin oxide glass substrate (ITO) using two different precursor materials for photo voltaic applications. Among one dimensional nanostructures, TiO_2 nanorods have gained significant interest over the past decade due to its unique optical, electrical and photoelectrochemical properties. Our work shows that titania precursors such as Titanium tetra-isopropoxide (TTIP) and Titanium tetrachloride ($TiCl_4$) have significant effects on the structural, morphological and optical properties of as-synthesized nanorods. X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray analysis (EDAX) and UV-Visible (UV-Vis) absorption spectroscopy were used to characterise the samples. Distinct rutile –phase TiO_2 peaks were observed in both the samples synthesized using different precursors. Using Scherrer's formula, the average crystallite size calculated was found to be of a uniform value ~15 nm with TTIP precursor whereas it possessed varying values in the range of 11-17nm for nanorods with $TiCl_4$. The surface morphology as observed from the FESEM images showed that the nanorod arrays were successfully synthesised on the substrate. It also revealed that the faster hydrolysis rate of TTIP led to the growth of vertically aligned nanorods with the length reaching 4.7 µm, whereas it is comparatively smaller with lengths of about 0.4 µm in case of $TiCl_4$. EDAX spectrum revealed the high purity nature of the synthesised samples, comprising only the elements of TiO_2. The prepared TiO_2 nanorod arrays exhibited high absorbance properties in the ultraviolet region (< 400nm) as expected but with an increased absorption range for TTIP precursor. We conclude from the findings that the titania nanorods synthesized using TTIP precursor with uniform crystallite size and higher absorption range would capitulate improved surface area and their longer nanorods would facilitate faster electron transport thus rendering a promising photoelectrode for photo voltaic applications.**

Index terms- **Hydrothermal; Precursors; Nanorods; Surface morphology; Photo voltaic applications.**

I. INTRODUCTION

Renewable energy sources have become an important approach for gaining independence from fossil fuels [1]. Utilizing solar energy is the most fascinating one as it can provide unmetered amount of energy in a clean way [2]. Photovoltaic solar cells are the most common form of light to electrical power convertors [3]. Employing nanostructured semiconductor materials have attracted much attention as fundamental building blocks for the development of next generation solar energy conversion devices [4].

Titanium di-oxide or titania is perceived as a stand-out among other wide band gap semiconductors due to its outstanding physical, optical and electrical properties [5]. An interesting property exhibited by this material is the generation of electron-hole pairs upon irradiation with UV-light which induces chemical reactions at its surface has propelled its effective utility as photoelctrodes in solar cells, photocatalysts and as gas sensors [6]. TiO_2 with its different morphologies including nanoparticles, nanotubes, nanorods, hollow spheres and nanofibres has been explored for various applications [7]. Among the above mentioned nanostructures, one dimensional TiO_2 nanorods have been reported to greatly increase electron diffusion length as they can offer direct and rapid transport pathways for injected electrons [8]. A number of methods such as sol-gel, chemical precipitation, hydrothermal, solvothermal and microemulsion have been used to synthesise TiO_2 nanorod structures [9]. Hydrothermal synthesis is considered as the most appropriate method to synthesise TiO_2 nanorods arrays because of its mild experimental conditions, lower cost and the advantage of control over desired morphology [10].

In the present investigation, we have successfully employed the facile hydrothermal approach to synthesise one dimensional TiO_2 nanorods directly on the conducting ITO substrate to facilitate an interfacial contact layer. In order to study the effect of titania precursor on structural, optical and morphological properties, we have used two different precursors such as Titanium tetra-isopropoxide (TTIP) and Titanium tetrachloride ($TiCl_4$), which is a scarcely reported work.

II. MATERIALS AND METHODS

A. Synthesis

The TiO_2 nanorod arrays were synthesized on the ITO substrate by hydrothermal method. Prior to coating, the ITO conducting substrates were ultrasonically cleaned with acetone and deionised water in sequence, for 10min each and finally dried in air. Titanium tetrachloride ($TiCl_4$) and Titanium tetra-isopropoxide (TTIP) were chosen as titania precursors. The TiO_2 sol solution was prepared by adding an appropriate amount of titania precursor to the mixture of deionised water and hydrochloric acid (1:1 ratio). The solution was stirred for few minutes to obtain a clear transparent solution. The pre-cleaned ITO substrates were then placed in a stainless steel autoclave for subsequent hydrothermal reaction for 2-4 hrs at 180º C. The autoclave was cooled down to room temperature and the substrates were rinsed with deionized water and dried in the air.

B. Characterisation

The crystal structure of the samples were investigated by X-ray diffraction (XRD) analysis using X-ray diffractrometer Rigaku (Japan) employing Cu Ka as a radiation source at 9 KW having wavelength of 1.5405 Aº. The surface morphology was characterized by Field Emission Scanning Electron Microscopy (FE-SEM) with a SUPRA-55, Carl Zeiss, (Germany) equipped with an Energy Dispersive X-ray spectrometer (EDAX) for compositional analysis. The optical absorption properties were studied in the range of 200–800 nm by using UV–Vis–Carry 5 spectrophotometer.

III. RESULTS & DISCUSSION

A. XRD Analysis

Fig. 1. shows the XRD pattern of the hydrothermally grown TiO_2 nanorods with $TiCl_4$. It was clearly evident from the figure that the TiO_2 nanorods grown on ITO coated glass substrates have tetragonal rutile structure (JCPDS card no 21-1276).

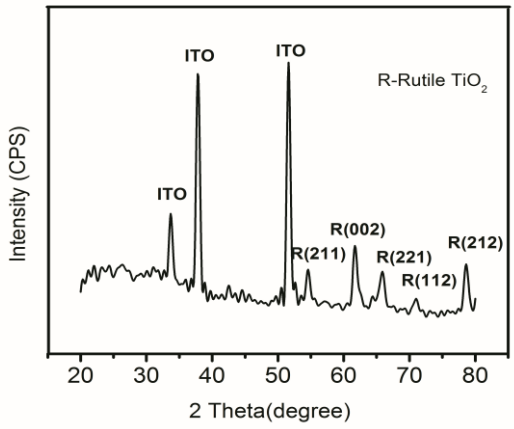

Fig. 1. XRD pattern TiO_2 nanorods with $TiCl_4$

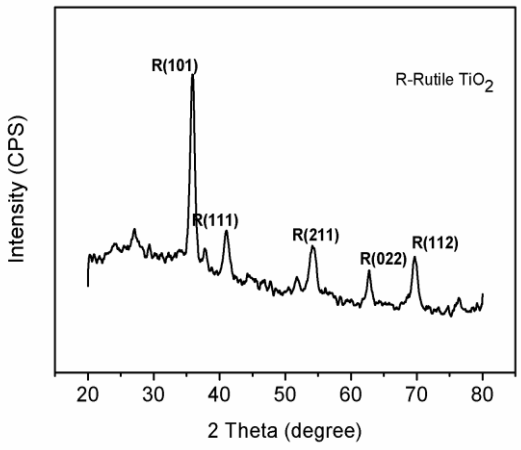

Fig. 2. XRD pattern TiO_2 nanorods with TTIP

The diffraction peaks at 2θ = 54.7°, 61.5°, 65.9°, 72.9 & 78.6° correspond to the (211), (002), (221), (112) & (212) planes of rutile TiO_2 except the signals from the ITO substrate which are found at about 34°, 38° & 51° (JCPDS card no 88-0773). The results are found to be in excellent agreement with the similar reported work [11].

Fig. 2. represents the crystal phase structure of TiO_2 nanorods synthesised using TTIP. The prominent peaks observed in the figures were indexed to rutile phase confirmed with (JCPDS card no 89-4920). The diffraction peaks at 2θ = 35.95°, 41.14°, 54.22°, 62.77° & 69.77° corresponds to the (101), (111), (211), (022) & (112) planes of rutile TiO_2. Few characteristic peaks of small intensities present at 35.95°, 41.14°, 54.22°, 62.77 & 69.77° could be assigned to the ITO substrate (JCPDS card no 88-0773) [12].

The average crystallite size of both the samples were estimated using Scherrer equation: $D = 0.89\lambda/(\beta\cos\theta)$,where λ is the employed X-ray wavelength, θ is the diffraction angle, and β is the full width at half maximum of the most intense diffraction peak (FWHM) [13]. The average crystallite size thus obtained in the case of TiO_2 nanorods using $TiCl_4$ was found to be in the range of 11-17 nm whereas it possessed a uniform value of 15 nm for nanorods with TTIP precursor. The occurrence of uniform crystallite size in the case of the latter could have been possibly due to the formation of a consistent seed layer during the growth of TiO_2 nanorods giving way for proper vertical orientation.

B. FESEM Analysis

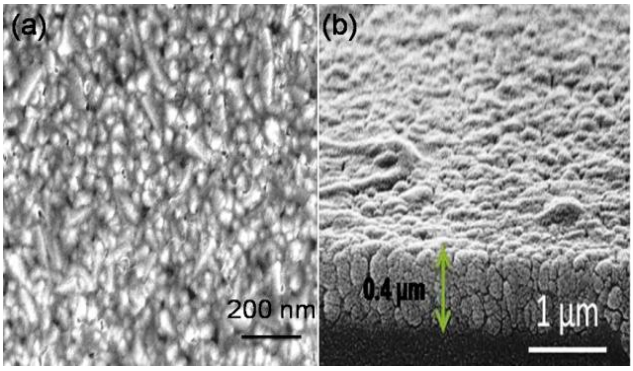

Fig. 3. FESEM image TiO_2 nanorods with $TiCl_4$; (a) Top view (b) Cross sectional view

From the above FESEM (Fig. 3a & 3b) image it was quite evident that the TiO_2 nanorods were formed with dandelion type morphology in a homogenous fashion with $TiCl_4$ precursor. The length of the nanorods found on the surface as measured from the SEM investigation was approximately 0.4 µm**.**

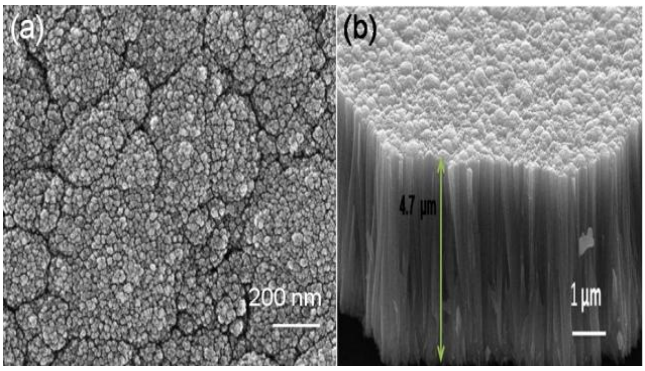

Fig. 4. FESEM image TiO_2 nanorods with TTIP; (a) Top view (b) Cross sectional view

Fig. 4a & 4b revealed the surface morphology of the nanorods with TTIP. Uniform and proper vertical orientation of TiO_2 nanorods was witnessed in this case with the length reaching 4.7 µm, much higher than those synthesised with $TiCl_4$. This behaviour could be due to the faster hydrolysis rate of TTIP precursor, which could have resulted in an accelerated growth of nanorods because of faster supply of titanium growth units [14]. Longer nanorods are anticipated to increase the surface area thus facilitating more dye molecules to be absorbed. Consequently, light harvesting would also be enhanced to promote faster electron transport with reduced electron-hole pair recombination which will substantially improve the current densities and thus the efficiencies of solar cells made from nanorods [15].

C. EDAX Analysis

Energy Dispersive X-ray Analysis (EDAX) was used to determine the elemental composition of the as-synthesized nanorod samples and is given in the Fig. 5 and 6. It was clearly evident that the samples in both cases possessed high levels of purity with the presence of only Ti and O elements.

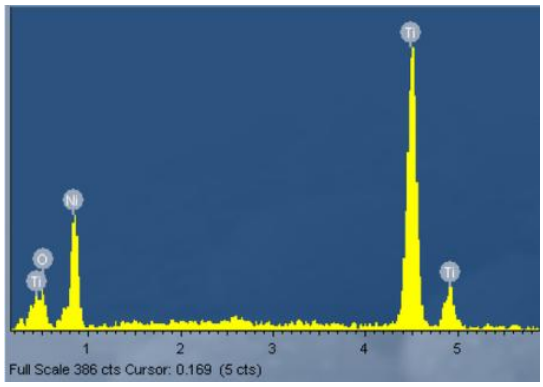

Fig 5 EDAX spectrum of TiO_2 nanorods with $TiCl_4$

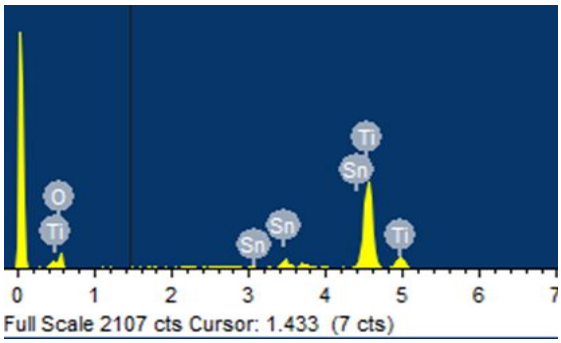

Fig. 6. EDAX spectrum of TiO_2 nanorods with TTIP

D. UV-Visible Absorption Spectra Analysis

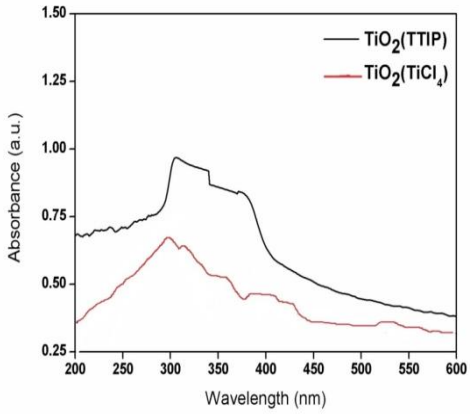

Fig 7 UV –Vis adsorption spectra of TiO_2 nanorods

Fig. 7. shows the UV –Visible absorption spectra of TiO_2 nanorods synthesised by using both precursors. The absence of absorption peaks in the visible region of the spectrum confirmed the wide band gap nature of TiO_2 in both cases [16]. An increased absorption with a red shift in the range of 300-500 nm was witnessed in the case of TTIP compared to $TiCl_4$ owing to its decreased particle size and proper vertical orientation. Hence, this nanostructure using TTIP precursor could be employed as a photoanode material due to its

absorption shift towards the visible region for solar cell applications.

IV. CONCLUSIONS

Facile hydrothermal approach was employed to synthesize titania nanorods directly on conducting ITO substrate. Different precursor materials such as Titanium tetra-isopropoxide (TTIP) and Titanium tetrachloride ($TiCl_4$) were found to influence the growth rate of the synthesized nanorods. XRD results confirmed the high crystallinity of the titania nanorods synthesized using both precursors with rutile phase. Vertically oriented nanorods with uniform crystallite size were reported in nanorods with TTIP precursor which promises enhanced light absorption thereby giving superior photoelectron conversion efficiency than those synthesized with $TiCl_4$. The optical property investigated using UV-Visible absorption spectroscopy shows an obvious sharp absorption edge at around 400 nm in both the samples as expected but with an increased absorption range in the UV-Visible region in the sample made with TTIP precursor. Our study has therefore concluded that the titania nanorods synthesized using TTIP are preferable candidates for use as photoelectrode material for high efficiency photovoltaic applications.

V. ACKNOWLEDGEMENT

The authors are grateful for the technical support extended by Loyola Insititute of Frontier Energy (LIFE), Chennai.

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