International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.3, pp 1563-1568, 2014-2015

ICONN 2015 [4th - 6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Synthesis of TiO_2 nanotubes from prepared TiO_2 nanoparticles by hydrothermal route and dye sensitized solar cell characteristics

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Abstract : A simple hydrothermal reaction among TiO_2 nanopowders and alkaline solution has been developed to synthesize low dimensional titanate nanostructures. The morphologies of the obtained nanomaterials depend on the process parameters: the structure of starting material, the nature and concentration of alkaline solution, reaction temperature and time, which suggests that the nanostructure synthesis could be controllable. Here we made an attempt to synthesize titanate nanotubes via hydrothermal reaction of TiO_2 crystals of anatase and NaOH solution in the range of 110-160°C. It seems to be titanate nanotubes obtained only at temperature 110°C with the diameter 10 nm. The phase of the obtained TiO_2 nanostructures were analyzed by X-ray diffraction (XRD) and Raman spectroscopy. The morphologies of the nanostructures were analyzed by several methods including Scanning electron microscope (SEM), High resolution transmission electron microscope (HRTEM).UV-Diffusion reflectance spectra (UV-DRS).The surface area and pore diameter of nanotubes were determined by Brauner-Emmett-Teller (BET) method. The flexible DSSC with light-to-electric energy conversion efficiency of 2.38% was achieved for optimized nanotubes under a simulated solar light irradiation of 100mWcm^{-2}.
Keywords: Titania, Hydrothermal treatment, Nanomaterials, Nanotubes, Dye-sensitizer.

1. Introduction

Dye sensitized solar cells have attracted immensely as an economical energy conversion device because of their low cost and high efficiency[1, 2]. Engineering materials such as ZnO, SnO_2, CdS, and TiO_2 contributed their major part in various applications like photocatalysis, environmental cleaning and protection, gas sensing, lithium ion batteries and solar cells. Among various metal oxide semiconductors TiO_2 have gained great interest because of its inconceivable performance in dye sensitized solar cells[3-6].

A typical DSSC device is made up of working electrode (photoanode), counter electrode and electrolyte. Different kinds of morphologies of the photoanode have been synthesized to improve the efficiency of the device. In DSSC, TiO_2 nanoparticles are working as photoanode[7-9]. To avoid the disadvantages like

ohmic loss, grain boundaries and recombination, 1 – dimensional TiO_2 nano structures are used as photoanodes instead of TiO_2 nanoparticles. Hence the 1-dimensional structures such as nanotube, nanowire, and nanorod are ideal materials for device fabrication[10-16].1-dimensional TiO_2 nano structures have been prepared by various established methods: 1) template 2) surfactant directed synthesis 3) alkali treatment under hydrothermal conditions[17-23]. The alkali treatment is an effective method to synthesis nanotubes under moderate hydrothermal conditions. The reaction temperature and reaction time are the two main factors which have control over the structure of morphology[24, 25].

In the present study we explored the formation of anatase TiO_2 nanotubes by hydrothermal growth using TiO_2 nanoparticles. The growth parameter for preparation of TiO_2 nanotubes by inexpensive route has also been presented. Optimized condition for the synthesized products has been characterized by XRD, UV, TEM, BET, and IV.

Karthik kinhal et al., had achieved the efficiency of 11.2 % in DSSC with the candidate of TiO_2 nanoparticles, as photoanode. Thus the performance of TiO_2 nanoparticles is still limited, due to the multiple disadvantages as described above. Therefore the use of 1-dimensional nano structures will definitely lead to a great improvement in efficiency due its better properties like electron diffusion length, high dye absorption, fast electron transport, and no grain boundaries.

2. Experimental

2.1 Preparation of TiO_2 nanoparticles

TiO_2 nanopowders were prepared via hydrothermal method using Tetra-n-butyl-titanate and deionized water as the starting materials. The concentration of the above chemicals were (the volume ratio of tetra-n-butyl titanate: deionized water) 1:6. Tetra-n-butyl titanate was added drop wise into the deionized water. The obtained gel was then autoclaved at 105°C for 10 hrs. The precipitate was washed with distilled water. Then the powder was dried in oven for 24 hours and then calcined at 450°C.

2.2 Preparation of TiO_2 nanotubes from as prepared TiO_2 nanoparticles:

In a typical preparation procedure 0.3 g of prepared TiO_2 white power was placed into a Teflon-lined autoclave of 100 ml capacity.10M NaOH was mixed with 20 ml of distilled water and stirred for 1 hour. The solution was transferred into autoclave and maintained at 110°C for 24 h. Then the autoclave was allowed to cool naturally to room temperature. The obtained products were collected and washed with HCl aqueous solution for several times until the pH value turned to 7. The products were then annealed at 400°C in air for 2h.

1.5 g of prepared TiO_2 nanotubes was mixed with ethanol and 1 drop of Triton-X and ground well. The mixture was then ultrasonicated for approximately 30 minutes. The mixture was sprayed onto the FTO substrate using a spray deposition technique. The resulting film was annealed at 450 °C for 2 h and then immersed for 12 h in an ethanolic solution containing 0.03M ruthenium (N-719) for dye adsorption. The dye-sensitized photoanode was clamped with a platinum electrode and filled with iodide redox electrolyte (0.6 M dimethyl propylimidazolium iodide, 0.1 M LiI, 0.01 M iodine, 0.5 M 4-tertbutylpyridine in acetonitrile).

2.3 Characterization methods

The structural analyses of the TiO_2 samples were examined with powder X-ray diffraction (XRD) using a X' Pert Powder XRD System equipped with Cu-Kα radiation. The data were collected for scattering angles (2θ) ranging between 10° to 80° with a step size of 0.2°. The external features and morphology of the samples were detected by scanning electron microscopy (SEM) using JEOL JSM-6700F and Transmission electron microscope. UV-visible (UV-Cary 5E) spectrophotometer was used to obtain optical absorption spectra of the samples.

Surface area of the samples was analyzed using a (BET) Micromeritics ASAP 2020 V3.00 H. Pore structure of the derived TiO_2 nanotubes was characterized by N_2 adsorption using an appropriate apparatus. Surface area of the samples was determined from the Brauner-Emmett-Teller (BET) equation. The pore size distribution was analyzed using the Barret-Joyner-Halanda (BJH) method.

3. Results and discussion

Figure.1 (a) shows the X-ray diffraction patterns of the as-synthesized TiO_2 nanoparticles (TNP) (b),(c) and (d) shows the XRD of TiO_2 nanotubes (TNT) prepared at 110 °C, 130 °C, 160 °C respectively. From fig. 1(a) the diffraction peaks indicate the formation of TNPs with a pure anatase phase with high intensity. In fig. 1(b) shows, the peaks are corresponding to anatase phase. Diffraction peaks in TNTs are weaker and low intensity than those in the TNPs. This is because of NaOH treatment on TNPs. At the moment of NaOH mixed with the TiO_2 nanoparticles, NaOH would rupture the Ti-O-Ti bonds, causing a lower crystallinity in the TNTs. When the temperature increased to 130 °C the phase transformation occurs from anatase to rutile phase.

Figure.1 (e), (f) and (g) shows Raman spectra of samples prepared at 110°C, 130°C, 160°C respectively. From figure 1(e) clearly shows the Raman peaks corresponding to the anatase phase of TiO_2 nanotubes prepared at 110 °C. The strong Raman peaks around 144, 197, 400, 515, and 640 cm^{-1} were assigned to the anatase structure.

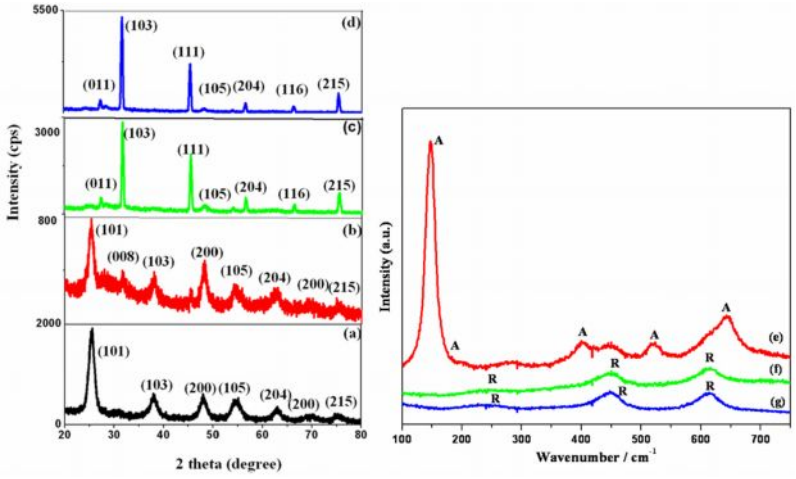

Figure.1 (a) shows X-ray diffraction pattern of the as-synthesized TiO_2 nanoparticle, (b), (c) and (d) shows the XRD of TiO_2 nanotubes prepared at 110°, 130°C, 160°C. Figure.1 (e, f, g) shows Raman spectra of samples prepared at 110 °C, 130 °C , 160 °C .

While the temperature was increased to above 130 °C and 160 °C the anatase phase began to transform to the rutile phase. Raman peaks around 235, 447 and 612 cm^{-1} assigned to the rutile phase of TiO_2 from figure 2 (f) and 2 (g)[25]. Peaks representing the anatase and the rutile form of TiO_2 are labeled A and R, respectively.

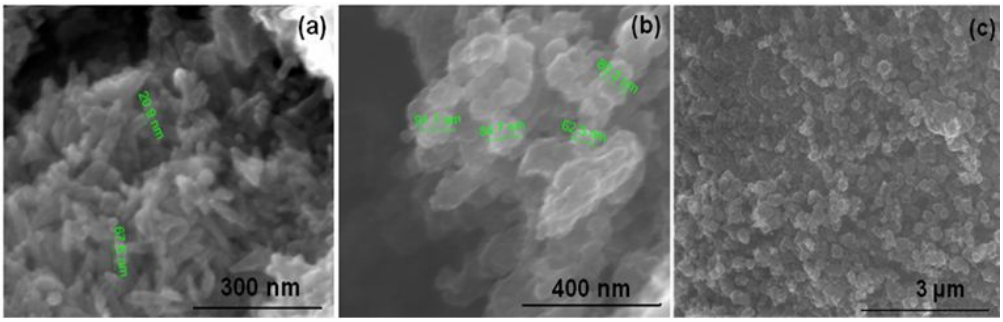

Figure. 2 (a), (b) and (c) shows the SEM images of TiO_2 nanotubes grown at 110°, 130°C, 160°C.

Fig 2 (a),(b) and (c) shows a sequence of SEM images taken from the samples grown at 110 °C, 130 °C, 160 °C. From image 3(a) observed that the TiO_2 nanotubes grown only at 110 °C, with the diameter around 10 nm and length 60 nm. Upon an increase of hydrothermal temperature (130 °C) the nanotubes were started to disintegrate with the particle size of 80-90 nm and some of them aggregated together shows in figure (b). At 160 °C the nanotubes were fully converted into spherical particles with sizes of 150-180 nm shows in figure (c).

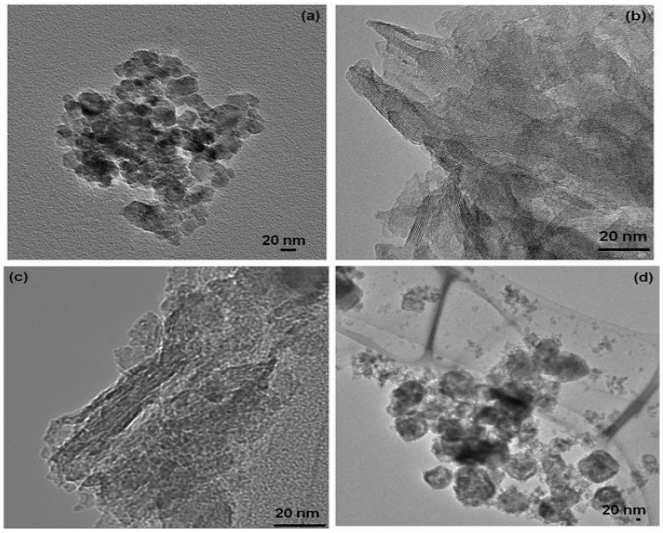

Figure. 3 (a) shows TEM images of TiO_2 nanoparticles, (b), (c) and (d) shows the TEM images of TiO_2 nanotube prepared at 110°, 130°C, 160°C

Figure.3 (a) shows the TEM images of TiO_2 nanoparticles, (b), (c) and (d) shows the TEM images of samples prepared at 110 °C, 130 °C, 160 °C. Fig. 3 (b) shows the TEM image of the sample which was grown at 110 °C for 24 h, showing a pure tube-like structure. The width of the tube is about 20 nm. Fig.3 (c) shows the TEM image of the sample prepared at 130 °C for 24 h. At this temperature nanotubes started to disappear. Fig.3 (d) exhibit the sample prepared at 160 °C and there is no existence of nanotubes in this system and the diameter of the particle is about 60 nm.

Figure.4 .(a,) (b) and (c) shows UV- spectra of prepared sample at 110°, 130°C, 160°C.The absorption onset at a) 428 nm, b) 401 nm c) 385 nm respectively. According to the Lambert–Beer's law, higher absorbance means the higher adsorption of the dye. It is well known that the photocurrent of the flexible DSSC is correlated directly with the amount of the dye molecule, the more dye molecules are adsorbed, more incident light are harvested, and the larger photocurrent occurs[26, 27].

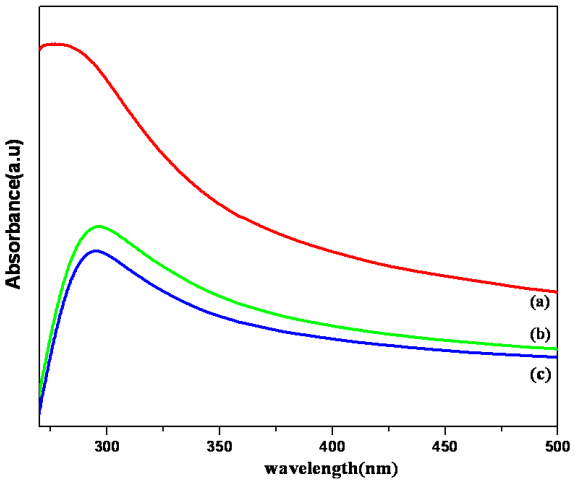

Figure.4. Shows UV- spectra of prepared sample at 110°, 130°C, 160°C

A typical isotherm for nitrogen adsorption on the surface of TiO_2 nanotube is shown in Fig.5 (a). These isotherms exhibit obvious hysteresis behavior, indicating that the products are mainly mesoporous. Basically, TiO_2 nanoparticles derived from hydrolysis methods were employed as the starting materials. The resulting nanotubes exhibited surface areas in a range of 20 and the pore volume is 0.1208 cm^3/g (Inset Figure b). Since the morphology of TiO_2 m^2/g nanotubes strongly depends on the size and crystalline phase of the TiO_2 source, use of the (TiO_2 nanoparticles- lab made) as the starting materials has the advantage in the property control of the nanotube products.

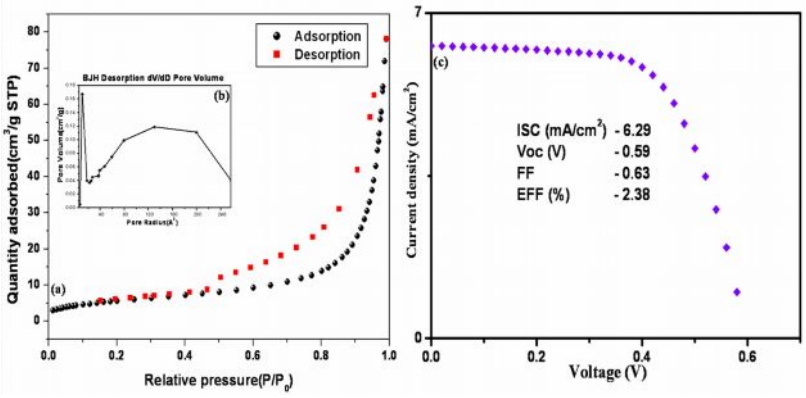

Figure.6 (a) Nitrogen adsorption–desorption isotherm and pore size distribution curve . Inset: pore diameter distribution spectra of the TiO_2 NTs. (c) I-V Characteristics of TiO_2 nanotubes prepared at 110°C.

I-V characteristics of prepared TiO_2 nanotubes are shown in fig.5 (c). TiO_2 nanotubes exhibited short circuit current densities (I_{sc}) of 6.29 mA/cm^2, open circuit voltages (V_{oc}) of 0.59 V, and fill factors (FF) of 0.63, respectively. The efficiency obtained for prepared TiO_2 nanotube device is 2.38 %.

4. Conclusion:

Anatase TiO_2 nanotubes with a length of 400 nm and diameter of 10 nm were prepared from synthesized TiO_2 nanoparticles using hydrothermal method. Formation of TiO_2 nanotubes were confirmed by SEM and BET surface area analysis. This method were new and cheapest method to produce nanotubes at 110° C for 24 hrs. Transformation from TiO_2 nanotube (110° C) to spherical particles (160° C) clearly revealed by TEM. Based on this result dye sensitized solar cells were fabricated for prepared TiO_2 nanotubes. The flexible DSSC with light-to-electric energy conversion efficiency of 2.38% was achieved under a simulated solar light irradiation of 100mWcm^{-2}.

Acknowledgement

One of the authors G.Arthi is thankful to the Shizuoka University, Research Institute of Electronics for providing necessary infrastructure to carry out this research.

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