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Hydrothermal synthesize of nano tree trunk TiO₂ as a 1-D structure used in anode of dye sensitized solar cell

M. Jalali^{a,*}, Kh. Sadrnezhaad^a, R. Siavash Moakhar^a, M. Mehdipour^b, N. Riahi-Nouri^b

^a Department of Materials Science and Engineering, Sharif University of Technology, Tehran, 11365-9466, Iran ^b Niroo Research Institute, Chemistry and Materials Center, Non-Metallic group, Pounak Bakhtari Avenue, Tehran, Iran

*jalali.mahsa.mse@mehr.sharif.ir

Abstract: In this paper we have synthesized a novel structure of TiO_2 called nano tree trunk shaped (NTT) as an anode for dye sensitized solar cell (DSSC) by the means of hydrothermal method. The morphology and crystalline structure of the nano particles (NP) and NTT were characterized by field emission scanning microscopy (FESEM) images, and X-ray diffraction (XRD), respectively. FESEM images presented a unique morphology of the assynthesized nano tree trunk shaped TiO_2 which has 200 nm thickness and particle size of 50 nm. XRD results showed high purity of anatase- TiO_2 crystalline both for NP and NTT. This novel structure combining with TiO_2 nano particles showed superior current density short circuit as well as efficiency in comparison with widespread DSSC with only TiO_2 nano particles.. DSSC with 20% NTT and also 80% NP used in anode had efficiency of 6.2% which is better than common DSSC of TiO_2 nano particle (i.e. 5.8%).

Keywords: Nano tree trunk shaped TiO₂; DSSC, Hydrothermal method

Introduction

TiO₂ has found extremely novel applications in several fields as well as high efficiency dye-sensitized solar cells [1,2], pigments [3], inorganic membrane[4], environmental purification[5] and catalysis[6].

Significant endeavours have been constructed due to controlled the morphologies of TiO_2 [7]. Among the different shapes of TiO_2 , low dimensional materials such as one dimensional (1-D) nanostructures such as nanorods, nano-wires and nanotubes and 2-D nanostructures containing nanosheet and nanoflakes have motivated substantial research interest because of their ability in conducting electrons [8].

In this paper, hydrothermal has been used to synthesize novel structure of TiO called tree trunk shaped (NTT) which has both beneficial of 1D structure for fast electron path and large surface area. FESEM and XRD have been employed in order to study the morphology and crystalline structure of NP and NTT, respectively.

Materials and method

 TiO_2 nanoparticles (NP) were prepared by hydrothermal operation. Titanium tetraisopropoxide (TTIP) with a purity of 97% (Sigma-Aldrich, UK) was used as a titanium precursor; as a catalyst 0.2 moles of acetic acid (CH₃COOH) was added gradually to it under magnetic stirring at room temperature. The sol was stirred for 30 min at room temperature then 300 ml deionised water

quickly added while severer stirring. After an hour stirring 10ml nitric acid 65% (Merck) was added. The mixture was heated with the rate of 1.5 degree/min until 70 centigrade degrees and peptized for 75 minutes.

After that it was charged into a 50 ml autoclave to fill 80 percent of its volume and placed in an oven with temperature of 180°C for 24 hours.

Nano tree trunk-shaped (NTT) TiO₂ was prepared by a two sequential hydrothermal operation. In a typical synthesis, 1g of TiO₂ (Degussa P25 with a particle size of about 20-30 nm) was added to 40 ml 10 M aqueous NaOH solution. The resultant suspension was stirred for 1 hour and transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL. The autoclave was heated at 180°C for 72hours and then cooled to room temperature. The obtained hydrogen titanate was dispersed in HCl solution until pH 2 was reached. After washing several times with distilled water, it was dispersed in 25ml ethylene glycol and by adding distilled water reached volume of 40 ml. the suspension stirred for 1 hour while after 30 min 2ml dimethylamine was added. The mixture transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL and heated at 180°C for 10hours.

Three diverse TiO_2 pastes were prepared from nanoparticles (NP), nano tree trunk shaped (NTT) and mix of them (NP 20% and NTT 80%).

The DSSC was assembled briefly as followed: The asprepared paste was spread on FTO coated glass (15 Ω /square, thickness 3 mm) TiCl₄ (40 mM) pre treated



using screen print technique. Then it was annealed at 450 °C in air. In order to enhance uniformity resulting increasing the photovoltaic properties, these films were post treated with TiCl₄ and then cured at 450 °C in air for 60 min. After cooling to 80 °C, the TiO₂ electrode was immersed in 0.5 mM N719 (DyeSol) solution in ethanol and kept at room temperature away from light for 24 h. The photoelectrode and counter electrode were sealed ogether with a 60 mm thick surlyn polymer foil (DyeSol) as the spacer and the electrolyte was injected to the space between them. The electrolyte solution consisted of 0.6 M 1-methyl propyl imidazolium iodide, 0.1 M lithium iodide, 0.05 M iodine and 0.5 M tert-butyl pyridine in acetonitrile (all the chemicals were purchased from Merck).

The morphology and crystalline structure of the NP and NTT were characterized by FESEM images, and X-ray diffraction (XRD), respectively. The photovoltaic characteristics of the DSSCs were measured using a Solar Simulator under 1.5 AM (100 mW/cm²) irradiation and the current density versus voltage (I-V) obtained.

Results and Discussion

Fig 1 (a) and (b) shows TiO_2 NP and NTT, respectively.



Fig.1: FE-SEM images of surface morphology of TiO_2 a)NP b)NTT

As it shown in Fig 1 (a), NP has particle size of 14-20 nm which is distributed uniformly. Fig 1 (b) presented a

unique morphology of the as-synthesized nano Tree Trunk shaped TiO_2 which has 200 nm thickness and particle size of 50 nm. In fact through the synthesis of NTTs nano wires formed, at first, then increasing pressure caused crack initiation. since propagation of cracks happened to the extend, enhanced electron paths were formed, respectively.

Fig 2 represent the X-ray diffraction patterns (XRD) of TiO_2 different morphologies. Conquering peak at $2\theta=25^{\circ}$ present high purity of anatase-TiO₂ crystalline.



Fig.2: XRD patterns of a)NTT and b)NP TiO₂

As it can see in Fig.2 (b) the broaden peak of NP TiO_2 pattern indicates small nanoparticles in comparison with NTT TiO_2 narrow peaks which represent 1-D structure.

Three DSSCs were prepared according to the experimental section, DSSC-1 made from a single layer NP, DSSC-2 made from a single layer NTT and mixture of NP 20% and NTT 80% formed DSSC-3. The solar cell's performances and their photovoltaic parameters were summarised in table1.

Table1: Table type style, example of table headnote.

DSSC	V _{oc} [mV]	J_{sc} [mAcm ⁻²]	FF [%]	η [%]
DSSC-1	0.780	-11.3	0.7	5.8
DSSC-2	0.780	-9.9	0.7	5.3
DSSC-3	0.780	-14.2	0.6	6.2

Additionally, the I-V curves of DSSC made are shown in Fig 3.



Fig 3: I-V curves for NP/NTT, NP and NTT TiO₂

Fig.3 presents the TiO₂ photoanode made by nanoparticles demonstrated overall energy efficiency (η) of 5.8%. As in DSC-2 which made of single layer of NTTs TiO₂ as anode dye loading decreased, the efficiency was 5.3% which was lower. To have enhanced electron paths and adequate surface area simultaneously 20% NTT and also 80% NP used to derived DSC-3's photoanode which performance's was 6.2%.

Conclusions

To sum up, nano tree trunk shaped TiO_2 has been synthesized hydrothermally and used as an anode for DSSC. FESEM images presented a unique morphology of the as-synthesized NTT TiO₂ which has 200 nm thickness and particle size of 50 nm. XRD results showed high purity of anatase-TiO₂ crystalline both for NP and NTT. Furthermore, broaden peak of NP TiO₂ pattern indicates small nanoparticles in comparison with NTT TiO₂ narrow peaks which represent 1-D structure. DSSC made with 20% NTT and 80% NP TiO₂ as a DSSC's anode had an efficiency of 6.2% which is better than common DSSC of TiO₂ nano particle (i.e. 5.8%).

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