Design and Development of ZNO Nanotube Based Photo-Electrodes for Dye-Sensitized Solar Cells

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Abstract- Surface-grown ZnO nanotubes have been synthesized by a chemical solution method, hydrothermal method and by surfactant- assisted in-situ chemical etching on a glass plate coated with ZnO seed layer via thermally decomposing zinc acetate at 280°C. The morphological and structural analyses have been investigated by optical polarizing microscope, Atomic Force Microscopy (AFM), Field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) spectral analysis. It was found that the ZnO nanotubes synthesized via surfactant-assisted in-situ chemical etching strategy produced mesoflower-like structures with hexagonal structure everywhere and has been confirmed through FE-SEM analysis. The ZnO nanotube based photo-anodes produced by the present investigations are highly expected to contribute towards the improvement in the efficiency of nanocrystalline Dye-Sensitized Solar Cells (DSSCs).

Index Terms- ZnO nanotubes, Dye-sensitized solar cell, Wet-Chemical Method, in-situ Chemical Etching, zinc nitrate hydrate

I. Introduction

Dye-sensitized solar cells (DSSC) have been studied extensively as a potential alternative to conventional inorganic solid solar cells. Considerable efforts have been devoted to the development of more efficient photoanode materials including ordered meso-structured materials. Highly ordered semiconductor oxide nanotube arrays are particularly attractive, which enhances power conversion efficiency due to its enhanced surface area for the attachment of dye molecules on the photoactive oxide material. ZnO is a promising, but less explored wide band gap semiconductor oxide used for DSSC fabrication. It's much higher carrier mobility is more favorable for the collection of photo induced electrons. Taking into account of these factors the present problem is framed to have a detailed study of the effect of morphological and structural parameters on the fabrication of photoelectrodes for DSSC applications. The present investigation provides simple and efficient methods for the construction of nanostructured photoelectrodes for solar cell applications and also provides a strategy for constructing self-powered nano devices.

II. Experimental Methods

A. Synthesis of ZnO Nanotubes: Wet-Chemical Method

In this method (seed layer deposition) ZnO seed layers were first deposited on glass substrates. Zinc acetate dehydrate (0.005M) was dissolved in anhydrous ethanol with continuous stirring for 45 minutes Clean glass substrates were dipped into this clear solution for 10 minutes and drawn out at 2 cm/min and dry in the air, then the second time dipping was carried out. The process was repeated for many times. Subsequently, the substrates were heat-treated at 280°C for 2-hours to obtain seed layers. In the second step for nanotubes growth, zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$) (0.025M) and Tri-ethyl amine (TEA) solution (0.025M) were mixed and stirred to get a uniformly growth solution, then the substrate with ZnO seed layers was horizontally suspended in aforementioned growth solution at 85°C for 6 hours, then the growth solution was cooled down to room temperature naturally. The substrate was pulled out and thoroughly washed with and allowed to dry in air at room temperature.

B. Surfactant-Assisted In-Situ Chemical Etching

In this method[3], the glass substrates with seed layers were suspended upside down in an autoclave filled with an aqueous solution of 6 ml ammonia (25 wt%) and 80 ml zinc chloride solution (0.1 M) at 95°C for 70 min (growth step). After growth, the glass plates were thoroughly rinsed with de-ionized water and suspended once again into a 90 ml solution containing ammonia (0.5 wt%) and cetyltrim-ethyl ammonium bromide (CTAB; 0.5 wt%) at room temperature for 3.5 h (etching step) and then washed with de-ionized water.

C. Hydrothermal Method

An equimolar (0.1M) aqueous solution(MilliQ, 18.2MΩ cm) of zinc nitrate, $Zn(NO_3)_2.4H_2O$, and diethyl amine was prepared in a bottle with an auto-clavable screw cap. A glass substrate with seed particles was placed inside. The bottle is then heated at a constant temperature of 90°C for 2 days in a hot air oven. Subsequently, the homogenous thin films are thoroughly washed with (MilliQ) water to remove any contamination from residual salts or amino complex [4].

III. Results and Discussion

Surface Grown ZnO Nanotubes are produced by Chemical Methods. The preparation of ZnO nanotubes was carried out through all of the three procedures mentioned in the experimental session and the characterization of as-synthesized ZnO nanotubes were done using AFM, SEM and XRD. The seed layers served as nucleation centers for the subsequent growth of nanotubes. The surface morphology of the ZnO nanotubes was studied using Atomic Force Microscopy Fig.1(A-B) shows the 2 and 3-Dimensional AFM images of ZnO nanotubes grown on the glass substrates respectively.

Further morphological characterization of the ZnO nanotubes was performed by FE-SEM.

FE-SEM images (Fig.1(C-D)) at low magnification indicated that ZnO nanotubes grow uniformly in large area. The size of the ZnO nanotubes is estimated to be about 1-5 µm which is much larger than the nanotubes synthesized by the reported chemical solution method. This implied that the as-prepared ZnO nanotubes films had high porosity and large surface area which would be of benefit to adsorption of more dyes, when the ZnO nanotubes films are used as photo-anodes of dye sensitized solar cell, the light harvest efficiency can be improved.

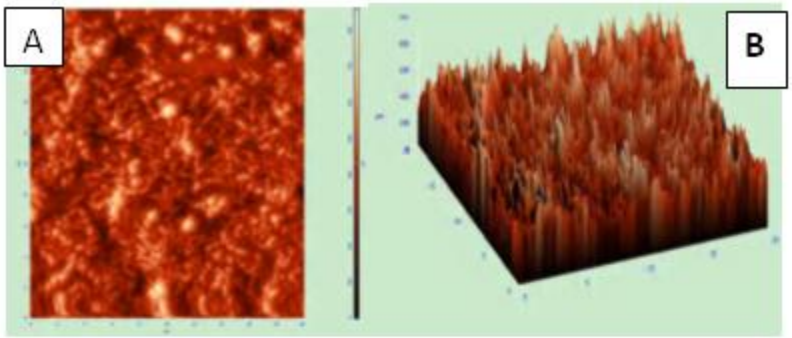

Fig.1: (A) 2-Dimensional, (B) 3-Dimensional images of ZnO nanotubes

A. ZnO Nanotubes Prepared by Surfactant -assisted In-situ Chemical Etching

Fig.2 A and B shows the FE-SEM images of the mesoflower – l ike ZnO nanotubes obtained using surfactant- assisted in-situ chemical etching method in which the nanotubes with an average size of about 5-10 µm and flat termination can be clearly seen. The mesoflower-like structures have been formed; which may be due to the aggregation of the seed particles during dip-coating in the first step, leading to the formation of mesoflower-like nanotubes. Representative SEM images showing the contrast between the tube wall and the inner part can be clearly observed, providing a direct evidence of the tubular structure.

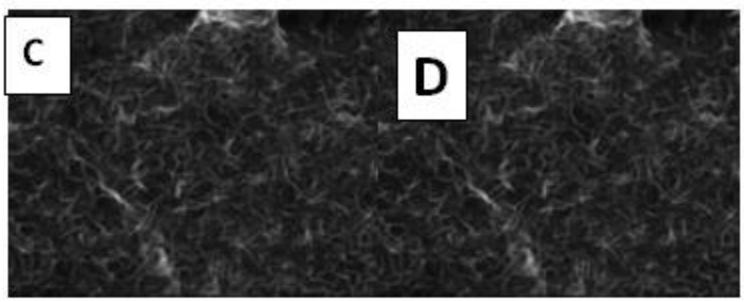

Fig. 2: (C-D) FE-SEM images of ZnO Nanotubes

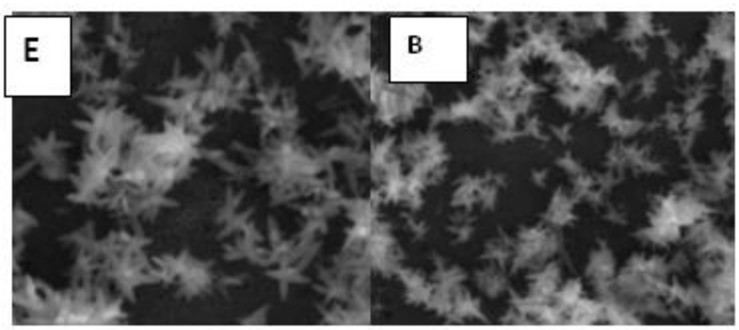

Fig. 2: (E-B) FE-SEM images of ZnO nanotubes exhibiting mesoflower-like structures

Fig.3 shows the XRD spectra for the ZnO nanotubes prepared by the surfactant-assisted Chemical etching taken for two different reaction conditions. The XRD spectra for then a no tubes were indexed using JCPDS data base and found that the peaks where exactly matching with the standard diffraction pattern of wurtzite ZnO nanostructures.

B. ZnO Nanotubes Prepared by the Hydrothermal Method

Using this method, ZnO micro tubes were formed successfully on the glass substrates and the morphological characterization was performed using AFM (Fig. 4). The presence of tubular structure can be seen from the 2-Dimensional image of ZnO tubes as well as in the 3-Dimensional image.

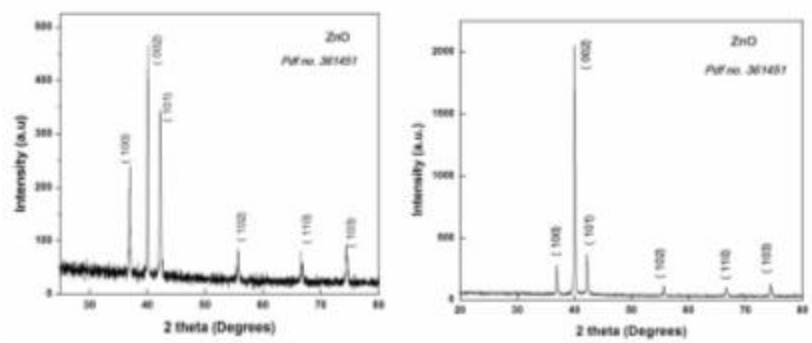

Fig.3: XRD pattern of the ZnO nanotubes prepared by the surfactant-assisted chemical etching

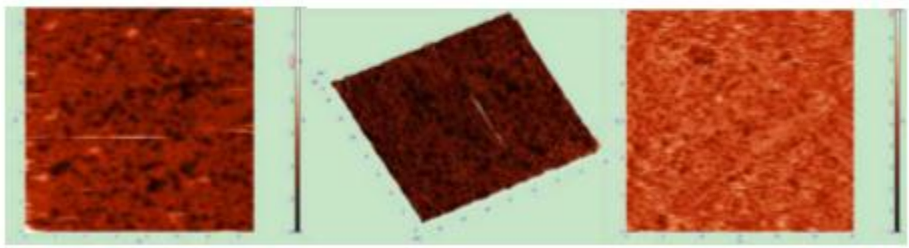

Fig. 4: AFM images (2-D and 3-D) of ZnO tubes prepared by the hydrothermal method

IV. CONCLUSION

In conclusion, ZnO nanotubes were synthesized via a simple chemical solution method, hydrothermal method and a surfactant-assisted chemical strategy. The as-prepared ZnO nanotubes were characterized by AFM, FE-SEM and X-ray diffraction analysis. The ZnO nanotubes synthesized via surfactant-assisted chemical etching method is found to have a meso-flower-like structure which has confirmed through FE-SEM studies and the ZnO nanotubes were found to have hexagonal structure. Since the nanotubes have high surface area and porosity it can be utilized as the photo-anodes in the formation of the DSSCs.

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