Journal of Solid State Chemistry 214 (2014) 17–23

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Low temperature grown ZnO@TiO_2 core shell nanorod arrays for dye sensitized solar cell application

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ARTICLE INFO

Available online 1 December 2013

Keywords:
Zinc oxide
Nanorod
Core shell
Solution method
Dye sensitized solar cell

ABSTRACT

High aspect ratio ZnO nanorod arrays were synthesized on fluorine-doped tin oxide glasses via a low temperature solution method. By adjusting the growth condition and adding polyethylenimine, ZnO nanorod arrays with tunable length were successfully achieved. The ZnO@TiO_2 core shells structures were realized by a fast growth method of immersion into a $(NH_4)_2 \cdot TiF_6$ solution. Transmission electron microscopy, X-ray Diffraction and energy dispersive X-ray measurements all confirmed the existence of a titania shell uniformly covering the ZnO nanorod's surface. Results of solar cell testing showed that addition of a TiO_2 shell to the ZnO nanorod significantly increased short circuit current (from 4.2 to 5.2 mA/cm^2), open circuit voltage (from 0.6 V to 0.8 V) and fill factor (from 42.8% to 73.02%). The overall cell efficiency jumped from 1.1% for bare ZnO nanorod to 3.03% for a ZnO@TiO_2 core shell structured solar cell with a 18–22 nm shell thickness, a nearly threefold increase.

1. Introduction

Demand for world energy is expected to double in the next 50 years. However, fossil fuel supplies are limited and will run out soon. Therefore, renewable energy sources from nature such as wind, biomass, tidal, geothermal and solar radiation have all been considered alternative sources. Among these, solar energy is commonly considered to be the ultimate solution to our need for clean, abundant and renewable energy resources for the future. Solar power can be converted directly into electrical power by photovoltaic (PV) solar cells. The first modern PV solar cells based on single-crystalline silicon (Si) were developed by Chapinet at Bell Laboratories in 1954. Although the Si based solar cell offer adequate efficiency to be used commercially, the cost of PV solar cells are still very high due to high production costs (the purification of crystalline Si from quartz and sand in nature).

Gratzel and his coworkers introduced the first dye-sensitized solar cells (DSSCs) which mimic natural photosynthesis, where chlorophyll absorbs photons but does not participate in charge transfer [1]. They are promising alternatives to conventional solid state photovoltaic devices that can provide efficient solar-to-electric energy conversion at low costs [1–3]. In DSSCs, the dye-sensitized nanocrystalline semiconductor film as a photo-anode plays a significant role in converting photons into electrical energy. So far, the most impressive DSSCs are the ones based on titanium dioxide (TiO_2) nano-crystalline particle films loaded with a ruthenium–polypyridine complex dye (such as N3 and N719 dyes) and a remarkable conversion efficiency of 11.18% [4]. Further increase in conversion efficiency is difficult due to large energy loss from detrimental recombination between electrons and either oxidized dye molecules or electron-accepting species in the electrolyte during the charge-transport process. Such a recombination is related to the lack of a depletion layer on TiO_2 nanocrystalline surfaces and becomes relatively serious as the thickness of the photo-anode film increases. Thus, semiconductor photo-anode materials that bridge the dyes and the electron collecting anode, while optimizing the electron-transfer energetics and kinetics are needed.

In this regard, the wide-band-gap semiconductor zinc oxide (ZnO) has attracted much attention as a fascinating alternative to TiO_2 photo-anode in DSSCs. This is because ZnO and TiO_2 exhibit similar lowest conduction band edges and electron injection process from the excited dyes. Additionally, the lifetime of carriers in ZnO is significantly longer than that in TiO_2. More importantly, in comparison with TiO_2, ZnO has a higher electron mobility, which is favorable for electron transport [5]. Therefore, it is expected that reduced recombination would be achieved when ZnO is used as photo-anode in DSSC due to rapid electron transfer and collection. Among the many ZnO growth methods (e.g. CVD, MOCVD, MBE, PLD) aqueous solution chemical methods have

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0022-4596/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2013.11.035

attracted more interest and has become the mainstream route to obtaining large-scale nano/micro-structured ZnO as photo-anode materials [6,7].

As reported, ZnO nanorods are not chemically stable. They are prone to being dissolved, leading to the formation of Zn^{2+}/dye complex layer on the surface [8–10]. To overcome this issue, a chemically stable shell can be coated onto the ZnO nanorod's surface. This conformal shell reduces recombination by forming an energy barrier between the photoinjected electrons and the oxidised species in the electrolyte, by forming a tunnelling barrier to confine the photoinjected electrons within the core, and by passivating the recombination centres on the core surface [9]. The coating of shell materials such as Al_2O_3 [9,11], SiO_2 [11], MgO [12], and TiO_2 [9,13–17] have been attempted and anatase TiO_2 appears to be the most promising due to the reported enhancements in efficiencies ranging from 1.91 times to 6.25 times [9,13–17]. However, the state of the art for the synthesis of anatase TiO_2 shells on the ZnO nanorod core utilises methods including atomic layer deposition (ALD) [9,13], sol–gel [14,17], radio-frequency sputtering [15], and atmospheric pressure chemical vapour deposition [16], each with one or more limitations such as the need for vacuum environments, slow growth rate, limited conformity, non-uniformity, and difficulty in the control of shell thickness.

Here, a simple and low cost solution method was used to synthesize ZnO@TiO_2 core shell nanorods with high aspect ratio (>100). First, the growth of ZnO nanorods was carried out in a zinc precursor solution containing hexamethylenetetramine and polyethylenimine. Optimum growth conditions were achieved which significantly improved the current densities and efficiencies of cells made from ZnO nanorods. The ZnO nanorod array was then immersed into the TiO_2 growth solution to coat a thin layer of TiO_2 on the surface of individual ZnO nanorods. In order to demonstrate their energy conversion behaviour, the ZnO@TiO_2 core shell nanorod array was used as the anode for a DSSC. A triple enhancement of cell efficiency was observed by the core–shell structured DSSCs, compared to the bare ZnO nanorod DSSCs. To the best of our knowledge, this is the first report of an all-solution method to synthesize low cost ZnO@TiO_2 core shell structures with nanocrystalline properties for solar cell applications. This novel method of coating a TiO_2 shell on the ZnO core has numerous advantages compared to the state of the art [9,13–17]. First, the shell can be grown at atmospheric pressure, negating the need for vacuum systems. Second, this method also overcomes challenges associated with conformity and uniformity. Lastly, this method is easily scalable to coat ZnO nanorod arrays of larger dimensions at low cost.

2. Experimental procedure

ZnO nanorods were grown on a fluorine-doped tin oxide (FTO) substrate that was seeded with a nanostructured ZnO thin film, as demonstrated by Greene et al. [18]. Briefly, 0.002 M zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 98%) was added into ethanol, dripped onto the FTO substrate and blown dry. This cycle was repeated 3 times and annealed for 1.5 h at 300 °C. For rod growth, the seeded FTO substrates were placed face down in a zinc nitrate hexahydrate (25 mM $Zn(NO_3)_2 \cdot 6H_2O$, 98%), 25 mM hexamethylenetetramine (HMT) and 5–7 mM polyethylenimine (PEI) solution bath in glass beaker. The growth temperature was set at 90 °C and growth duration ranged up to 96 h to vary the aspect ratio of the nanorods.

As for the coating of TiO_2, ZnO nanorod arrays grown on FTO were immersed into a solution consisting of 0.1 M ammonium hexafluorotitanate, $(NH_4)_2 \cdot TiF_6$, and 0.3 M of H_3BO_3 at 90 °C for various durations. The coated arrays were then rinsed with deionised water and followed by heat-treatment in air at 400 °C for 30 min.

Finally, these samples were fabricated into dye-sensitized solar cells using the ruthenium-based N719 dye (Solaronix) and iodolyte *AN-50*, (Solaronix) as the electrolyte was used. Platinum-coated FTO glass was used as the counter-electrode. ZnO nanorod-based dye sensitized solar cells with an effective area of 0.25 cm^2 were all characterized under simulated AM 1.5 sunlight with an intensity of 100 mW/cm^2. The incident light intensity was calibrated using a standard solar cell.

Field emission scanning electron microscope (FESEM) images were taken using a JEOL JSM-6700F instrument. High resolution transmission electron microscope (HRTEM) images, energy dispersive x-ray spectroscopy (EDX), and selected area electron diffraction (SAED) measurements were obtained using a Philips CM300 FEG TEM. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). Current density–voltage (J–V) measurements were performed at AM1.5 using a Newport Oriel Class A Solar Simulator (92,250 A).

3. Results and discussion

Fig. 1 shows a schematic of the formation of ZnO nanorods on FTO substrate covered with a ZnO seedlayer for growth in an aqueous solution at 90 °C. The decomposition of HMT and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) solutions was first described by Vayssieres [19] where Zn^{2+} ions originate from zinc

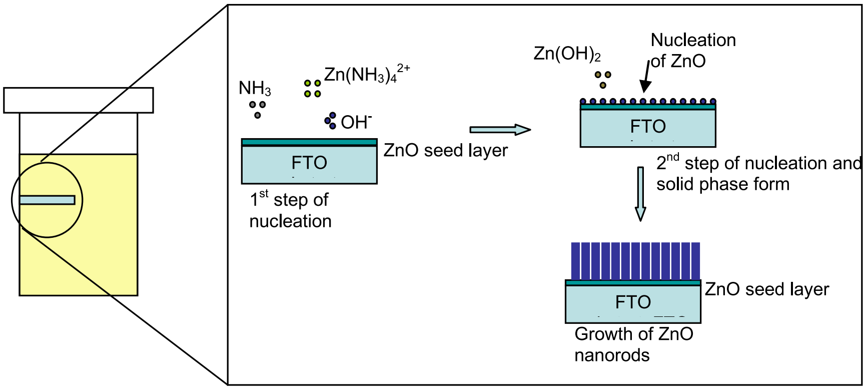

Fig. 1. Schematic diagram of ZnO nanorod formation under hydrothermal conditions.