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Hierarchical zinc oxide pomegranate and hollow sphere structures as efficient photoanodes for dye-sensitized solar cells

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ABSTRACT

The hierarchically structured ZnO pomegranates as well as hollow spheres have been prepared in a solvothermal assisted process using ethylene glycol as a solvent and L-ascorbic acid and oxalic acid as additives/surfactants respectively, without using water as solvent. Depending on the surfactant used, the morphology of the ZnO hierarchical nanostructures has changed dramatically which can be attributed to the reaction kinetics affected by presence of generated solvents, evolved gases. The structural analysis reveals the formation of wurtzite hexagonal crystalline structure. Electron microscopy images show the pomegranate and hollow sphere like morphology. The secondary nanoscale growth has been observed on the shell of pomegranate like ZnO microspheres. The synthesized ZnO hierarchial nanostructures have been used as photoanode in dye sensitized solar cells (DSSCs) which showed enhanced light harvesting properties than the commercial ZnO. Pomegranate like structure has displayed better light conversion efficiency (4.35%) as compared to ZnO hollow sphere structures (3.28%). This enhancement in photocurrent and power conversion efficiency could be due to interesting pomegranate like architecture of ZnO coupled with secondary 1-dimensional growth which provided more specific surface area for dye loading.

1. Introduction

The exhaustible nature of non-renewable energy resources provides an impetus to search an alternative source to fulfill the growing energy demand, which is everlasting. The new resources should have low production cost, easy to fabricate and highly efficient to be commercialized. The attention of researchers in dye-sensitized solar cell (DSSC) has increased due to its superior performance, uncomplicated engineering and low production costs. Among various known metal oxides, TiO_2 is essential material for dye-sensitized solar cells for exhibiting the highest overall light conversion efficiency ~11% and good long-term stability [1,2]. Beside this ZnO has been explored as materials of semiconductor for DSSCs due to its: 1) Similar band gap with TiO_2 i.e. 3.2 eV; 2) high electron mobility ~115–155 $cm^2\ V^{-1}\ s^{-1}$ than the anatase TiO_2 which is reported to be ~10^{-5} $cm^2\ V^{-1}\ s^{-1}$ [3,4]. and 3) possibility of producing simple tailor made modifications in the morphology and surface structure of ZnO nanomaterials as compared to TiO_2. The third point carries profound importance as optimization of surface structure, porosity; particle size and shape of nanomaterials are the important factors which can enhance the performance of DSSCs via increasing specific surface area for greater dye percolation. Hierarchical nanostructures affix further benefits of providing better pathways for cumulative charge conduction. All these factors can be easily tailored in case of ZnO nanostructures by exploiting different reaction parameters of solution growth and wet chemical method. Hydrothermal, microemulsion, solvothermal, template assisted and sol–gel syntheses are the important solution phase technique for the synthesis of ZnO nanomaterials [5–13].

As far as ZnO nanostructures synthesis is concerned, the solvothermal route enjoys an edge over other wet chemistry routes due to its precise control over the size, shape distribution, and crystallinity of products. Diverse array of experimental parameters such as reaction temperature, reaction time, solvent type, surfactant type, and precursor type are available to alter these

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characteristics. Additionally, hierarchical shapes can be easily obtained by properly tuning these reaction parameters. Different reaction parameters have been used in the glycol-assisted solvothermal synthetic route for the synthesis of ZnO nanoscale particles with hierarchical structures [14–26], and it had been observed that the glycol concentration in the reaction mixture plays a key role for determining the morphology and microstructure of ZnO particles. However, addition of additives/surfactants can further change the morphological features of obtained ZnO nanostructures, an effect which is not yet fully studied.

In this context, the present study reports on the morphological, optical and opto-electrical attributes of hierarchical ZnO pomegranate and hollow spheres like structures synthesized through solvothermal route using ethylene glycol as a solvent and L-ascorbic acid as well as oxalic acid as additives. Furthermore, solvothermally synthesized pomegranate like ZnO by using L-ascorbic acid with 1 dimensional (1-D) secondary growth of nanorods on the upper surface has been reported for the first time owing to the interesting architecture with enhance active surface area for its application in DSSC as photo-anode material. The structural, optical and morphological features were characterized for the synthesized nanostructures and photovoltaic parameters were calculated using the hierarchal as well as commercial ZnO material as photoanode through corresponding *J-V* curve and action spectrum. Solar cell characteristics reveal that nanostructures possessing pomegranate like structures having secondary growth exhibit highest solar cell efficiency and can be employed in the future generation of DSSCs.

2. Experimental

2.1. Materials

Zinc acetate (Merck), ethylene glycol (Merck), L-ascorbic acid (Qualigens) and oxalic acid (Qualigens) were used as received. For cell electrolyte, acetonitrile (Merck) was used as the medium of electrolyte, LiI (Aldrich) and I2 (BDH) were used as redox couple without further purification. Platinum catalyst (T/SP) (for making counter electrode), the sealing agent (SX1170-60, 50 μm, for packing the assembly) and N719 dye (as photosensitizer) were used in these experiments and were obtained from Solaronix. Conductive glass plate (15 Ω/cm) was obtained from Pilkington, USA.

2.2. Preparation of ZnO powder

In a typical experimental process, zinc acetate (0.2 M) was dissolved in 50 mL ethylene glycol (EG) with constant stirring for 20 min at 50 °C. Subsequently, 0.2 M oxalic acid was added in the reaction mixture and stirred for 10 min. The whole reaction mixture was placed in stainless steel lined with Teflon container and kept in oven at 200 °C for 24 h. The precipitate obtained was subsequently washed with water (3 × 15 ml) and with acetone (3 × 15 ml) and finally dried in air. The similar experimental procedure was repeated for the synthesis of another batch of ZnO. However, 0.2 M of L-ascorbic acid was used instead of oxalic acid. For the sake of meaningful comparison, the physic-chemical and opto-electrical performance of synthesized ZnO powders was compared with commercial ZnO powder (henceforth referred as Z-1). ZnO powder prepared using oxalic acid and L-ascorbic acid as additive/surfactant are labeled as Z-2 and Z-3, respectively.

2.3. Preparation of ZnO electrode (photoanode) and counter electrode

The ZnO thin film was prepared by making the paste of as-prepared ZnO powders in ethanol. The paste was spread on the conductive glass plate using doctor's blade technique and annealed at 450 °C for half an hour in air with the rate of 4 °C min^{-1} to obtain a thin film of ~ 5–6 μm thickness. The photosensitizer (N719 dye) was anchored onto the ZnO surface by dipping the ZnO-coated electrodes in an ethanolic solution of N719 dye for 6 h. The unadsorbed dye was washed off with anhydrous ethanol. The platinum counter electrode was prepared by deposition of Pt catalyst (T/SP paste, Solaronix SA) using screen printing method on conductive glass plate and annealed in tubular furnace at 400 °C for half an hour in air with the rate of 4 °C min^{-1}.

2.4. DSSC assembly

The dye-sensitized ZnO electrode and platinum coated counter electrodes were placed over each other in face to face sandwich manner leaving the space for making contact to connect with external load. This sandwich type assembly was sealed from three sides by using the hot melt sealant/spacer leaving one side open through which the electrolyte solution (0.05 M iodine, 0.05 M LiI and 0.5 M 4-tert. butypyridine in acetonitrile) was injected between the electrodes. Finally the open side of the cell assembly was also sealed. Copper wires were fixed on both the electrodes using silver paste and araldite for getting electrical contact.

2.5. Instrumentation and characterization

The crystal structure of as synthesized ZnO powders was characterized by XRD using Bruker AXS model D-8 equipped with a monochromator and Ni-filtered Cu-Kα radiation (λ = 1.54 Å) at 2θ varying from 20° to 80° with a scan speed of 4° min^{-1}. The morphology of the samples was investigated by field emission scanning electron microscope (FESEM) by using Hitachi S-4800 at an accelerating voltage of 5 kV and 10 kV. The high resolution transmission electron microscopy (HRTEM) images were obtained by TEM Techni G2 at an acceleration voltage of 200 kV. UV–Vis spectra of the samples were recorded using Shimadzu UV–Vis–NIR spectrophotometer- Model: UV-3600 in solution form by dispersing the samples in ethanol. The surface area of the samples were examined using Brunauer–Emmet–Teller (BET) analysis of nitrogen adsorption–desorption on a Tristar 3030 system (Micrometrics Instrument Corporation), after degassing over night at 150 °C.

The photoelectrochemical performance, including the short-circuit current (J_{sc}, mA/cm^2), open-circuit voltage (V_{oc}, V), fill factor (*FF*), and overall energy conversion efficiency (η) were determined from the J–V curve obtained by using a digital Keithley 236 SMU under an irradiation of white light from a 1000 W/HS Xenon arc lamp at a 100 mW/cm^2 light intensity with 1.5 AM.

The incident photon-to-electron conversion efficiency (IPCE) was measured by using a 300 W Xe lamp light source joined to a monochromator (Oriel). A reference Si photodiode calibrated for spectral response was used for the monochromatic power-density calibration. Electrochemical impedance spectroscopy (EIS) measurements of fully assembled DSSC were performed using electrochemical impedance spectra (EIS) in the dark at −0.70 V applied forward bias using a computer-controlled potentiostat (VersaSTAT 3). The spectra were scanned in a frequency range of 10^{-2}–10^5 Hz at room temperature with alternating voltage amplitude set at 10 mV.

3. Result and discussion

The crystalline nature of the hierarchically-structured ZnO (Z-2 and Z-3) and commercial ZnO powders was analyzed by using XRD. Fig. 1 shows the X-ray diffraction (XRD) patterns corresponding to