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Zinc stannate nanoflower (Zn_2SnO_4) photoanodes for efficient dye sensitized solar cells

M. Mary Jaculine [a], C. Justin Raj [b], Hee-Je Kim [c], A. Jeya Rajendran [d], S. Jerome Das [a,*]

[a] *Department of Physics, Loyola College, Chennai 600034, India*
[b] *Department of Chemistry, Dongguk University-Seoul, Jung-gu, Seoul, 100-715, South Korea*
[c] *Department of Electrical Engineering, Pusan National University, Jangjeong-Dong, Gumjeong-Ku, Busan 609 735, South Korea*
[d] *Department of Chemistry, Loyola College, Chennai 600034, India*

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ABSTRACT

Ternary zinc stannate (Zn_2SnO_4) nanoparticles were synthesized using the green hydrothermal technique at 200 °C for different reaction times and they were used as photoanodes for dye sensitized solar cells (DSSCs). The photovoltaic performance of the DSSC cells was characterized by measuring the *J–V* curves in dark, and under illumination. Among the three DSSC cells, the photoanode based on Zn_2SnO_4 nanoflower synthesized at 200 °C for 48 h recorded the highest conversion efficiency of 3.346% under 1 sun illumination (AM 1.5 G, 100 mW cm^{-2}) with improved short-circuit current density of 7.859 mA cm^{-2}, and comparable open-circuit photovoltage (0.626 V) and fill factor (0.679). This enhancement of characteristics is primarily attributed to the higher current density owing to its better crystalline quality as well as the larger surface area of Zn_2SnO_4 nanoflowers, all of which are the results of longer reaction time. The findings are further substantiated by means of open-circuit photovoltage decay experiment, dye loading behavior and electrochemical impedance spectroscopy.

1. Introduction

Energy scarcity is a global concern today. The increasing limitedness of hydrocarbon energy is pushing up the overall cost of living which results in mass poverty and social unrest. Against this background, scientists and engineers have been working relentlessly to develop alternative and sustainable sources of energy especially using solar power. But despite decades of research and developmental efforts, solar cells are still expensive and wanting in high efficiency, making it an uncompetitive alternative to fossil fuels. One of the main reasons for the high cost of traditional semiconductor photovoltaic solar cells is their poor design. In fact, the amount of energy converted from light into electricity finally depends on how many electrons that can pass across the interface between the two layers. One way to increase the creative efficiency is to create very high surface areas at the interface. The cell that could possibly achieve very high surface area at the interface is the third generation solar cell that is known as dye-sensitized solar cell (DSSC), or Gratzel cell – named after its inventor [1]. These cells are more flexible, and they can operate even in low lighting conditions. Since the dye is much larger than the actual area of the cell, it increases the surface area by more than a thousand times. Therefore as an alternative to amorphous conventional solar silicon cells, DSSCs offer a realistic option for harvesting sunlight into electrical energy, with appreciable high conversion efficiency along with other advantages of being environment friendly, easy to fabricate and economically viable [2–4].

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[*] Corresponding author. Tel.: +91 44 2817 5662; fax: +91 44 2817 5566.
E-mail addresses: sjeromedas2004@yahoo.com, jerome@loyolacollege.edu, jeromedas.s@gmail.com (S.J. Das).

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In a DSSC, light is absorbed by a dye sensitizer adsorbed on the surface of a wide-band gap semiconductor. Charge separation takes place at the interface via photo-induced electrons from the lowest unoccupied molecular orbit (LUMO) of dye sensitizer into the conduction band of the semiconductor and transported through the conduction band of the semiconductor to the external circuit [5]. The semiconductor oxide electrode material is a critical factor determining the performance of DSSCs [6]. Several binary semiconductor oxide materials have been studied in developing DSSCs such as Nb_2O_5 [7], ZnO [8,9], SnO_2 [10], WO_3 [11], In_2O_3 [12] and TiO_2 [13–16]. Among these, nanocrystalline TiO_2 and ZnO are found to be the most excellent materials owing to their high performance in DSSC. Besides these binary oxides, special attention is also paid to the ternary oxides, which provide more freedom to tune the chemical properties of the material and band structure [17]. To the best of our available knowledge, $SrTiO_3$ ($\eta=1.8\%$) and Zn_2SnO_4 ($\eta=3.7\%$) are the only two ternary oxides reported for DSSCs applications [18]. The most commonly used material for charge transport in DSSCs is a mesoporous network of TiO_2 nanoparticles, which have shown excellent photoelectric conversion efficiency [19,20]. However there have been research attempts in the recent times to identify new materials for improving the electron transport as well as for reducing the recombination rate which will eventually replace the widely used TiO_2. Zinc stannate (Zn_2SnO_4), being a wide-band gap semiconductor (band gap $E_g=3.6$ eV and electron mobility of 10–15 $cm^2\,V^{-1}\,s^{-1}$) is widely proposed as an anode material for dye-sensitized solar cells (DSSCs). Zn_2SnO_4 is particularly interesting because of its physical and electrical properties while also possessing good chemical, thermal stability and low visible absorption. Because of their large band gap (3.6 eV), Zn_2SnO_4 cells could have greater photostability against UV light than TiO_2 [18]. Further the electron lifetime is proven to be larger for Zn_2SnO_4 than for TiO_2 [18]. Zn_2SnO_4 also shows dramatically reduced acid etching rate in comparison with ZnO [17]. The above stated facts have been confirmed by several research results. Aviles et al. [18] reported that Zn_2SnO_4 is an interesting material for dye-sensitized photoanodes since the large band to band transition substantially diminishes photo-bleaching and presents a lower electron-triiodide recombination rate. Villarreal in his study concluded the position of the conduction band (C_B) for Zn_2SnO_4 located at higher energy level than for TiO_2, which tends to transport photo injected electrons much faster [21]. In this work, we have demonstrated the photovoltaic performance of DSSCs fabricated using the samples synthesized with green hydrothermal technique at 200 °C for different reaction times. Further dye loading behavior and charge transfer kinetics were analyzed using UV–vis spectral analysis and electrochemical impedance spectroscopy (EIS).

2. Experimental details

2.1. Synthesis of Zn_2SnO_4 nanoparticles

All reagents were of analytical grade purchased from Merck and used as received without further purification. Zinc chloride ($ZnCl_2$) and tin chloride dihydrate ($SnCl_2\cdot 2H_2O$) were used as precursors and NaOH as the mineralizer for the hydrothermal synthesis of Zn_2SnO_4. The process began by dissolving $SnCl_2\cdot 2H_2O$ (3 mmol) and $ZnCl_2$ (3 mmol) with 20 mL of double distilled water separately to form two transparent solutions. There after 20 mL of NaOH (1 M) solution was added little by little facilitated by magnetic stirring into the tin chloride dihydrate transparent solution. Finally, zinc chloride solution was added drop by drop into the above mixed solution under stirring using magnetic stirrer. The mixed solution under room temperature was continuously stirred for 1 h until it leads to the formation of white precipitate of the hybrid complex. In the end, the white hybrid complex was transferred into a 100 mL Teflon-lined stainless autoclave with a fill factor of approximately 70%. The autoclave was sealed and maintained in a furnace at 200 °C for varying time durations, in order to examine the influence of the reaction time on the product structure and morphology. The autoclave was cooled naturally to room temperature and the precipitate thus obtained was washed several times in double distilled water and in absolute ethanol by repeated centrifugation and ultrasonication. Finally, the product was dried in an oven at 80 °C for 20 h.

2.2. Fabrication of Zn_2SnO_4 photoanodes

The photoanode was deposited on FTO (fluor-doped SnO_2 glass) glass substrate by adopting doctor blading technique. The paste was prepared by adding as synthesized 0.5 g Zn_2SnO_4 nanopowder to 3 mL of an ethanol–water mixture (3:1) with 0.08 g of ethylene cellulose, 0.5 mL of acetyl acetone and 1 mL of Triton X-100 solution as surfactant. The mixture was ground thoroughly by ball milling for 30 min under 500 rpm followed by an ultrasonication for 1 h and made into a paste by optimized drying condition. The resultant paste was doctor bladed (area$=0.25\ cm^2$) over ultrasonically cleaned FTO substrate and was sintered at 450 °C for 30 min. The thicknesses of the films were found to be about 15 μm and were used for the fabrication of DSSCs.

2.3. Fabrication of DSSCs

The photoelectrodes were soaked in a 0.2 mM N719 dye (cis–bis (isothiocyanato) bis (2, 20-bipyridyl-4, 40-discarboxylato)-ruthenium (II)-bis-tetrabutylammonium, $RuC_{58}H_{86}N_8O_8S_2$) solution for overnight in ambient temperature and the excess dye was removed by soaking the photoanode in 99.9% ethanol. Platinum counter electrodes were deposited from a commercial platinum paste (Solaronix, platinum catalyst T/SP) on a FTO glass substrate, which was subsequently heat treated at 400 °C for 30 min in air. Finally, the photoanodes and the counter electrodes were sealed together using a 25 μm hot-melt sealing sheet (SX 1170-25, Solaronix) and the internal space was filled with a redox liquid electrolyte of 0.5 M LiI, 0.05 M I_2 and 0.5 M 4-tertbutylpyridine in acetonitrile.

2.4. Characterization

Phase formation of synthesized samples was identified by using SEIFERT JSO DEBYEFLEX 2002, Germany make X-ray diffractometer with CuKα radiation ($\lambda=1.540598$ Å)