Optical Materials 78 (2018) 325–334

Contents lists available at ScienceDirect

Optical Materials

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

Nanostructured zinc oxide photoelectrodes by green routes M-SILAR and electrodeposition for dye sensitized solar cell

M.A. Gaikwad [a], M.P. Suryawanshi [b], P.S. Maldar [a], T.D. Dongale [c], A.V. Moholkar [a, *]

[a] Thin Film Nanomaterials Laboratory, Department of Physics, Shivaji University, Kolhapur 416-004, M. S., India
[b] Optoelectronics Convergence Research Center, Department of Materials Science and Engineering, Chonnam National University, 300, Yongbong-Dong, Buk-Gu, Gwangju 500-757, South Korea
[c] School of Nanoscience and Biotechnology, Shivaji University, Kolhapur 416-004, M. S., India

ARTICLE INFO

Article history:
Received 11 November 2017
Received in revised form
13 February 2018
Accepted 19 February 2018

Keywords:
ZnO
Nanorods
Nanosheets
Growth mechanism
Dye-sensitized solar cell

ABSTRACT

Surfactant-free, ultrasound assisted modified successive ionic layer adsorption and reaction (M-SILAR) method and home-made microcontroller based low-cost potentiostat system are employed to prepare zinc oxide (ZnO) nanostructure based thin films. The comparison between physicochemical as well as photoelectrochemical (PEC) properties of the nanostructures prepared via two different template free, simplistic and cost-effective green routes have been discussed in detail. X-ray diffraction and Raman analysis confirm the formation of phase pure ZnO with the hexagonal crystal structure. Surface morphology significantly affects the physicochemical as well as PEC properties of ZnO thin films. Nanorods (NRs) and nanosheets (NSs) based ZnO thin films sensitized with N3 dye have been directly used as photoelectrodes in the dye-sensitized solar cell (DSSC). The power conversion efficiency (PCE) of 0.59% is achieved with J_{sc} of 4.04 mA/cm^2 and V_{oc} of 0.44 V for the DSSC in which the M-SILAR deposited 1-D ZnO NRs based thin film is used as the photoanode. While relatively less PCE of 0.29% with J_{sc} of 2.53 mA/cm^2 and V_{oc} of 0.36 V is obtained for DSSC prepared using electrodeposited 2-D ZnO NSs. In the NSs like 2-D surface morphology, the presence of multiple grain boundaries are acted as traps for the diffusing electrons, which reduces the electron mobility through it.

1. Introduction

To get rid of chemically hazardous and rare earth ingredients, third generation solar cells have been designed. They possess a great potential using nanomaterials and have gained a great breakthrough since Gratzel put forward the concept of a dye-sensitized solar cell (DSSC) [1]. In the past two decades, a large number of binary metal oxides such as TiO_2, ZnO, SnO_2, WO_3 and Nb_2O_5 have been tested as photoelectrode materials in the DSSCs [2–6]. Until now using TiO_2 as the DSSC photoanode, the power conversion efficiency (PCE) of more than 9% has been achieved with ruthenium-based N3 sensitizer [7]. Moreover, the 13% PCE has been achieved with porphyrin sensitizers using TiO_2 as a photoanode [8]. Up to now record PCE of 8.03% have been achieved with ZnO based DSSCs [9], which is much lower than that of TiO_2-based DSSC, still ZnO is regarded as a potential substitute for TiO_2 photoelectrode because of its similar electron affinity, wide band gap of 3.4 eV and exciting binding energy level (60 meV) with stable wurtzite structure [4]. Also, it possesses higher bulk mobility (100 cm^2/V^{-1}s^{-1}) indicating lower charge recombination [10]. Numerous kinds of ZnO nanostructures, particularly, one-dimensional (1-D) nanowires (NWs) or nanorods (NRs), and two-dimensional (2-D) nanosheets (NSs) or nanoplates (NPs) have been synthesized using the various physical and chemical methods including pulsed laser deposition (PLD), spray pyrolysis technique (SPT), hydrothermal method, chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR) and electrodeposition (ED) method [11–16]. In comparison, the PLD and SPT methods require high temperature with rigorous and complex conditions for the operation. From the technological point of view, SILAR and ED method offers much more inexpensive experimental setup, a rapid and economical method for preparation of large-area ZnO nanostructures with low-temperature processing, arbitrary substrate shapes, and offer precise control of film parameters [17,18]. Using the SILAR method, the thickness, composition and phase purity of thin films can be easily controlled just by regulating the growth parameters such as

* Corresponding author.
E-mail address: avm_phy@unishivaji.ac.in (A.V. Moholkar).

https://doi.org/10.1016/j.optmat.2018.02.040
0925-3467/

adsorption and reaction time, deposition cycles and precursor concentration [19–21]. Additionally, the deposition electrolyte of ED method can be reused, while the deposition solutions for other methods could be used only once.

In the DSSC, photoelectrode made up of wide band gap semiconducting material acts as the heart of the DSSC. Researchers are trying to improve the electron transport properties of the material by changing the morphology of the samples, such as 1 dimensional (1-D) nanowires (NWs), NRs or nanotubes (NTs), as every possible point of electron injection is directly connected to the substrate with a minimum number of interfaces and grain boundaries in between, which further improves the charge transport in the device [19]. 1-D ZnO nanostructures afford a direct conduction pathway for the photogenerated electrons, which is favorable for rapid electron transport in photoelectrode with reduced recombination loss [20]. The 2-D nanostructure of ZnO like NSs has also attracted much interest because of their unique advantages, such as the large surface area for the adsorption of sensitizers and enhanced light scattering capacity, which especially beneficial for applications in photoelectrochemical (PEC) cells [22].

Çakar et al. synthesized the ZnO plates, rods and nanoparticles using microwave assisted hydrothermal method and achieved 1, 0.83 and 0.41% power conversion efficiency for the respective samples with Fe-tannic acid complex dye as photosensitizer [23]. Marimuthu et al. prepared seed layer assisted ZnO nanorods as photoelectrode by ED method and obtained 3.75% PCE with Ru based N719 dye [24]. Using hydrothermal and dip-coating methods, Feng et al. prepared the ZnO/TiO_2 composite NRs for DSSC application. The top ZnO NRs facilitated large surface area for dye adsorption and TiO_2 NRs provided a direct pathway to the photogenerated electrons which results in a PCE of 4.36% [25]. Patil et al. have achieved the PCE of 2.9% by photonic sintering of a ZnO nanosheet based photoanode prepared by using solid-state synthesis with flash white light combined with deep UV irradiation [26]. Hedgehog-like hierarchical ZnO needle-clusters developed by Qu et al. by hydrothermal synthesis provides the high surface area for dye adsorption and also avoids extensive grain boundary formation which results in 2.2% PCE of the DSSC [27].

The limiting and time-consuming factor for traditional SILAR method is the slow growth rate. With the use of ultrasound-assisted M-SILAR method, nanostructured photo-electrodes can be directly prepared with less deposition time. The ultrasound works on the principle of the acoustic cavitation effect. The deposition rate and the film quality are expected to increase with the modification **i**n the deposition process of ZnO nanostructure by the cavitation effect. Therefore, M-SILAR method has been used for the deposition of the nanostructured ZnO photo-electrodes to be used in DSSC's [28]. For ED, the microcontroller based low-cost potentiostat has been designed and developed. In the extensive literature survey, there are fewer reports on the synthesis of DSSC photoelectrodes by employing the simplistic M-SILAR and Electrodeposition green routes. So, in the present investigation, surfactant-free 1-D ZnO NRs have been grown without prior seed layer by changing the M-SILAR cycles and 2-D ZnO NSs have been deposited by employing ED method with variation in the deposition time. The probable growth mechanism processes of these nanostructures are also discussed. The comparison between physicochemical as well as PEC performance of ZnO nanostructures prepared by two different green routes is also debated in the present study.

2. Experimental

2.1. Preparation of ZnO thin films by M-SILAR method

ZnO thin films have been deposited using zinc-ammonia complexed precursor ($Zn(NH_3)_n^{2+}$) as cationic source and 1% diluted hydrogen peroxide (H_2O_2) kept at 353 K temperature as an anionic source with slight modifications as discussed in our previous report [29]. The schematic setup used for M-SILAR deposition of ZnO thin films is as shown in Fig. 1 (A). The M-SILAR cycles have been repeated successively for 50, 100, 150 and 200 times and the as-deposited films were annealed at 673 K in an air for 1 h to remove the hydroxide phase and to increase the crystallinity. The films are denoted as SZ-5, SZ-10, SZ-15 and SZ-20 samples for 50, 100, 150 and 200 deposition cycles, respectively and these samples were further used for their structural and morphological studies.

2.2. Preparation of ZnO thin films by ED method

In this study, Atmel AT89C51 microcontroller is used to generate basic electrical output such as constant current, constant voltage, and forward and reverse pulse with pulse width modulation (PWM) capabilities. The total cost of the system nearly equals to 50 USD. A typical block diagram of the proposed system is shown in Fig. 1 (B). The microcontroller can produce 0–5000 mV voltage with the help of 8 bit digital to analog converter DAC0808 (Texas Instruments). The operational amplifier (Op-Amp) circuits are responsible for the precise control of constant voltage, constant current, and forward and reverse pulse with pulse width modulation (PWM). The constant current is generated using Op-Amp and Zener diode circuit, whereas the PWM is achieved by conventional triangle-wave generator circuits. The software code of the present system is written in the Keil integrated development environment (IDE). ED of ZnO thin films was performed with the microcontroller based potentiostat in a standard three electrodes system. The block diagram of microcontroller based potentiostat used for the ED of ZnO NSs is as shown in Fig. 1 (B). Graphite and saturated calomel electrode (SCE) are used as the counter electrode and the reference electrode, respectively. The flexible stainless steel (SS) and fluorine doped tin oxide (FTO) substrates were used as working electrode. The electrolyte was 0.05 M Zn $(NO_3)_2$ aqueous solution and 0.1 M KCl was introduced into it as a supporting electrolyte. ZnO thin films were obtained by potentiostatic electrodeposition at −1.0 V (versus SCE) at the constant temperature of 80 °C by varying deposition time for 5, 10, 20 and 30 min. The as-deposited films were annealed at 673 K in an air for 1 h to remove the hydroxide phase included if any. The films are denoted as EZ-5, EZ-10, EZ-20 and EZ-30 samples for 5, 10, 20 and 30 min deposition time, respectively.

2.3. Assembly of ZnO-based DSSCs

The optimized M-SILAR and electrodeposited ZnO samples have been soaked in ethanolic 0.3 mM *cis*-Bis (isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato ruthenium) (II) i.e. N3 dye solution at room temperature for 12 h and then washed cautiously in ethanol, afterward the dye-loaded films have been dipped in acetonitrile and dried up in an air. Compact DSSCs have been fabricated using a typical two electrode configuration with an active area of 0.25 cm^2. Dye-loaded ZnO samples have been used as photoelectrode and platinum (Pt) coated FTO as the counter electrode. The predrilled FTO substrates were ultrasonically washed and the Pt counter electrode is prepared by drop cast method using the 10 mM hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) in 2-propanol solution with annealing at 450 °C for 10 min. The two electrodes have been assembled using the thermoplastic (1 mm). The space between the electrodes is filled with an electrolyte comprising of 0.1 M lithium iodide and 0.05 M iodine in acetonitrile through the predrilled hole in the counter electrode.