Journal of Photochemistry and Photobiology A: Chemistry 295 (2014) 64–69

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

DSSCs synergic effect in thin metal oxide layer-functionalized SnO_2 photoanodes

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ARTICLE INFO

Article history:
Received 7 July 2014
Received in revised form 18 August 2014
Accepted 1 September 2014
Available online 16 September 2014

Keywords:
Wet-chemical method
SnO_2 nanosheets
Surface passivation
Charge transport and recombination

ABSTRACT

DSSCs synergic effect, for reducing charge recombination and energizing charge transfer, in SnO_2 photoanodes functionalized with thin layers of several metal oxides including ZrO_2, MgO, $CaCO_3$ and ZnO etc., for boosting overall dye-sensitized solar cells (DSSCs) performance is investigated. The SnO_2 photoanodes composed with upright-standing nanosheets were initially fabricated using a simple and cost-effective wet chemical method. Both pristine and functionalized SnO_2 photoanodes were explored in DSSCs application in addition to other photoelectrochemical properties where, functionalized photoanodes exhibited remarkably improved light-to-electrical power conversion efficiencies compared to that of pristine one. To corroborate synergic effect and for probing the charge transport properties including charge transfer resistance and electron life time in thin metal oxide functionalized SnO_2 photoanodes, electrochemical impedance spectroscopy measurement was undertaken.

1. Introduction

Dye sensitized solar cells (DSSCs) have attracted considerable attention in solar cell research community. The low-cost, easy manufacturing process, possible flexible device fabrication and a competitive photo-to-electron conversion efficiency have made it a possible alternative to existing silicon solar cells. TiO_2 is one of the most accepted photanode materials for DSSCs application. Basically, the high photoconversion efficiency (~15%) in DSSCs is attributed to high surface area of photoanode that exhibits high light harvesting despite of monolayered dye adsorption [1], which is also undesirably responsible for limiting the DSSCs performance by incorporating the most viable probability of electron recombinations [2] at the photoanode–electrolyte interface resulting in recombinations of the injected electrons of the anode with the oxidized species in the electrolyte [3–7]. Faster electron recombination, insufficient light harvesting and low dye loading amount are few major reasons for obtaining lower power conversion efficiencies. Some of the main approaches used to solve the recombination problems (including TiO_2) are use of; organic additives in the electrolyte [8,9], fibrous nanostructures for fast transport [10] or a thin metal oxide blocking layer on the photoanode for inhibiting back electron transfer to redox electrolyte [7]. As for the approach of a blocking layer, it is believed with investigation on interpreting the functional role of the blocking layer along with its fundamental understanding which proved essential to prevent the recombination reaction by forming a potential barrier between the anode and the electrolyte thus consequently DSSCs performance in most of the cases is tested with surface treatment including MgO, Al_2O_3, ZrO_3 etc. [9,10]. In general, uses of thin layers are restricted to insulating or wide-band-gap oxide materials. Few reports suggest that the use of even a small band gap semiconductor can form an effective blocking layer. Due to its smaller thickness a quantum confinement effect is more active [11].

Characteristics including open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power energy conversion efficiency (η) are important for any type of solar cells. At the same time, researchers are looking for a controlled synthesis for developing various micro and nanostructure-based photoanodes for best photoconversion efficiency [12–16]. Various reports suggest that the surface treatment of $TiCl_4$ is responsible for remarkable enhancement of cell performance; however, it is also responsible for the modification of nanostructures

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http://dx.doi.org/10.1016/j.jphotochem.2014.09.004
1010-6030/

morphology, which is undesirable for a specific application [17]. As previously discussed, among most viably studied and highest performance reported TiO_2 [18], which shows a fairly slow electron transport in its nanoparticulate state [19,20], and hence the DSSCs system also requires a slow redox shuttle; in other words, the electrolyte with slow rate of reduction and oxidation with respect to interception of injected electrons, typically I^-/I_3^- is more suitable for this purpose. The lethargic reactivity of the electron transport shuttle requires approximately 600 mV energy for attending its regeneration to initial state. The insertion of this lashing force hampers the achievable V_{oc} almost by a factor of half and hence many groups are indulged into the findings of alternative redox shuttles to tackle this loss in voltage [21–23]. The second alternative to this problem can be addressed by employing another semiconductor with higher electron mobility and high surface area-based photoanode where electron transport would be relatively faster [24]. Among, the various semiconductors that have been considered to replace TiO_2; SnO_2 is an unceasing candidate with many advantages including a faster rate of electron interception by the redox electrolyte, higher electronic mobility, low sensitivity to UV degradation due to its larger band gap and hence the better long-term stability, etc. [25]. Moreover, the lower conduction band edge (more positively located) position of SnO_2 facilitates the higher efficiency of electron injections from the adsorbed dye molecules [26]. However, the use of SnO_2 as the high surface area electrode also inherits some prominent drawbacks which includes, more positive located conduction band position, responsible for low V_{oc} and secondly, the rate of electron interception by the redox electrolyte is much higher [27]. That is, the back electron transfer rate from SnO_2 (to the redox electrolyte) is in the microsecond range which is roughly three orders of magnitude faster than that of TiO_2 [28]. In order to overcome these drawbacks, there are only two possibilities which includes either to develop and use a fast redox shuttle or to slow down the rate of electron interception by coating the photoelectrode with a thin layer of a higher band gap metal oxide compared to SnO_2 such as MgO [28], ZrO_2 [29], SiO_2 [30], Nb_2O_5 [31] and with an insulator like $CaCO_3$ [32], Al_2O_3 [33] which could passivate these states and make the rate of electron interception slower. Usually, different techniques are employed for developing a thin passivating layer which includes chemical bath deposition, chemical vapor deposition, successive-ionic-layer adsorption and reaction method, dip-coating etc. [34,35].

The key objective of our approach is to enhance the DSSCs performance of N719-based SnO_2 photoanodes by modifying them with different thin metal oxide layers so called functionalization. In this work, we have grown upright-standing nanosheets of SnO_2 using wet chemical method at ambient temperature. The presence of passivating layers of different metal oxides obtained by spin coating method, whose speed rate and rotation time were kept constant, was confirmed. The functionalized photoanodes exhibited remarkable improvement in DSSCs performance, without distorting the original morphology. The DSSCs performance of SnO_2 photoanode was increased to 3.18% for ZnO, 3.96% for ZrO_2, 5.17% for $CacO_3$ and 5.25% for MgO after functionalization which was only 1.38% for pristine electrode. For the first time, a passivating layer of $CaCO_3$ was used for enhancing DSSCs performance of SnO_2 photoanode.

2. Experimental details

2.1. Electrodes synthesis

All the chemicals were purchased from Sigma–Aldrich and used without further purification. For the synthesis of SnO_2 nanosheets, initially 0.3 M tin tetrachloride ($SnCl_4$) was dissolved in ethanol (50 ml), 0.6 M thioacetamide was further added into the same solution. The solution was then sealed in the falcon tube of 50 ml capacity with two fluorine-tin-oxide (FTO) substrates of $8 \times 2.5\ cm^2$ dimensions inserted and placed vertically into it, facing in opposite directions. Prior to deposition, FTO substrates were cleaned with detergent solution, *iso*-propanol and acetone solution through ultrasonication for 30 min each, dried in an argon gas flow and then treated in ozone for 30 min. The wet chemical method was carried out at 70 °C for 3 h. It must be noted that, if the time period exceeds above 3 h, photoanode of SnO_2 starts to peel-off out from the substrate surface. The photoanodes thus obtained were washed with ethanol and naturally dried in air and then annealed at 450 °C for 1 h. Thus, the photoanode obtained by this method was about 4 micron thick, white in appearance and fairly transparent in nature.

The surface functionalization was achieved by using a spin coater, which is reliable to get uniform film coverage along with zero probability of sample damage. Different solutions including zinc chloride, zirconium nitrate, magnesium acetate and calcium chloride (0.05 M) were prepared in ethanol solvent then coated by fixing the rotary pump at 10^{-3} torr and adjusting the speed of motor to 2000 rpm with time period of 5 min each. Furthermore, these spin-coated functionalized SnO_2 photoanodes were air-annealed at 500 °C for 30 min so as to form metal oxide layer of respective precursor solution before measuring structure,

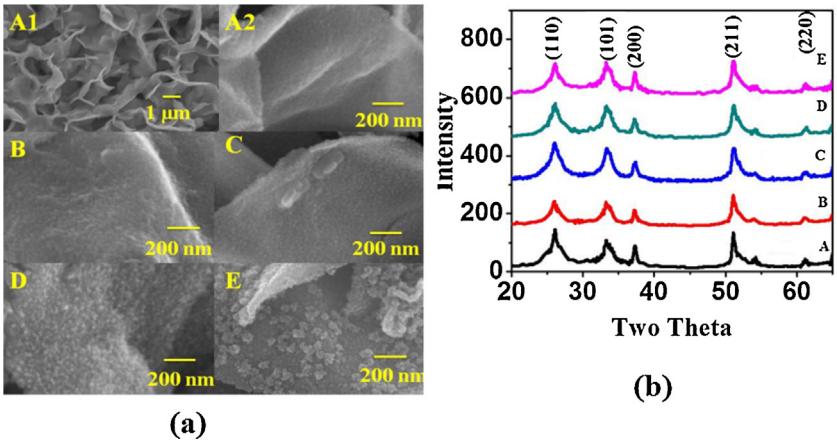

Fig. 1. FE-SEM images of (a) (A1 and A2) pristine, and (B–E) $ZnCl_2$, $Mg(CH_3OO)_2$, $CaCl_2$ and $ZrCl_4$ treated SnO_2 photoanodes; (b) XRD spectra (of A–E as in (a)).