Calcium carbonate electronic-insulating layers improve the charge collection efficiency of tin oxide photoelectrodes in dye-sensitized solar cells

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ABSTRACT

In dye-sensitized solar cells (DSSCs), a surface passivation layer has been employed on the tin oxide (SnO_2) photoanodes to enhance the charge collection efficiency, and thus the power conversion efficiency. Herein, we demonstrate that the electronic-insulating layering of calcium carbonate ($CaCO_3$) can improve the charge collection efficiency in dye-sensitized solar cells designed with photoanodes. In order to evaluate the effectiveness of $CaCO_3$ layering, both layered and pristine SnO_2 photoanodes are characterized with regard to their structures, morphologies, and photo-electrochemical measurements. The SnO_2-6L $CaCO_3$ photoanode has demonstrated as high as 3.5% power conversion efficiency; 3.5-fold greater than that of the pristine SnO_2 photoanode. The enhancement in the power conversion efficiency is corroborated with the number of the dye molecules, the passivation of surface states, a negative shift in the conduction band position, and the reduced electron recombination rate of photoelectrons following the coating of the $CaCO_3$ surface layer.

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1. Introduction

It is imperative to develop environmentally sustainable energy technologies to overcome environmental pollution concerns and the energy crisis. Among the various renewable energy technologies, the photovoltaic cell is considered to be one of the most promising because of its large solar energy capacity that can fulfill the increasing global energy consumption demand [1]. Dye-sensitized solar cells (DSSCs) are one type of photovoltaic cell, and have generated a great deal of attention as a result of their low production cost, environmentally friendly fabrication processes, durability, and relatively comparable solar-energy-conversion efficiency [2]. To achieve high solar-to-electrical power conversion efficiency, metal oxide based photoanodes, as one of the important components in DSSCs, have been developed to possess features such as wide band-gap ($\sim$3–4 eV), good electron transport abilities,

chemical stability, mechanical robustness, and large surface [3]. In addition, the lowest unoccupied molecular orbital (LUMO) energy level of the dye molecules has to closely match with the conduction band of the photoanode for efficient electron injection from the dye to the photoanode [4].

To date, TiO_2 nanostructured metal oxide film electrodes have frequently been used as a photoanode material for DSSCs application, however they have disadvantages such as a high surface state and a fast electron recombination rate. These problems associated with TiO_2 metal oxide have an adverse effect on the electron mobility and charge transport kinetics, which in fact is responsible for low power conversion efficiency [5]. Therefore, many researchers have tried to substitute TiO_2 with other metal oxide photoanodes such as ZnO, Bi_2O_3, WO_3, SnO_2, and Nb_2O_5 etc. [6].

Among these metal oxide photoanodes, SnO_2 has intrinsic attractive properties such as a high electron mobility (100–$200\,cm^2\,V^{-1}\,S^{-1}$) and a large band-gap (3.6 eV). The high electron mobility in SnO_2 promotes faster transportation of photo-injected electrons to the conducting current collector. Additionally, the large band-gap creates fewer oxidative holes in its valence band, thereby minimizing the dye-degradation rate and improving the long-term stability of DSSCs [7,8]. In addition,

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various physical and chemical synthesis methods allow for SnO_2 photoanode preparation in a variety of morphologies for the purpose of improving the performance of DSSCs with regard to excess dye loading, light harvesting, and direct transportation *etc.* Up until now, methods such as spray pyrolysis, sol–gel, thermal plasma, wet chemical, microwave-assisted synthesis, and electrodeposition etc., [9] have been applied to develop different morphologies such as nanofibers, nanowires, nanoflowers, nanoparticles, nanorods, and hollow microspheres etc., of the SnO_2 photoanodes [10]. Despite these advantages, SnO_2 photoanodes still suffer from low power conversion efficiency because of fast electron recombination kinetics and a positive shift in their conduction band edge with decreased photovoltage. Furthermore, the poor dye uptake capacity of the SnO_2 photoanode surface is associated with a low isoelectric point (isoelectric point ∼5.5 at low pH) which results in a reduced photocurrent [11].

The surface passivation layer on the photoanode can shift the conduction band edge position of the host photoanode, and it can block recombination pathways in DSSCs because it can; (i) reduce the density of surface traps through which recombination occurs, (ii) form an energy barrier layer that allows electron injection but hinders the back flow of electron transfer at the photoanode/dye/electrolyte interfaces, and (iii) generate an interface dipole that shifts the conduction band position of the photoanode material with respect to the redox potential [12,13]. Furthermore, in general, the surface layers are responsible for changing the surface pH, which can eventually increase the dye adsorption, or the dye surface concentration [14]. So far, various surface passivation materials including TiO_2, Al_2O_3, MgO, ZnO, ZrO_2 and SiO_2 etc., [15,16] have been demonstrated to enhance the overall performance of the above mentioned photoanodes.

In the present work, we synthesized SnO_2 nanoparticle-photoanodes using a hydrothermal route with an environmental friendly oxidizing agent (i.e. sugar) as an easily scalable and low-cost solution process. Next, we demonstrated use of new insulating layer (i.e. $CaCO_3$) enhanced the power conversion efficiency of the DSSCs, as a passivation layer on the SnO_2 photoanode surface (Scheme 1) could be achieved. A simple successive ionic layer adsorption and reaction (SILAR) method has been applied in order to coat various $CaCO_3$ layers on the SnO_2 photoanode. To the best of our knowledge, this is the first example of the fabrication of $CaCO_3$ thin layers on SnO_2 photoanode surfaces, which demonstrates an enhanced DSSCs performance. The $CaCO_3$ surface layer contributes to; (i) enhancement in dye adsorption, as confirmed by UV–vis and incident photon-to-current conversion efficiency (IPCE) measurements, (ii) decrease in surface defects and electron recombination rate, as revealed by

photoluminescence (PL), electrochemical impedance spectroscopy or Complex-plane plot (EIS), and open-circuit photovoltage decay (OCVD) spectra, and (iii) a negative shift of flat band potential, as confirmed through the Mott–Schottky analysis.

2. Experimental Details

### 2.1. Hydrothermal synthesis of SnO_2 nanoparticles-photoanode

All chemicals were of analytical grade and were used without any further purification. The pristine SnO_2 nanoparticles were prepared using a simple one-step hydrothermal method using sugar as an oxidizing medium and $SnCl_4$ as a Sn precursor. In the standard experimental procedure, 2.80 g of $SnCl_4 \cdot 5H_2O$ (Sigma Aldrich, 99.9%) and 5 g of sugar were mixed in 80 mL distilled (DI) water (Milli-Q water; 18.2 MΩ cm). The mixture was maintained under constant stirring for 30 min and then transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and maintained at 190 °C for 24 h, followed by cooling to room temperature. The resulting black ($Sn(OH)_2$) product was centrifuged at 8000 rpm for 10 min and washed several times with DI water and ethanol (1:1 volume ratio) to remove undesired impurities, if there is any. The product was heated in air at 600 °C for 2 h to form a white powder of SnO_2. 1.0 g of SnO_2 powder was mixed in 4.0 ml ethanol, 0.2 ml acetic acid, 3.5 g α-terpineol, and 0.5 g ethyl cellulose, and stirred for 12 h to form homogeneous slurry in order to obtain SnO_2 photoanodes. The SnO_2 photoanodes were fabricated using the doctor-blade technique on thick fluorine-tin-oxide (FTO) glass slices (15 Ω, TEC 8, Pilkington glass). The FTO glass was ultrasonically cleaned sequentially in DI water (20 min), acetone (20 min), and iso-propanol (20 min) prior to the application of the doctor-blading technique. Finally, the SnO_2 photoanodes were heat-treated at 450 °C for 1 h in order to evaporate solvents and to form compact SnO_2 photoanodes.

2.2. $CaCO_3$ layering

A $CaCO_3$ electronic-insulating layer was coated on the SnO_2 photoanodes using the SILAR method. A cycle (called a layer, L) was performed by initially immersing the SnO_2 photoanode in an ethanolic solution of 0.2 M calcium nitrate (1:1, ethanol: water) for 1 min, rinsing with water and subsequently immersing in 0.4 M sodium hydroxide (1:1, ethanol: water) for 1 min, and finally rinsing with water again. It is known that during the first immersion into the calcium nitrate solution, ions of calcium/nitrate are adsorbed onto the SnO_2 photoanode, whereas during the next half cycle, a layer of Ca $(OH)_2$ is obtained through NO_2 release. Different numbers of cycles (1, 6, and 12L) were applied to the SnO_2 photoanodes. During the SILAR cycle deposition, a $Ca(OH)_2$ layer was formed on the SnO_2 photoanode surface. The SnO_2 photoanodes were washed with deionized water to remove loosely bonded ionic species. Lee *at al.* reported the conversion of $Ca(OH)_2$ into CaO through a process of N_2 atmosphere decomposition. After additional annealing in air, the CaO layer transformed into a $Ca(OH)_2$ layer *via* a vigorous reaction between CaO and CO_2 [17]. Here, both pristine SnO_2 and the SnO_2–$CaCO_3$ photoanodes were annealed in an oxygen container at 450 °C for 30 min so as to have same annealing effect and also development of $CaCO_3$. In final stage, they were subsequently immersed into a 0.03 mM N719 dye solution (1:1 volume ratio, ethanol: acetonitrile) for 24 h.

2.3. Characterization techniques

The surface morphologies of the pristine SnO_2 and the SnO_2–$CaCO_3$ photoanodes were obtained from field-emission scanning electron microscopy (FE-SEM, Nova nano SEM200-
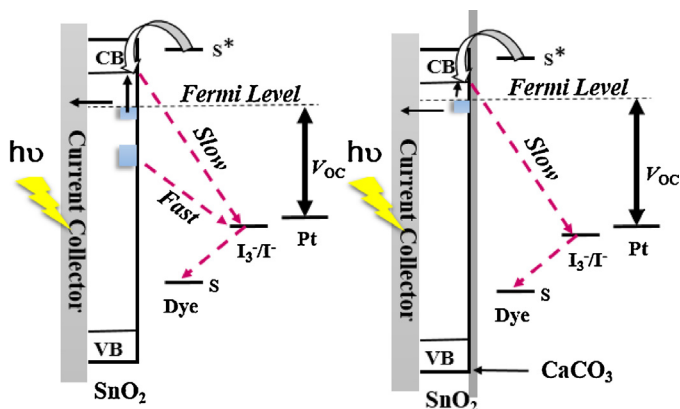
Scheme 1. Representative image of SnO_2 nanoparticles covered with a $CaCO_3$ surface passivation layer.