TiO₂ coated urchin-like SnO₂ microspheres for efficient dye-sensitized solar cells

Amit Thapa¹§, Jiantao Zai²§, Hytham Elbohy¹, Prashant Poudel¹, Nirmal Adhikari¹, Xuefeng Qian² (✉), and Qiquan Qiao¹ (✉)

¹ Center for Advanced Photovoltaics, Department of Electrical Engineering, South Dakota State University, Brookings, SD, 57007, USA
² School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China
§ These authors contributed equally to this work.

ABSTRACT

Urchin-like SnO₂ microspheres have been grown for use as photoanodes in dye-sensitized solar cells (DSSCs). We observed that a thin layer coating of TiO₂ on urchin-like SnO₂ microsphere photoanodes greatly enhanced dye loading capability and light scattering ability, and achieved comparable solar cell performance even at half the thickness of a typical nanocrystalline TiO₂ photoanode. In addition, this photoanode only required attaching ~55% of the amount of dye for efficient light harvesting compared to one based on nanocrystalline TiO₂. Longer decay of transient photovoltage and higher charge recombination resistance evidenced from electrochemical impedance spectroscopy of the devices based on TiO₂ coated urchin-like SnO₂ revealed slower recombination rates of electrons as a result of the thin blocking layer of TiO₂ coated on urchin-like SnO₂. TiO₂ coated urchin-like SnO₂ showed the highest value (76.1 ms) of electron lifetime (τ) compared to 2.4 ms for bare urchin-like SnO₂ and 14.9 ms for nanocrystalline TiO₂. TiO₂ coated SnO₂ showed greatly enhanced open circuit voltage (Vₜ₉₃), short-circuit current density (Jₛₛ₃) and fill factor (FF) leading to a four-fold increase in efficiency increase compared to bare SnO₂. Although TiO₂ coated urchin-like SnO₂ showed slightly lower cell efficiency than nanocrystalline TiO₂, it only used a half thickness of photoanode and saved ~45% of the amount of dye for efficient light harvesting compared to normal nanocrystalline TiO₂.

1 Introduction

Dye-sensitized solar cells (DSSCs) are of great interest as an alternative to the conventional silicon based solar cells because of their low-cost, simple fabrication process, and environmental advantages [1–6]. DSSCs
are generally composed of a photoanode and counter electrode (CE) separated by the redox pair (I−/I3−) based electrolyte [7–9]. The photoanode is usually a porous layer of TiO2 nanoparticles deposited on fluorine-doped tin dioxide (FTO) sensitized by dye molecules, while the CE is generally FTO glass substrate coated with platinum (Pt) [7–9] and carbon nanostructures [10]. Since the evolution of the first DSSCs, an extensive amount of work has been carried out in order to understand the behavior of TiO2 as a photoanode. Although mesoporous TiO2 shows good results when used as a photoanode in DSSCs, its lower electron mobility and poor long term stability is a concern.

Several studies on other alternative metal oxides such as ZnO, SnO2 and Nb2O5 have been conducted [11–22]. Among these, SnO2 has a higher electron mobility (100–200 cm²·V−1·s−1) than TiO2 (0.1–1 cm²·V−1·s−1) and a larger band gap (3.6 eV) than TiO2 (3.2 eV) [13, 22]. The higher electron mobility of SnO2 can result in good charge transport which will lower the total series resistance and improve device performance. Furthermore, the smaller band gap (3.2 eV) of TiO2 will result in a large number of oxidative holes in the valence band of TiO2 under UV illumination which has adverse effects on the performance of organic dyes and electrolytes [13, 22]. These oxidative holes can be suppressed if we use metal oxides with larger band gap such as SnO2. Thus, DSSCs containing SnO2 will be less sensitive to UV degradation, which should improve long-term stability [13, 22]. However, so far the reported performance of SnO2 based DSSCs has been lower in comparison to those based on nanocrystalline TiO2. To the best of our knowledge, the highest known efficiency for bare SnO2 based DSSCs is 3.2% [19]. Poor performance of SnO2 based DSSCs has been attributed to low open circuit voltage and fast interfacial electron recombination resulting from the 300 mV positive shift of the conduction-band edge of SnO2 with respect to nanocrystalline TiO2 [22, 23]. Moreover, the lower isoelectric point (iep, at pH = 4–5) than anatase TiO2 (iep, at pH = 6–7) leads to less adsorption of dye molecules such as N719 with acidic carboxylic groups [22, 24, 25]. To tackle this problem, there have been attempts to coat a thin layer of other metal oxides including TiO2, ZnO, Al2O3 or MgO to improve the performance of SnO2 based DSSCs by reducing the interfacial recombination rate and increasing dye attachment [17, 21, 22, 24–26]. As reported by others [22, 25], a thin layer of TiO2 coating will not create sufficient oxidative holes to cause UV degradation, because such a negligible amount of TiO2 will not absorb enough UV light. However, a pure nanocrystalline TiO2 photoanode with a typical thickness of 10–20 μm will be able to absorb sufficient UV light to cause degradation. Therefore, the larger band gap of SnO2 makes the DSSCs less sensitive to UV degradation if a thin layer of TiO2 is used as a coating.

In addition to coating an additional metal oxide layer onto the photoanode, control of material morphology is another important strategy to improve DSSC performance. Three-dimensional (3D) micro/nanostructures have been extensively studied in an attempt to enhance sunlight absorption in solar cells [27–30]. Compared to other 3D structures such as porous thin films, hollow structures, and nanorod arrays, the 3D urchin-like nanostructures show more promising performance in solar cells [31–36] and photocatalysis [37]. 3D urchin-like structures can lead to higher light absorption efficiency compared with planar thin film structures due to enhanced light trapping by scattering. The morphology of omnidirectionally grown nanorods in urchin-like structures provides random light incidence angles and scattering, leading to high light trapping and carrier generation efficiencies [31–36]. Furthermore, the tapered nanorods and domed-tip arrays enhance device efficiency by absorption through wider angles of light incidence [38]. These advantages have been demonstrated by urchin-like structures of TiO2 [31–33], ZnO [34–36] and Bi2S3 [37]. urchin-like SnO2 structures have been synthesized by solvothermal methods with mixed solvent [39–41] and oxidation-hydrothermal process [42, 43] and show enhanced lithium storage and gas sensitive properties. However, to best of our knowledge, there has been no report of the use of urchin-like SnO2 in DSSCs.

In this paper, we synthesized microsized urchin-like SnO2 for use in DSSCs by a novel organic acid/alkali pair (mercaptoacetic acid/urea) assisted hydrothermal process. Both bare and TiO2 coated urchin-like SnO2 microspheres are used as new photoanode materials.