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Balancing surface area with electron recombination in nanowire-based dye-sensitized solar cells

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Abstract

Dye-sensitized solar cells (DSSCs) represent a promising technology in the renewable energy portfolio. In this study, tin-doped-indium oxide (ITO) nanowires are used to prepare DSSC photoanodes that overcome charge transport limitations associated with conventional nanoparticle-based photoanodes. Vertically-aligned ITO nanowires are grown by a thermal evaporation method and a porous TiO_2 shell layer is uniformly coated on the nanowire surfaces to ensure high dye-loading. It is found that cell efficiency increased to 4.85% from 2.81% when a dense HfO_2 blocking layer is inserted between ITO nanowire surfaces and the porous TiO_2 shell. While more photoactive surface area associated with longer nanowires improves device performance, nanowires longer than 20 μm show reduced efficiency from an increase in electron recombination. Therefore, 20-μm-long nanowires show the best efficiency, which is attributed to the balance of surface area and electron recombination in the photoanode. Although decreasing TiO_2 annealing temperatures from 600 to 400 °C increases electron recombination, the smaller TiO_2 nanoparticles at 400 °C lead to much higher dye-loading and, ultimately, the highest device efficiency of 5.59%.

Keywords: Dye-sensitized solar cell; Nanowire; Tin doped indium oxide; Surface area; Electron recombination

1. Introduction

Dye-sensitized solar cells (DSSCs) represent a reliable and affordable renewable energy technology and they have garnered a lot of attention in the scientific community (Hardin et al., 2012; Ye et al., 2014; Hagfeldt et al., 2010; Li et al., 2014a, 2014b). The photoanode of a DSSC typically consists of a nanoparticle-based TiO_2 thin film (~10 μm in thickness) deposited on a transparent conductive oxide (TCO). In the TiO_2 nanoparticles, charge transport is generally dictated by a multiple trapping/detrapping process, where electrons in the conduction band fall into the shallow traps (sub-bandgap states) and are then detrapped through thermal vibration (Wang et al., 2011). The rate of charge transport in TiO_2 nanoparticles is 2–3 orders of magnitude slower than in bulk TiO_2 due to the many defects and grain boundaries in TiO_2 nanoparticles (Fisher et al., 2000; Law et al., 2005). The slow charge transport in TiO_2 nanoparticles makes electrons susceptible to recombination, which results in major electron loss and is one of the limiting factors on DSSC performance (Chandiran et al., 2014).

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One strategy to reducing electron recombination is to insert blocking layers at the interfaces of the photoanode. For instance, HfO_2 blocking layers were coated onto TiO_2 nanoparticle surfaces by a sol–gel method and DSSC efficiency was improved by 69% (Ramasamy et al., 2013). Palomares et al. (2002) investigated the effectiveness of SiO_2, Al_2O_3, and ZrO_2 blocking layers, where Al_2O_3 showed the greatest efficiency enhancement (35%) due to its high point-of-zero-charge. The improvements in efficiency have been attributed to the blocking layers passivating the surface states in the photoanode (Li et al., 2009; Prasittichai and Hupp, 2010). To achieve the best results, the blocking layer should be thin and compact. Compact blocking layers establish a physical separation between the photoanode and the electrolyte, which reduces the probability of electrons travelling back to the electrolyte. Thinner blocking layers (less than a few nanometers) allow most of the passing electrons to tunnel through, thus maximizing the current flow.

Alternatively, increasing the rate of charge transport in the photoanode reduces the probability of electron recombination and consequently enhances DSSC efficiency. Using nanowires as the photoanode is an effective approach to increase the rate of charge transport due to the presence of an interfacial electric field within the nanowires that is not present in nanoparticles (Hill et al., 2011; Du Pasquier et al., 2006; Martinson et al., 2006). Hill et al. (2011) showed that photoanodes fabricated from core-shell nanowires resulted in the injected electrons within the semiconductor shell layer being quickly swept into the core by the radial electrical field in the shell. The benefits of reducing trap-limited electron transport may be especially beneficial at high illumination conditions (Du Pasquier et al., 2006). Using photomodulation techniques, Martinson et al. (2006) revealed that electron transport is tens to thousands of times faster in ZnO nanowire-based DSSCs than in nanoparticles. Noh et al. (2011) obtained similar results in ITO nanowire-based DSSCs.

Annealing the TiO_2 layer is usually required to achieve high device efficiency. Mohammadpour et al. (2016) fabricated TiO_2 nanotubes by anodization and annealed the structures at temperatures between 400 and 800 °C. The highest efficiency was reached at 600 °C due to remarkably fast charge transport at 600 °C. Higher annealing temperatures resulted in lower dye loading. On the other hand, Atta et al. (2011) reported lower efficiency at similar TiO_2 annealing temperatures between 450 and 650 °C, which was attributed to the larger pore size and higher surface area for TiO_2 structures annealed at 450 °C.

Depending on the photoanode structure, the primary electron recombination pathways may be from TiO_2 to the electrolyte (I/I_3^-) or from TCO to the electrolyte. In TiO_2-nanoparticle-based DSSCs, electron recombination from TiO_2 to the electrolyte may dominate due to the slow electron transport in TiO_2 nanoparticles. Consequently, most existing studies focused on inserting various blocking layers on TiO_2 in nanoparticle-based DSSCs (Ramasamy et al., 2013; Palomares et al., 2002; Li et al., 2009). In nanowire-based DSSCs, electron recombination from TiO_2 to the electrolyte is greatly alleviated due to the rapid charge transport from TiO_2 to the nanowires. On the other hand, electron recombination from TCO (nanowires) to the electrolyte is exacerbated because of the dramatically higher surface area of the nanowires that are exposed to the electrolyte.

In this study, HfO_2 blocking layers are inserted by atomic layer deposition (ALD) to reduce electron recombination in ITO nanowire-based DSSCs. The balance of higher surface area and lower electron recombination is investigated for different nanowire length and TiO_2 annealing temperatures, which lead to the highest device efficiency of 5.59%.

2. Fabrication and characterization of DSSCs

2.1. ITO nanowire synthesis

ITO nanowires are synthesized following our previous work (Li et al., 2015). Briefly, transparent ITO/glass (Thin Film Devices, USA) substrates were consecutively cleaned in deionized water, acetone, and ethanol using ultrasonication. A 3-nm Au film was deposited on ITO as the catalyst for nanowire growth. High-purity metallic powders of indium (99.99%) and tin (99.995%) were mixed with a spatula in an atomic ratio of 10:4.5. The mixed powder was put in a quartz boat and loaded in the middle of a quartz tube furnace. The substrate was placed a few centimeters downstream from the powder. A stream of 0.5% O_2 (balance Ar) was fed through the tube at a flow rate of 40 sccm and the furnace was rapidly heated to 750 °C. A vacuum pump was used to maintain a vacuum level below 0.3 Torr.

2.2. Photoanode preparation

A thin layer of HfO_2 was deposited onto the ITO nanowire surfaces via ALD (Cambridge Nano Fiji 200). Water and tetrakis (dimethylamido) hafnium (IV) were used as the O and Hf source, respectively. A total of 16 ALD cycles were performed. Subsequently, a porous TiO_2 shell was coated on the nanowires by $TiCl_4$ treatment. To prepare the $TiCl_4$ coating solution, a 4.7 M $TiCl_4$ stock solution was first prepared by placing ice cubes quickly into refrigerated $TiCl_4$ (caution: this reaction is vigorous and should be done in the fume hood while wearing adequate personal protective equipment). The thick, yellowish stock solution can be stored in a refrigerator indefinitely. The stock solution was diluted to 0.1 M and nanowires were immersed for 8 h at room temperature. This coating process was repeated 12 times for all nanowire samples. After coating, nanowires were annealed between 400 and 600 °C for 1 h in air.