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 TiO₂ 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 HfO₂ blocking layer is inserted between ITO nanowire surfaces and the porous TiO₂ 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 TiO₂ annealing temperatures from 600 to 400 °C increases electron recombination, the smaller TiO₂ 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.[1-5] The photoanode of a DSSC typically consists of a nanoparticle-based TiO_2 thin film ($\sim 10 \mu\text{m}$ 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.[6] 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.[7, 8] 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.[9]

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%.[10] Palomeres *et al.* [11] 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.[12,13] 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.[14-16] Hill *et al.*[14] 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.[15] Using photomodulation techniques, Martinson *et al.*[16] revealed that electron transport is tens to thousands of times faster in ZnO nanowire-based DSSCs than in nanoparticles. Noh *et al.*[17] obtained similar results in ITO nanowire-based DSSCs.

Annealing the TiO₂ layer is usually required to achieve high device efficiency. Mohammadpour *et al.*[18] fabricated TiO₂ 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.*[19] reported lower efficiency at similar TiO₂ annealing temperatures between 450 and 650 °C, which was attributed to the larger pore size and higher surface area for TiO₂ structures annealed at 450 °C.

Depending on the photoanode structure, the primary electron recombination pathways may be from TiO₂ to the electrolyte (I/I₃⁻) or from TCO to the electrolyte. In TiO₂-nanoparticle-based DSSCs, electron recombination from TiO₂ to the electrolyte may dominate due to the slow electron transport in TiO₂ nanoparticles. Consequently, most existing studies focused on inserting various blocking layers on TiO₂ in

nanoparticle-based DSSCs.[10-12] 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.[20] 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 hours 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.

2.3 DSSC cell fabrication

N719 dye (Dyesol, Australia) was dissolved in ethanol to give a concentration of 3 mM. TiO_2 -coated ITO nanowires were immersed in the dye solution for ~12 h and used as the photoanode. A counter-electrode solution (CELS, Dyesol) was spin-coated onto clean ITO/glass and annealed at 430 °C for 10 min. Scotch tape was used as the spacer and an iodine-based solution (EL-HPE, Dyesol) was used as the electrolyte. A schematic of the cell is shown in Scheme 1.

2.4 Characterization

An X'Pert Powder XRD (PANalytical, USA) was used to collect the XRD spectra of ITO nanowires. SEM images were obtained using a FEI Nova NanoSEM 430. TEM imaging was performed on a JEOL 2010F TEM. To measure cell efficiency, a light source (XPS 200 coupled with 16S, Solar Light Company, USA) was used to produce a

global AM 1.5 spectrum with a power density of $100 \text{ mW}\cdot\text{cm}^{-2}$. Before cell testing, the light intensity was calibrated by a Si reference cell (RCSi65, PV Measurements, USA). Current-voltage characteristics were recorded by a potentiostat (VersaSTAT 3, Princeton Applied Research, USA). A two-terminal setup was established by combining the working/sensing electrodes and the reference/counter electrodes. DSSC cells were illuminated through a black aperture with an area of 0.08 cm^2 . For each type of cell 3-4 devices were tested. The reported cell performance statistics was determined by Pierce's criterion. Open-circuit voltage decay (OCVD) curves were recorded with the same potentiostat. During OCVD measurement, cells were illuminated and the open-circuit voltage was monitored. Illumination was then interrupted and the transient voltage was recorded at dark. Dye loading of the photoanodes was determined by a UV-vis spectrometer (Perkin-Elmer Lambda 800). The photoanodes were submerged in a 0.1 M NaOH water/ethanol (1:1 v/v) solution for 2 h for the dye to desorb. Dye solutions of known concentrations were prepared in the same solvents. The UV-vis spectra are included in Supporting Information.

3. Results and discussion

3.1 ITO nanowires

Figure 1a shows a typical SEM image of the as-grown ITO nanowires on a ITO/glass substrate. The diameters of the nanowires were 100-200 nm and their lengths can be controlled by the growth time. Most of the nanowires were vertically aligned, which could provide direct pathways for charge collection during DSSC operation. Figure 1b is the XRD pattern for ITO nanowires. These nanowires can be indexed to an In_2O_3 cubic structure (bixbyite) with a JCPDS # 06-0416. The strongest (400) peak indicates that the growth direction of ITO nanowires is along [100].

3.2 Different nanowire lengths

ITO nanowires with lengths between 10 and 28 μm were coated with a thin HfO_2 blocking layer by ALD. During ALD, nanowires were alternately exposed to Hf and O precursors, which were separated by an Ar purging step. ALD boasts excellent coating uniformity on high aspect-ratio nanostructures. The same coating thickness and quality from nanowire top to bottom were observed. The nanowires were subsequently coated with a porous TiO_2 shell via TiCl_4 treatment. All TiO_2 shells were annealed at 500 $^\circ\text{C}$ in air. Figure 2a and b are TEM images of ITO nanowires before and after the deposition of HfO_2 blocking layer, respectively. The HfO_2 blocking layer has a thickness of ~ 1.3 nm after depositing 16 ALD cycles. Compact and thin blocking layers, such as the one shown in b, are advantageous in reducing electron recombination in DSSCs. Figure 2c shows a TEM image of a nanowire coated with a porous TiO_2 shell. The TiO_2 shell uniformly covered nanowire surfaces, which provides maximum surface area for dye attachment.

Figure 3 shows the current-voltage response of DSSCs fabricated using nanowires of different lengths. Their photovoltaic properties are summarized in Table 1. It is seen that, for 20- μm nanowires, both the short-circuit current (J_{sc}) and the open-circuit voltage (V_{oc}) increased dramatically upon deposition of 1.3 nm of HfO_2 . Consequently, cell efficiency increased from 2.81% to 4.85%. The increase in J_{sc} is attributed to the reduction of electron recombination by HfO_2 from ITO nanowire surfaces to the electrolyte. The reduced electron recombination is also evidenced by lower dark current upon HfO_2 deposition (Figure 3b). Electron transport from the TiO_2 shell to the ITO core is not expected to be impacted since most electrons can tunnel through the thin HfO_2 layer.[4, 5, 9] The V_{oc} of a DSSC is determined by the difference between the Fermi level of the TiO_2 and the Fermi level of the redox couple in the electrolyte. The increase in V_{oc}

seen in Figure 3a may result from the reduction of electron recombination, which could increase the Fermi level of the TiO_2 .

In Figure 3a, as nanowire length increased from 10 to 28 μm , the efficiency first increased to 4.85% for 20- μm nanowires and then decreased slightly. The initial increase is due to the the increase of active surface area in nanowires, which enabled higher dye loading and, in turn, higher current density (Table 1). When nanowire length is further increased to 28 μm , dye loading and current density continue to increase. However, an increase in electron recombination led to lower efficiency. This is witnessed by the higher dark current seen in Figure 3b. The higher dark current for longer nanowires is likely due to electrolyte transport issues. Due to the confinement of electrolyte between nanowires, the increased length of the photoanode causes dye regeneration problems that lead to electron loss (REF Hill Thesis).

Figure 4a shows the open-circuit voltage decay (OCVD) curves of DSSCs fabricated with nanowires of different length. The 20- μm nanowires showed the slowest decay, which indicates that these nanowires can retain the highest concentration of electrons. Electron lifetime (τ_n) can be determined from the OCVD curves using the expression $\tau_n = (-k_B T / e) (dV_{oc} / dt)^{-1}$, [21] where k_B is the Boltzmann constant, T is the absolute temperature, and e is the positive electron charge. The results are shown in Figure 4b. It is seen that the 20- μm nanowires have the longest electron lifetime. Because there is no current flux during OCVD measurements, the differences in electron lifetime may be associated with the different charge distribution within different components of the photoanode (TiO_2 , ITO nanowires, and the substrate). Different components have different charge recombination rates, [20] which results in differences in the observed voltage decay and hence the electron lifetime. The long electron lifetime for 20- μm nanowires contributed to their best efficiency, as seen in Table 1.

Although electron lifetime was calculated using the expression $\tau_n = (-k_B T/e)(dV_{oc}/dt)^{-1}$, [19] a long electron lifetime may not necessarily correspond to a high V_{oc} during J-V measurement. This is because the V_{oc} in the above expression is a transient voltage that is monitored after illumination has been interrupted. Therefore, it is a “dark” voltage. On the other hand, the V_{oc} during J-V measurement (Figure 3a) is the open-circuit voltage under continuous illumination. Therefore, both electron lifetime and open-circuit voltage are important characteristics of a DSSC.

3.3 Different TiO_2 annealing temperatures

Cell efficiency is optimized using different TiO_2 annealing temperatures. A 1.3 nm HfO_2 blocking layer was first deposited on 20- μm ITO nanowires. Subsequently, these nanowires were identically coated with a porous TiO_2 shell by $TiCl_4$ treatment. The TiO_2 shell was annealed at temperatures between 400 and 600 °C in air. Figure 5 shows TEM images of the porous TiO_2 shell annealed at different temperatures. It is seen that the thickness of the TiO_2 shell is ~70 nm and the size of TiO_2 nanoparticles increased with increasing annealing temperatures.

Figure 6 shows the current-voltage response of cells when TiO_2 was annealed between 400 and 600 °C. Their photovoltaic properties are listed in Table 2. It is seen that the J_{sc} increased with decreased annealing temperatures. This response is partly attributed to higher dye-loading at lower TiO_2 annealing temperatures, as seen in Table 2. Lower annealing temperatures led to smaller TiO_2 nanoparticles (Figure 5), which provides larger surface area for dye attachment. Similarly, Han *et al.*[21] investigated ITO nanowire-based DSSCs and reported increased efficiency despite higher dark current when TiO_2 annealing temperatures decreased from 600 to 500 °C. Their efficiency increase was also attributed to higher dye loading at 500 °C.

Each of the devices exhibited similar V_{oc} even though the TiO_2 was annealed at different temperatures. The similarity in V_{oc} is attributed to the identical HfO_2 blocking layers deposited on the nanowire surfaces of each photoanode. The identical blocking layers would be expected to induce similar Fermi levels in the TiO_2 layer of each photoanode, even when annealed at different temperatures. The similarity in the blocking layers across different photoanodes result in the same shunt resistance for each device. When similar V_{oc} is observed between DSSCs, the dark current would typically be expected to have similar magnitude. This relationship is because the Fermi level of the TiO_2 , which determines V_{oc} , also dictates the energy barrier during dark current flow. However, different dark current is observed in Fig. 6b, with lower annealing temperatures resulting in a higher magnitude of dark current. This relationship between V_{oc} and dark current assumes that there are no changes to contact area. The higher porosity within the TiO_2 shell when annealed at lower temperatures is expected to cause more intimate contact between the nanowire and the electrolyte. The higher contact area increases the probability of electron recombination, resulting in the higher dark current. However, the higher dye-loading led to higher current density, counteracting the negative effects from increased electron recombination, ultimately leading to higher device efficiency at lower annealing temperatures.

4. Conclusions

ITO nanowire-based DSSCs were fabricated to overcome the electron-transport limitations of conventional nanoparticle-based DSSCs. Although the core-shell nanowires have a radial electric field, the high surface area of ITO exposed to the electrolyte still caused significant electron recombination. Therefore, nanowire surfaces were deposited with a thin HfO_2 blocking layer by ALD to reduce electron recombination. A porous TiO_2 shell was subsequently coated onto the nanowire surface to ensure high

dye-loading. It was found that the HfO_2 blocking layer increased cell efficiency from 2.81 to 4.85%. Cell efficiency was further optimized by using nanowires of different lengths and annealing the TiO_2 shell at different temperatures. The 20- μm nanowires showed the highest efficiency because they have the longest electron lifetime, as shown by OCVD measurement. When TiO_2 annealing temperatures are decreased from 600 to 400 °C, the short-circuit current increased while the open-circuit voltage remained the same, leading to the highest device efficiency of 5.59%.

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Supporting Information

The UV-vis spectra of the photoanodes are included in Supporting Information.

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Table 1: Photovoltaic properties of DSSCs with different nanowire lengths.^{a)} All TiO₂ shells were annealed at 500 °C in air.

	V _{oc} (V)	J _{sc} (mA·cm ⁻²)	FF (%)	η (%)	Dye loading (10 ⁻⁸ mol·cm ⁻²)
20 μm without HfO ₂	0.53±0.05	9.94±0.08	53.5±0.6	2.81±0.05	1.52±0.16
10 μm + HfO ₂	0.72±0.04	10.84±0.07	55.2±0.8	4.30±0.06	0.94±0.11
20 μm + HfO ₂	0.70±0.04	12.14±0.04	57.0±0.5	4.85±0.07	1.60±0.20
28 μm + HfO ₂	0.70±0.06	12.37±0.05	53.2±0.7	4.59±0.11	2.21±0.17

a) Average values and standard deviations are based on 3-4 cells.

Table 2: Photovoltaic properties of DSSCs when the porous TiO₂ shell was annealed between 400 and 600 °C.^{a)}

	V _{oc} (V)	J _{sc} (mA·cm ⁻²)	FF (%)	η (%)	Dye loading (10 ⁻⁸ mol·cm ⁻²)
400 °C	0.69±0.04	15.96±0.06	50.6±0.8	5.59±0.06	2.28±0.18
500 °C	0.70±0.04	12.14±0.05	57.0±0.5	4.85±0.07	1.60±0.20
600 °C	0.70±0.03	11.80±0.11	50.3±0.5	4.13±0.05	1.24±0.15

a) Average values and standard deviations are based on 3-4 cells.

Figure captions

Figure 1: (a) A typical SEM image and (b) XRD pattern of as-grown ITO nanowires on the ITO/glass substrate.

Figure 2: TEM images of (a) as-grown ITO nanowires, (b) ITO nanowires coated with a 1.3 nm HfO_2 blocking layer by ALD, and (c) ITO nanowires coated with a porous TiO_2 shell by TiCl_4 treatment.

Figure 3: Current-voltage response of DSSCs fabricated with nanowires of different length (a) under AM 1.5 illumination and (b) dark conditions. All TiO_2 shells were annealed at 500 °C in air.

Figure 4: (a) Open-circuit voltage decay (OCVD) curves and (b) corresponding electron lifetime of DSSCs fabricated with nanowires of different length. All TiO_2 shells were annealed at 500 °C in air.

Figure 5: TEM images of the porous TiO_2 shell surrounding ITO nanowires annealed at different temperatures: (a) 400, (b) 500, and (c) 600 °C. The red dotted lines indicate the boundaries of the TiO_2 shell.

Figure 6: Current-voltage response of DSSCs when TiO_2 was annealed between 400 and 600 °C under (a) AM 1.5 illumination and (b) dark conditions.

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Scheme 1. Diagram showing the structure of a nanowire-based DSSC.”

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