

Research Article

Tin-Doped Indium Oxide-Titania Core-Shell Nanostructures for Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) hold great promise in the pursuit of reliable and cheap renewable energy. In this work, tin-doped indium oxide (ITO)-TiO₂ core-shell nanostructures are used as the photoanode for DSSCs. High-density, vertically aligned ITO nanowires are grown via a thermal evaporation method and TiO₂ is coated on nanowire surfaces via TiCl₄ treatment. It is found that high TiO₂ annealing temperatures increase the crystallinity of TiO₂ shell and suppress electron recombination in the core-shell nanostructures. High annealing temperatures also decrease dye loading. The highest efficiency of 3.39% is achieved at a TiO₂ annealing temperature of 500°C. When HfO₂ blocking layers are inserted between the core and shell of the nanowire, device efficiency is further increased to 5.83%, which is attributed to further suppression of electron recombination from ITO to the electrolyte. Open-circuit voltage decay (OCVD) measurements show that the electron lifetime increases by more than an order of magnitude upon HfO₂ insertion. ITO-TiO₂ core-shell nanostructures with HfO₂ blocking layers are promising photoanodes for DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted a lot of attention in recent years due to their promising properties, including low cost, ease of fabrication, and flexibility in material selection [1, 2]. A DSSC typically consists of a dyed TiO₂-based photoanode, a platinized counter electrode, and a liquid electrolyte containing a redox couple (such as I⁻/I₃⁻). Under illumination, electrons in the dye are excited from the HOMO to the LUMO level. These electrons are then injected into the conduction band of TiO₂. A transparent conduction oxide (TCO) collects these electrons, which pass through the external circuit and generate power.

TiO₂ nanoparticle-based thin films are conventionally used as the photoanode of DSSCs. TiO₂ nanoparticles provide large surface area for maximum dye attachment, which enables high current densities and high efficiencies. However, electrons in TiO₂ nanoparticles are transported via random walk [3–5], which limits the effective thickness of the TiO₂ thin film to be ~10 μm [6]. The slow kinetics also leads to major electron losses via electron recombination from TiO₂

to the electrolyte, from TiO₂ to the dye, and from TCO to the electrolyte. Electron recombination is the limiting factor for increasing the efficiencies of DSSCs [7].

Core-shell nanostructures can be used to facilitate electron transport and suppress electron recombination. For instance, in ITO-TiO₂ core-shell nanostructures, the accumulation of positive and negative charges in the space-charge layers in the TiO₂ shell establishes an electric field [3, 6, 8–10], which could draw electrons in the TiO₂ layer towards the ITO core during DSSC operation. The rapid transport of electrons in TiO₂ could greatly suppress electron recombination from TiO₂ to the electrolyte. The direct contact between the single-crystalline ITO nanowires and the current collector ensures efficient electron collection as well.

Establishing compact blocking layers in the photoanode is also an effective approach to reducing electron recombination [11]. TiO₂ has a bandgap of 3.2 eV [12]; therefore, the high bandgap of HfO₂ [7, 13], Al₂O₃ [14–16], SiO₂ [14, 17], and ZrO₂ [18] (typically >5 eV) creates an energy barrier. This energy barrier acts as a blocking layer to electron transport that suppresses electron recombination with the electrolyte.

However, the blocking layers need to be extremely thin (<a few nm) so that forward electron transport is minimally impacted.

In this study, DSSCs based on ITO-TiO₂ core-shell nanostructures are investigated. Vertically aligned ITO nanowires are grown directly on ITO/glass substrates by a thermal evaporation method. Core-shell nanostructures are formed by coating the nanowires with TiO₂ through TiCl₄ treatment. HfO₂ blocking layers are deposited on ITO nanowire surfaces by atomic layer deposition (ALD). Photovoltaic properties of devices based on these core-shell nanostructures are evaluated.

2. Experimental Section

2.1. ITO Nanowire Growth. ITO nanowires were grown using a thermal evaporation method. Tin (99.995%) and indium (99.99%) powders were mixed in a 4.5:10 atomic ratio by a spatula. The mixed powder was loaded into the center of a quartz tube on a quartz boat. Glass slides with a predeposited 400-nm-thick ITO thin film (Thin Film Devices, Inc., USA) were coated with a 3 nm Au film by a sputter coater (Electron Microscopy Sciences, Inc., USA). The glass slides were placed a few centimeters from the metal source. A 0.5% oxygen gas stream (balance argon) was fed into the quartz tube at a flow rate of 50 standard cubic centimeters per minute (sccm). The vacuum level in the quartz tube was maintained below 170 mTorr for successful nanowire growth. The tube furnace was heated to 750°C for 30 min and cooled down. After each growth, scanning electron microscopy (SEM) was used to examine the nanowires. All nanowires used in this work have a length of $15 \pm 1 \mu\text{m}$.

2.2. ITO-TiO₂ Core-Shell Nanostructures. For maximum dye attachment, the nanowire surfaces were coated with a layer of TiO₂ by TiCl₄ treatment, resulting in ITO-TiO₂ core-shell nanostructures. Nanowires were immersed in a 0.1M TiCl₄ solution for 8 h and this process was repeated 12 times. After coating, TiO₂ was annealed at temperatures between 350 and 600°C for 1 h in air. To investigate the effect of blocking layers on device performance, a compact layer of HfO₂ was deposited on nanowire surfaces by atomic layer deposition (ALD) before TiCl₄ treatment. Tetrakis(dimethylamido)hafnium and H₂O were the Hf and O sources for ALD, respectively. The nominal thickness of HfO₂ for each ALD cycle is 0.11 nm and a total of 16 ALD cycles were performed on nanowire surfaces.

2.3. DSSC Device Fabrication. N719 dye (Dyesol) was dissolved in ethanol to make a 3 mM solution. The annealed core-shell structures were soaked in dye solution for ~14 h for dye attachment. Counter-electrode solution (CELS, Dyesol) was spin-coated on ITO/glass and annealed at 430°C for 10 min. The core-shell nanostructure photoanode and the counter electrode were held together by clips with Scotch tape as the spacer. An I⁻/I₃⁻ solution was used as the electrolyte (EL-HPE, Dyesol).

2.4. Characterization. The morphologies and length of nanowires were examined by a SEM (FEI Nova NanoSEM

430). ITO-TiO₂ core-shell structures were characterized by a JEOL 2010F transmission electron microscopy (TEM). The simulated global AM 1.5 spectrum ($100 \text{ mW}\cdot\text{cm}^{-2}$) for device testing was produced by a light source (XPS 200 and 16s, Solar Light Company, USA). Current-voltage (*J-V*) response and open-circuit voltage decay (OCVD) were recorded by a potentiostat (VersaSTAT 3, Princeton Applied Research, USA). For each type of cell, 3-4 devices were tested. OCVD measures the change of open-circuit voltage (V_{oc}) with time after illumination was interrupted. Electron lifetime (τ_n) was calculated from the slope of the decay curve [19], $\tau_n = (-k_B T/e)(dV_{oc}/dt)^{-1}$, where k_B is the Boltzmann constant, T is the absolute temperature, and e is the positive electron charge. Dye loading was determined by desorbing the dye in 0.1M NaOH water/ethanol (1:1 v/v) solution and measuring its absorption spectrum using a Perkin-Elmer Lambda 800 UV-Vis spectrometer. The crystallinity of the TiO₂ shell after annealing at different temperatures was investigated by a Renishaw inVia micro-Raman spectrometer equipped with a 785 nm laser.

3. Results and Discussion

Figure 1(a) shows the SEM image of ITO nanowires grown on ITO/glass substrate. When used as the photoanode, the vertically aligned nanowires are expected to efficiently transport electrons to the substrate where the current is collected. These nanowires have high density, which enables high dye loading and high current density during device operation. Figure 1(b) shows a TEM image of a nanowire coated with TiO₂ by TiCl₄ treatment. The radial electrical field in the ITO-TiO₂ core-shell structures could facilitate electron transport during DSSC operation by drawing electrons to the ITO core [3, 6].

Figure 2(a) shows the *J-V* characteristics of devices without HfO₂ blocking layers under illumination and Figure 2(b) at dark conditions when TiO₂ was annealed between 350 and 600°C. The corresponding photovoltaic properties are listed in Table 1. It is seen that both open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) increase with the increase of annealing temperatures, which resulted in the highest efficiency of 3.39% when the annealing temperature for TiO₂ shell was 500°C. The increase in efficiency is attributed to two reasons. (a) Higher annealing temperatures resulted in better crystallinity of the anatase TiO₂ shell, as evidenced by the Raman spectra of samples annealed at different temperatures shown in Figure 3. The better crystallinity led to better conductivity and charge transport. (b) Higher annealing temperatures suppressed electron recombination from ITO to the electrolyte, as evidenced by the smaller dark current in Figure 2(b). It should be noted that when compared to conventional TiO₂ nanoparticle-based DSSCs, electron recombination from TiO₂ to the electrolyte in ITO-TiO₂ core-shell nanostructures is minimized due to the rapid transport of electrons from TiO₂ to ITO by the electric field in the TiO₂ shell [3, 6].

At 600°C, although the V_{oc} continues to increase, the J_{sc} decreased dramatically, leading to a decreased device efficiency of 2.76%. The decrease of efficiency is due to the

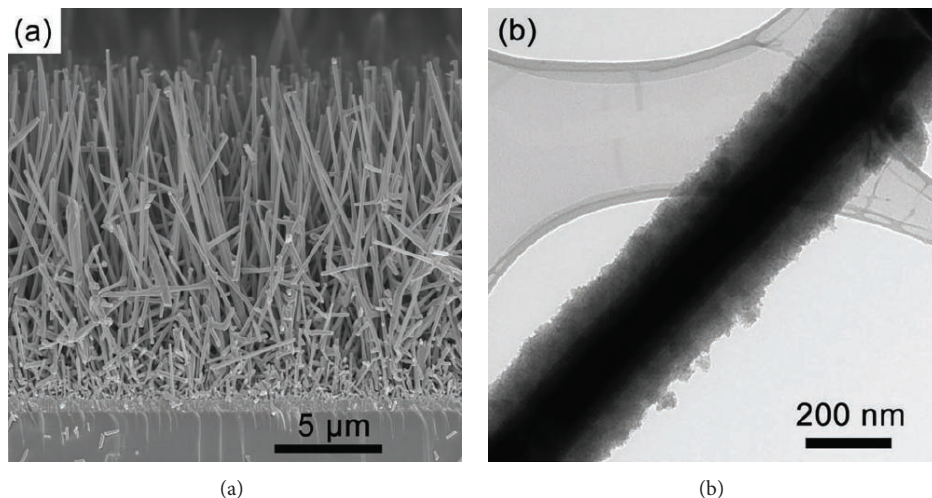


FIGURE 1: (a) SEM image of ITO nanowires grown by a thermal evaporation method and (b) TEM image of an ITO nanowire coated with TiO_2 by TiCl_4 treatment, forming an ITO- TiO_2 core-shell nanostructure.

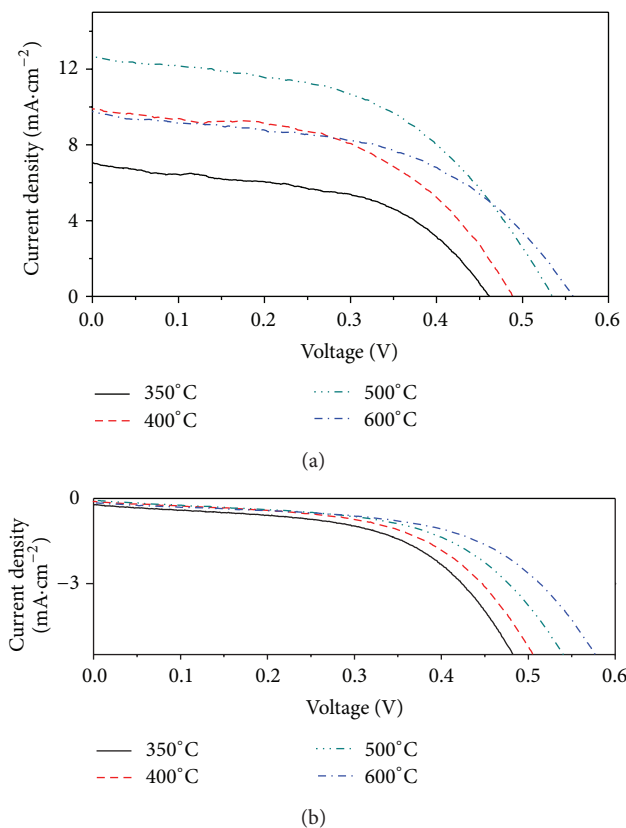


FIGURE 2: J - V characteristics of devices when TiO_2 shell was annealed between 350 and 600°C (a) under AM 1.5 illumination and (b) at dark condition.

decreased dye loading (see Table 1). The amount of dye loading directly dictates the current density in DSSCs. The decreased dye loading eventually resulted in lower efficiency despite the fact that the dark current continued to decrease at 600°C, as shown in Figure 2(b).

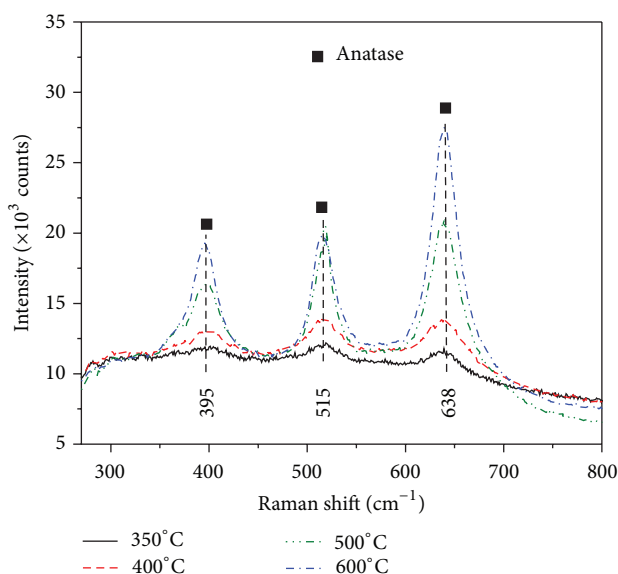


FIGURE 3: Raman spectra of ITO- TiO_2 core-shell nanostructures annealed between 350 and 600°C.

To further improve DSSC efficiencies, compact HfO_2 blocking layers were first deposited on nanowire surfaces. TiCl_4 treatment was subsequently performed to form core-shell nanostructures, which were then annealed at 500°C for 1 h. J - V curves of the devices based on these structures are shown in Figure 4. Upon HfO_2 insertion, the V_{oc} increased dramatically from 0.53 to 0.67 V. The V_{oc} of DSSCs is determined by the difference in Fermi level of TiO_2 and that of the redox couple in the electrolyte [20]. Since the conduction band edge position for HfO_2 is much higher than that for TiO_2 , the insertion of HfO_2 between ITO and TiO_2 could greatly raise the Fermi level of TiO_2 . Consequently, higher V_{oc} is seen in Figure 4(a).

The HfO_2 blocking layer also greatly increased the J_{sc} , as shown in Figure 4(a). From Table 2, HfO_2 barely affected

TABLE 1: Photovoltaic properties of devices when the TiO₂ shell was annealed between 350 and 600 °C^a.

	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF (%)	η (%)	Dye loading ($\times 10^{-8}$ mol·cm ⁻²)
350 °C	0.46 ± 0.03	7.05 ± 0.07	50.7 ± 1.0	1.65 ± 0.07	2.16
400 °C	0.49 ± 0.06	9.90 ± 0.08	50.6 ± 0.9	2.45 ± 0.08	1.80
500 °C	0.53 ± 0.03	12.61 ± 0.05	50.7 ± 0.6	3.39 ± 0.05	1.32
600 °C	0.56 ± 0.04	9.75 ± 0.05	50.5 ± 0.9	2.76 ± 0.07	1.01

^aAverage values and standard deviations are based on 3-4 devices.

TABLE 2: Photovoltaic properties of devices before and after the insertion of a compact HfO₂ blocking layer by ALD^a.

	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF (%)	η (%)	Dye loading ($\times 10^{-8}$ mol·cm ⁻²)
Without HfO ₂	0.53 ± 0.03	12.61 ± 0.05	50.7 ± 0.6	3.39 ± 0.05	1.32
With HfO ₂	0.67 ± 0.05	16.50 ± 0.06	52.7 ± 0.9	5.83 ± 0.07	1.36

^aAverage values and standard deviations are based on 3-4 devices.

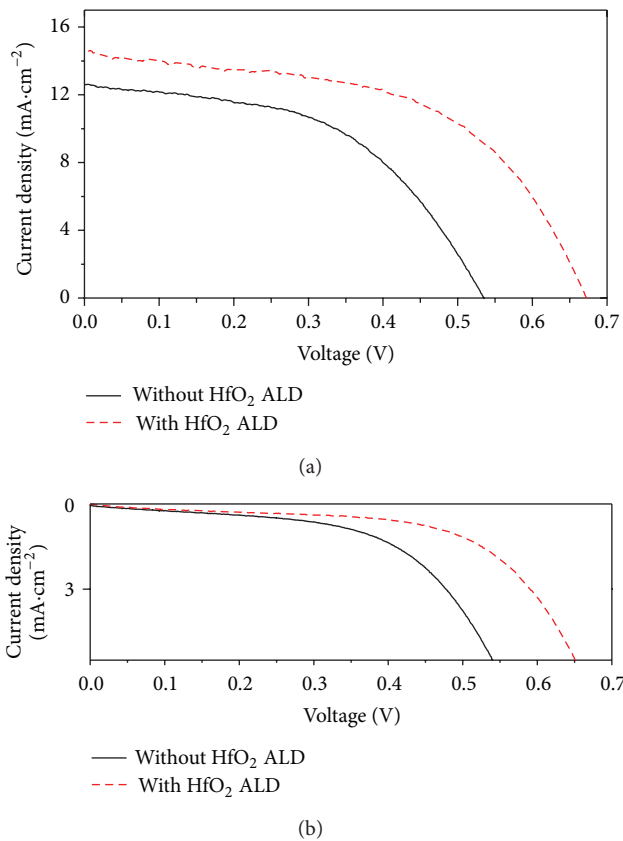


FIGURE 4: J - V characteristics of devices before and after the insertion of a compact HfO₂ blocking layer by ALD (a) under AM 1.5 illumination and (b) at dark condition.

dye loading. Therefore, the increase in J_{sc} is mainly attributed to the suppression of electron recombination by HfO₂, as indicated by the smaller dark current in Figure 4(b). The high bandgap of HfO₂ (5.9 eV versus 3.6 eV for ITO [7]) created an energy barrier that suppressed the back transfer of electrons from ITO to the electrolyte, while electrons in TiO₂ could tunnel through the thin layer of HfO₂ to reach ITO [1]. The axial electrical field in the TiO₂ shell expected for core-shell nanowires [6] should also assist in drawing electrons to the ITO core. The higher V_{oc} and J_{sc} eventually led to an efficiency

of 5.83% with HfO₂ insertion, corresponding to an increase of 72% from devices without HfO₂.

In order to investigate the electron transfer kinetics in DSSCs, OCVD measurements were performed and the results are shown in Figure 5. From Figure 5(a), higher TiO₂ annealing temperatures resulted in slower V_{oc} decay, which is indicated by a higher voltage at any given time in Figure 5(a). From Figure 5(b), longer electron lifetimes are observed at higher TiO₂ annealing temperatures. The slower V_{oc} decay and longer electron lifetimes are due to suppressed electron recombination at higher TiO₂ annealing temperatures, as discussed above.

From Figure 5(b), the electron lifetime increased dramatically upon HfO₂ deposition. For instance, when TiO₂ was annealed at 500 °C, HfO₂ deposition increased the electron lifetime by more than an order of magnitude from 0.031 to 0.38 s at 0.4 V. The increased electron lifetime ultimately led to the increased efficiency as seen in Table 2.

4. Conclusions

In summary, ITO-TiO₂ core-shell nanostructures are used as the photoanode of DSSCs. High-density, vertically aligned ITO nanowires are grown via a thermal evaporation method. Core-shell nanostructures are formed by coating the nanowires with TiO₂ through TiCl₄ treatment. TiO₂ are annealed between 350 and 600 °C and the photovoltaic properties of these devices are investigated. High annealing temperatures increase the crystallinity of the TiO₂ shell and suppress electron recombination. High annealing temperatures also result in lower dye loading. The highest efficiency of 3.39% is achieved when TiO₂ is annealed at 500 °C. Inserting HfO₂ blocking layers on nanowire surfaces further suppresses electron recombination from ITO to the electrolyte and a maximum efficiency of 5.83% is achieved. OCVD measurements indicate that HfO₂ blocking layers increase the electron lifetime by more than an order of magnitude.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

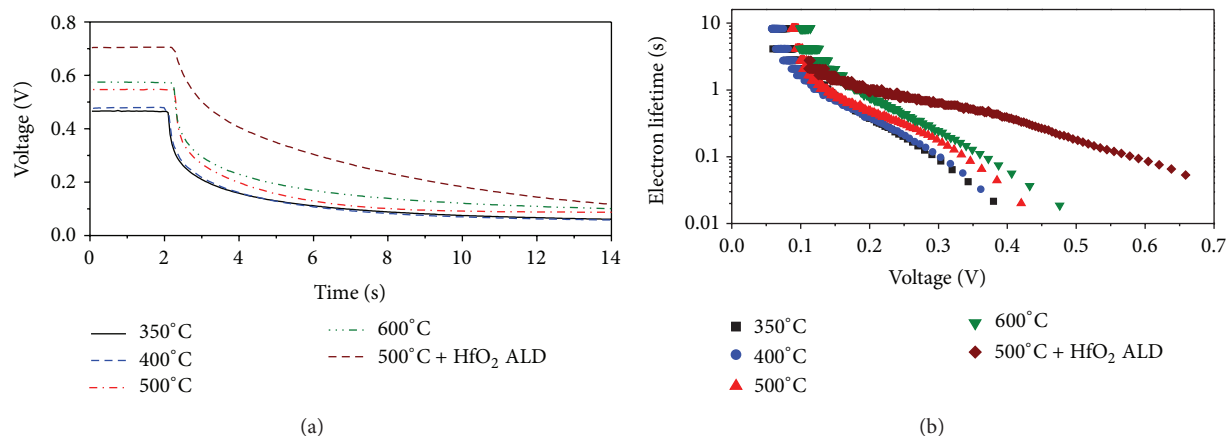


FIGURE 5: (a) Open-circuit voltage decay (OCVD) curves and (b) electron lifetimes of photoanodes annealed at temperatures between 350 and 600°C.

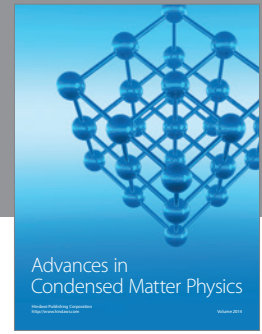
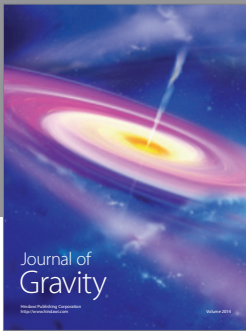
Acknowledgments

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