Planar Waveguide—Nanowire Integrated Three-Dimensional Dye-Sensitized Solar Cells

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ABSTRACT We present a new approach to fabricate three-dimensional (3D) dye-sensitized solar cells (DSSCs) by integrating planar optical waveguide and nanowires (NWs). The ZnO NWs are grown normally to the quartz slide. The 3D cell is constructed by alternatively stacking a slide and a planar electrode. The slide serves as a planar waveguide for light propagation. The 3D structure effectively increases the light absorbing surface area due to internal multiple reflections without increasing electron path length to the collecting electrode, resulting in a significant improvement in energy conversion efficiency by a factor of 5.8 on average compared to the planar illumination case. Our approach demonstrates a new methodology for building large scale and high-efficient 3D solar cells that can be expanded to organic- and inorganic-based solar cells.

KEYWORDS Dye-sensitized solar cell, ZnO, nanowire, optical slides, optical fiber

Solar energy is one of the most promising sustainable energy resources for the future.1–2 Excitonic solar cells (SCs),3–6 including organic and dye-sensitized solar cells (DSSCs), appear to have significant potential as a low-cost alternative to conventional inorganic photovoltaic (PV) devices. A typical high-efficiency DSSC7,8 consists of a TiO2 nanocrystal thin film that has a large surface area covered by a monolayer of dye molecules to harvest sunlight. However, the advantage offered by the increased surface area of the nanoparticle film is compromised by the effectiveness of charge collection by the electrode. For DSSCs, the traditional nanoparticle film was replaced by a dense array of oriented, crystalline nanostructures to obtain faster electron transport for improving solar cell efficiency.9–11 Despite the expected faster electron transport, the traditional nanowire (NW) solar cells are still of low efficiency, limited primarily by a smaller surface area compared to that of a nanoparticle structured film. To effectively take the advantages offered by the enhanced electron transport property and the surface area, we have introduced an optical fiber—NW hybrid based three-dimensional (3D) DSSC by introducing the solar light internally along the fiber.12 Such a structure is advantageous because it allows light to have multiple interactions with the dye molecules adsorbed on the NW surface without increasing the electron transport distance. Compared to the case of light illumination normal to the fiber axis from the outside of the device, the internal axial illumination enhances the energy conversion efficiency by a factor of up to six for the same device. Analogous approaches have been demonstrated by other groups by integrating planar waveguide and thin film DSSC.13 Fiber-based organic SCs have also been fabricated by constructing concentric thin films onto the fiber.14 An energy conversion efficiency of 0.6% has been measured under parallel to axial illumination.

The optical fiber—NW hybrid 3D structure shows an approach and methodology to make high-efficiency SCs that can be concealed and conformable, but its performance is limited by the geometry of the planar electrode located at one side of the fiber, which may impose difficulty in developing multifiber-based SC for large-scale applications. In this study, by replacing the optical fiber with a quartz slide, we introduce a new 3D DSSC by alternatively sandwiching the quartz slides covered with aligned NW arrays with planar electrodes. The ZnO NWs were grown normally to both surfaces of the quartz slide, which serves as a planar waveguide for light propagation. Each time when light reaches waveguide—NW interface, photons are coupled into the ZnO NWs and then are absorbed by the dye molecules to generate electricity. On average, the enhancement of energy conversion efficiency by a factor of 5.8 has been achieved when light propagating inside the slide is compared to the case of light illumination normal to the surface of the slide from outside; and the full sun efficiencies have been achieved up to 2.4% for ZnO NWs. This work demonstrates an effective approach for developing large scale 3D solar cells with high efficiency.

The waveguide—NW 3D DSSC is an alternative sandwiching of planar waveguides that are covered by aligned ZnO NW arrays and planar counter electrodes (Figure 1a). The detailed structure is shown in Figure 1b. The waveguide is first coated with indium tin oxide (ITO) film and followed by a ZnO seed layer. The ZnO NW arrays are grown from the seed layer and are uniformly covered by a monolayer of dye molecules. The waveguide—NW working unit is sandwiched between two platinum (Pt)-coated counter electrodes. The electrolyte is filled into the space between the working and counter electrodes. It is worth noting that...
waveguide is made by fused quartz, whose refractive index (1.45) is smaller than that of coated ITO (∼2) and ZnO (∼2) films. So it is a waveguide with moderate leakage. For each internal reflection at the waveguide–ITO–ZnO NW interfaces, light will cross the interface to reach the dye molecules through the NWs as an evanescent wave. The flat symmetric structure of a unit cell allows closely packed stacking of multiple cells in a layer-by-layer fashion to build a large-scale 3D SC, which can be manufactured in a way as shown in Figure 1a. The counter electrodes can be molded in a comb configuration, and waveguide–NW units are plugged into the counter electrode housing, then the internal space of the device is filled with electrolyte, and the SC is sealed and fully packaged.

The SCs were first fabricated by growing vertically aligned ZnO NW arrays with optimized density and uniform length (Figure 2b) onto a quartz slide (1–2.4 cm wide and 3–4 cm long with a thickness of 200 μm, served as waveguide). Quartz slides were ultrasonically cleaned in acetone, ethanol, and deionized (DI) water consecutively. The slide was coated with a 300 nm thick ITO layer with a sheet resistance of 30–50 Ω/square on one (both) side (sides) by radio frequency (RF) magnetron sputtering. The 300 nm thick ZnO seed layer was then sputtered on top of the ITO (Figure 2c). The aligned ZnO arrays were synthesized via hydrothermal (HT) method on the surface of the slide with desired morphologies, as tuned by changing the growth conditions. In general, NWs are longer, thicker, and denser at higher solution concentration and temperature and at longer time. Optimized ZnO NW arrays (Figure 2b) were synthesized in a solution containing 16 mM zinc chloride (Alfa Aesar) and 16 mM hexamethylenetetramine (HMTA) (Fluka) at 95 °C for 16 h in a Yamato convection box oven. Aspect ratio of the NW was controlled by adding (0–5 mL in 100 mL solutions) ammonium hydroxide (Aldrich, 28% in volume). All chemicals were reagent grade. The ZnO NW arrays were grown on one side of the slide by floating the substrate on the nutrient solution surface. While the ZnO NW arrays were grown on the double-side of the slide (Figure 3b-3e) by immersing the substrate into the solution with the slide surface normal to the nutrient solution surface. The NW-coated slide was rinsed using ethanol and air-dried in a drybox (humidity less than 1%) at room temperature for 24 h.

The NW arrays were sensitized in a 0.5 mM N719 dye solution in dry ethanol for one hour. A Pt (80 nm) layer was evaporated on a precleaned glass substrate with a Ti (20 nm) adhesion layer to serve as the counter electrode. The waveguide–NW unit was sandwiched between two Pt coated counter electrodes. The spacing was controlled using Surly film (60 μm thick, Solaronix), which also sealed the device when heated to 100 °C. The internal space of the device was filled with a liquid electrolyte (0.5 M LiI, 50 mM I2, and 0.5 M 4-tertbutylpyridine in 3-methoxypropionitrile (Fluka)) via capillary effect.

The solar cell was characterized using a solar simulator (300 W Model 91160, Newport) with an AM 1.5 spectrum distribution calibrated against a NREL reference cell to accurately simulate a full sun intensity (100 mW cm⁻²).
The thickness (200 µm) and width (1.2 cm) of the quartz slab, which is a multiplication of the edge of the quartz slide, as shown in Figure 1b. The light was coupled into the waveguide from the PS case. (b) Low-magnification SEM image of a quartz slide with uniformly grown ZnO NWs on DS surfaces. (c, e) High-magnification SEM image showing the densely packed ZnO NWs on top and bottom surfaces of the slide, respectively. (d) Image of a slide coated with grown ZnO NW arrays. The J–V curve was measured under two configurations: light illumination normal to waveguide surface (NS) and parallel to waveguide surface (PS). IPCE measurements were carried out using a 300 W Xe lamp light source coupled to a monochromator (Oriel). A reference Si photodiode calibrated for spectral response was used for the monochromatic power density calibration.

![Image](image_url)

**Figure 3.** ZnO NWs are coated on single side (SS) and double-side (DS) of the waveguide. (a) Current density J and voltage V curves of DSSCs under one full sun illumination for PS configuration. Inset, typical incident photon-to-electron conversion efficiency (IPCE) measured for single-side (SS) and double-side (DS) coated DSSCs in the PS case. (b) Low-magnification SEM image of a quartz slide with uniformly grown ZnO NWs on DS surfaces. (c, e) High-magnification SEM image showing the densely packed ZnO NWs on top and bottom surfaces of the slide, respectively. (d) Image of a slide coated with grown ZnO NW arrays.

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<table>
<thead>
<tr>
<th>solar cell type</th>
<th>average η-NS (%)</th>
<th>average η-PS (%)</th>
<th>average EEF</th>
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<tbody>
<tr>
<td>single-side coated waveguide</td>
<td>0.31</td>
<td>1.8</td>
<td>5.8</td>
</tr>
<tr>
<td>single-side coated rectangular fiber¹²</td>
<td>0.56</td>
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<tr>
<td>double-side coated waveguide¹⁰</td>
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### Table 1. Average Energy Conversion Efficiencies and Efficiency Enhancement Factors (EEF) of Planar Waveguide–NW and Fiber–NW¹² 3D DSSCs

For the SC with NWs coated on one side of the slide, the light can partially leak out from the side without NWs
We compared the photovoltaic characteristic between planar waveguide and optical fiber based solar cells (SCs) (Figure 4 and Table 1). The area covered by aligned ZnO nanowire (NW) arrays for three-dimensional (3D) waveguide—NW SC is about 100 times as large as that of a 3D fiber SC. Despite the large difference in the area covered by ZnO NW arrays, an average energy conversion efficiency of ~2% was obtained for both the waveguide and the fiber SCs in the PS configuration. The waveguide—NW SC has smaller variation of energy conversion efficiency among devices because of an easier and a more consistent packaging process, as in comparison to the fiber case. The waveguide SC has an average efficiency enhancement factor (EEF) of 5.8, while fiber SC’s EEF is 3.8 on average. The difference in the EEF between the waveguide and fiber SCs could be due to several factors. One is that ZnO NWs are grown on three sides of the rectangular optical fiber. While ZnO NWs are only grown on one side of the waveguide, which gives complete contact between the working and counter electrodes for better charge collection. The other factors, such as geometry and internal scattering sites in the planar waveguide/optical fiber, could also make a difference.

The planar waveguide—NW 3D DSSCs has certain advantages over the optical fiber—NW hybrid cell. First, it is easy to fabricate using general methods of making traditional flat (2D) DSSCs. The flat working and counter electrodes can be stacked layer-by-layer to form a volume-based SC without limitation. On average, the enhancement of energy conversion efficiency by a factor of 5.8 was achieved with light propagating inside the waveguide compared to the case of light illumination normal to the surface of the slide; and the full sun efficiencies have been achieved up to 2.4% (Figure 4) for the 3D solar cells with ZnO NWs grown on double side of the waveguide. More importantly, the planar waveguide allows a large-scale fabrication of the 3D SC, while the integration of the fiber-based SC with counter-electrode electrode is a rather challenging task.

In summary, we have demonstrated a new approach to fabricate waveguide—NW integrated 3D DSSC, whose energy conversion efficiency was enhanced as light propagating inside the waveguide compared to the case of light illumination normal to the surface of the waveguide. The unique configuration of the 3D hybrid SC effectively increases the light absorbing surface area due to multiple internal reflections without increasing the electron path length to the collecting electrode as well as an improved charge collection with the introduction of stacked planar electrodes, resulting in a significant improvement in energy conversion efficiency. The full sun efficiencies have been achieved up to 2.4% for the 3D solar cells with ZnO NWs grown on double sides of the waveguide. The planar waveguide—NW 3D SCs have the following features for scaling up. First, ZnO NWs can be grown on substrates uniformly on a large scale via chemical synthesis at temperatures below 100 °C. The material and growth processes are low cost and environmentally green. Second, this design can adopt the fabrication and package techniques from traditional 2D SCs. Third, the active area for electricity generation of the cell is much larger than that of fiber 3D SC, while the energy conversion efficiency remains the same, clearly indicating its potential for scale up. Lastly, the flat symmetric structure of a unit cell is feasible for close-packed stacking of multiple cells in a layer-by-layer fashion to build large scale SCs. It is possible to replace the quartz slide with highly transparent polymer substrates. The waveguide—NW 3D architecture provides a general ap-
approach for fabricating high-efficiency, large-scale excitonic SCs, such as dye-sensitized and organic SCs.

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Supporting Information Available. The transmission spectrum of the Pt-coated counterelectrode used for the 3D solar cell. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES
(20) The η-NS (%) was not studied for the double-side coated waveguide. For the double-side coated waveguide, the most effective charge generation portion is the top surface of the waveguide that directly faces the sunlight, while the sunlight is largely attenuated once it penetrates through the ZnO NWs, the ITO layer, and the waveguide to reach the bottom surface of the waveguide. The electrons/holes generated at the top surface cannot be collected since the top Pt counterelectrode is removed to allow the light to reach the solar cell. The photon generated electrons/holes can only be collected for the bottom surface, at which the incident light is significantly attenuated with consideration of the scattering and adsorption of the top surface layer. This attenuation results the low-energy conversion efficiency for the NS configuration and the high EEF.