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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 (DSSC), appear to have significant potential as a low-cost alternative to conventional inorganic photovoltaic (PV) devices. A typical high-efficiency DSSC[7,8] consists of a TiO_2 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

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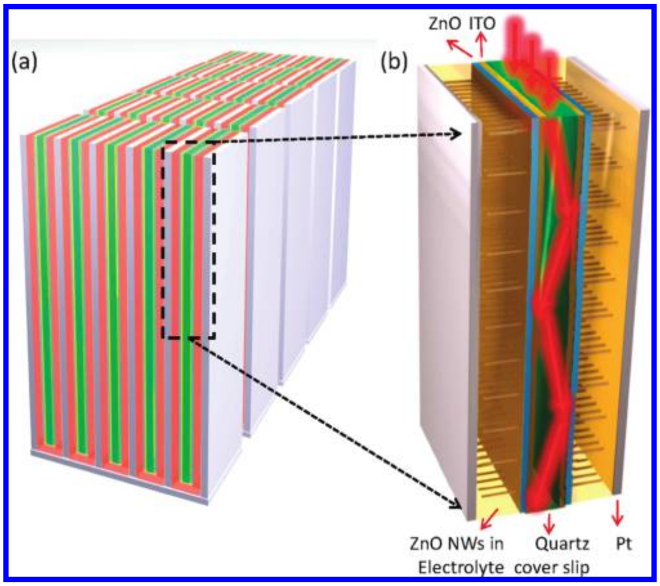

FIGURE 1. Design and principle of planar waveguide−NW integrated 3D DSSC. (a) Schematic architecture of large scale 3D DSSC. The waveguide−NW 3D unit SCs are plugged into the counter electrode housing and then sealed and fully packaged. (b) Detailed structure of a unit waveguide−NW 3D DSSC.

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[15] 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.[16] Optimized ZnO NW arrays (Figure 2b) were synthesized in a solution containing 16 mM zinc chloride (Alfa Aesar) and 16 mM hexamethylenetetramine (HMTA) (Fluka)

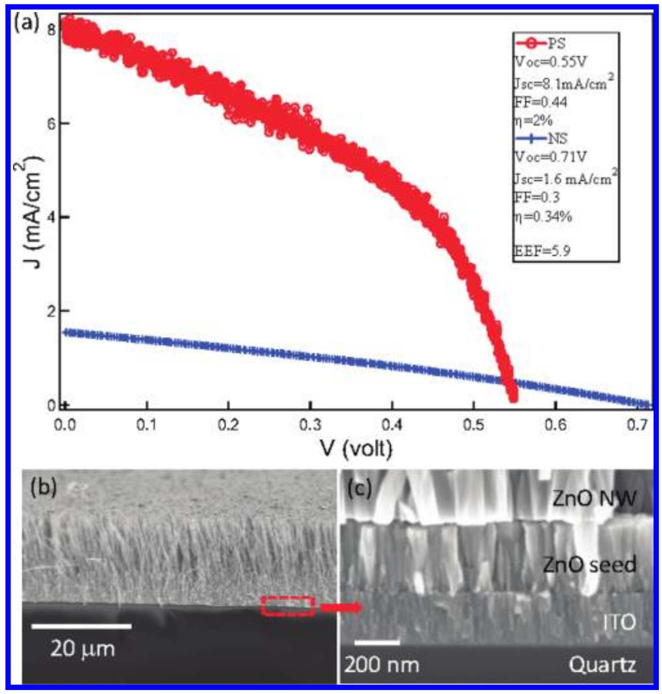

FIGURE 2. ZnO NWs are coated on single side (SS) of the waveguide. (a) Current density J and voltage V curves of the DSSC under one full sun illumination (AM1.5 illumination, 100 mW cm^{-2}). The characteristics of DSSC when illumination is normal to waveguide surface (NS) and is parallel to waveguide surface (PS). (b) Low-magnification SEM image of a quartz slide with uniformly grown ZnO NWs on one surface. (c) High-magnification SEM image showing the detailed quartz, ITO, ZnO film, and NWs interfaces.

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 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.[17] 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 I_2, 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

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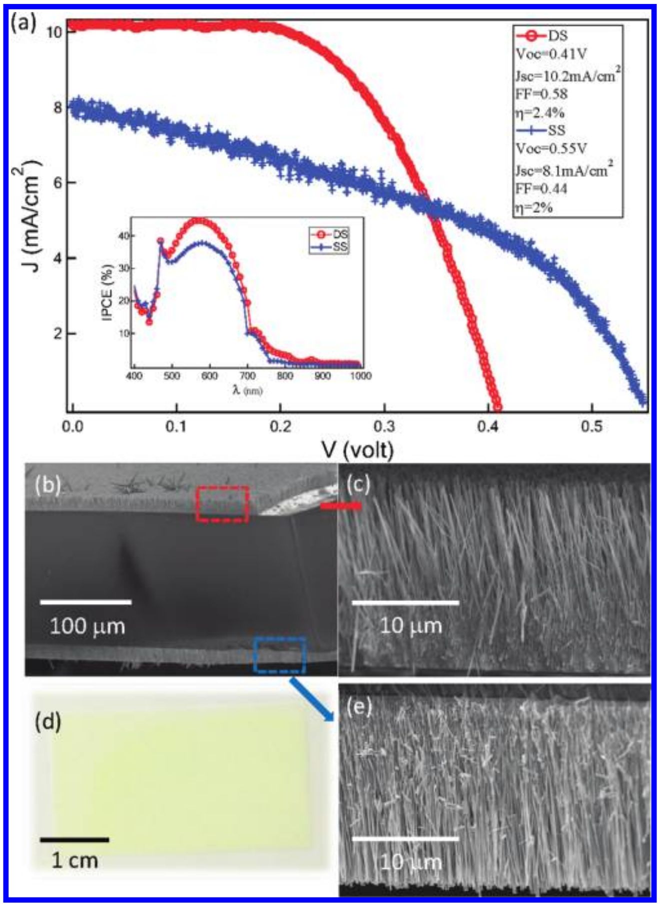

FIGURE 3. ZnO NWs are coated on single side (SS) and double-side (DS) of the waveguide. (a) Current density J and voltage V curves of DSSCs under one full sun illumination for PS configuration. Inset, typical incident photon-to-electron conversion efficiency (IPCE) measured for single-side (SS) and double-side (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.

$J-V$ 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.

We first studied the characteristics of SCs in NS and PS configurations with NWs coated on one side of the slide. For the PS case, the light was coupled into the waveguide from the edge of the quartz slide, as shown in Figure 1b. The light illumination area S_{PS} in the PS case was calculated using the cross-section of the quartz slab, which is a multiplication of the thickness (200 μm) and width (1−2.4 cm) of the waveguide. The waveguide surfaces coated with and without NWs were both covered by Pt-coated glass slides, which had a transmittance less than 2% with light illumination normal to the waveguide surface (see Supporting Information). The

TABLE 1. Average Energy Conversion Efficiencies and Efficiency Enhancement Factors (EEF) of Planar Waveguide−NW and Fiber−NW[12] 3D DSSCs

solar cell type	average η-NS (%)	average η-PS (%)	average EEF
single-side coated waveguide	0.31	1.8	5.8
single-side coated rectangular fiber[12]	0.56	1.9	3.8
double-side coated waveguide[20]		2.2	

low transmittance of the Pt counterelectrode prevents the light leakage from the waveguide−NW 3D SC. The power generated by the SC depends on the angle of incident light.[18,19] To obtain the highest output, the waveguide surface was initially placed in parallel to the incident light. Then the short circuit current was monitored to reach its maximum by rotating the SC. The $I-V$ characteristic was measured afterward. The current density $J = I/S_{PS}$ in the PS case was then calculated. An energy conversion efficiency of 2% was obtained (Figure 2a). The measurements of the solar cell in the NS configuration are straightforward as those of typical 2D flat solar cells. The $J-V$ curves for both PS and NS are shown in Figure 2a. The open circuit voltage V_{OC} of the PS case is significantly lower than that of the NS case, resulting from lower local incident light intensity at the ZnO−dye interface for the PS case due to multiple internal reflections in the waveguide.[12] The short circuit current density J_{SC} of the PS case is much higher than that of the NS casem as a result of better light absorption. Compared to the NS case, the PS configuration gives an average energy conversion efficiency enhancement factor (EEF) of η_{PS}/η_{NS} = 5.8 (Table 1).[20] The large J_{SC} for the PS case and the efficiency enhancement are based on a hybrid structure that integrates an optical waveguide and aligned ZnO NW arrays, which increases the light absorbing surface area due to multiple internal reflections and provides a fast electron transfer pathway along ZnO NWs. Light coupling between waveguide and NWs is effective due to the following processes. First, the light hits the waveguide−ITO interface upon the propagation down the waveguide. The refractive index of the waveguide (fused quartz) is ~1.45, which is smaller than that of the coating layers (ITO and ZnO) ~2. A high index of refraction material allows the light to escape into the dye from the waveguide. Second, the scatters (such as defects, air bubble, and impurities) in the waveguide can change the light traveling directions, which enhance the light coupling between the waveguide and the NWs. The SC's performance can be adjusted and optimized by engineering scatters inside the waveguide. Finally, evanescent wave coupling, by which electromagnetic waves are transmitted from one medium to another, should be considered.[21] The first two mechanisms dominate the light coupling between the waveguide and the NWs.

For the SC with NWs coated on one side of the slide, the light can partially leak out from the side without NWs

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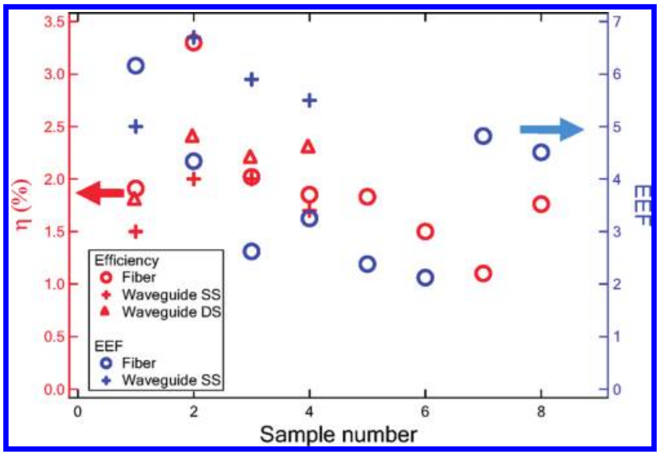

FIGURE 4. Comparison of energy conversion efficiencies and efficiency enhancement factors (EEF = η_{PS}/η_{NS}) of planar waveguide–NW and fiber–NW[12] 3D DSSCs.

coating, and efficiency is limited. By growing NWs on both sides of the slide, the active surface area is doubled from that of an one-side coated cell. This improved design takes advantage of larger and fully covered surface areas, which allows more efficient light collection with minimum light leakage, and higher energy conversion efficiency is expected. Compared to an one-side coated slide, double-side coated slide (Figure 3a) has a larger J_{sc} and fill factor (*FF*) because of more efficient photon collection; the smaller V_{oc} for the double-side coated slide is due to lower local incident light intensity. The highest efficiency received for a double-side coated slide was 2.4% (Figure 4), which was ∼20% higher than that for an one-side coated slide (note, the enhancement is not a factor of 2 because at the surface without NWs, there is a certain degree of total internal reflection at the quartz–air interface). The superior performance of the double-side coated waveguide was further evaluated by IPCE measurements (Figure 3a, inset). Single- and double-side coated SCs are both peaked at 570 nm, which suggests the more efficient collection of longer wavelength photons for waveguide–NW SC. The peak value of double-side coated waveguide is larger than that of the one-side coated waveguide, just as expected. From the architecture point of view, the double-side coated waveguide is a natural choice as the building block stacked layer-by-layer to form a volume based SC at a large scale.

We compared the photovoltaic characteristic between planar waveguide and optical fiber[12] 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 DSSC 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.[22] 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-

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proach 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.

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