# Fast Electron Transport in Metal Organic Vapor Deposition Grown Dye-sensitized ZnO Nanorod Solar Cells

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The electron transport in dye-sensitized solar cells with a MOCVD (metal organic vapor deposition)-grown ZnO nanorod array (ZnO-N) or a mesoporous film prepared from ZnO colloids (ZnO-C) as the working electrode was compared. The electrodes were of similar thickness (2 $\mu$m) and sensitized with zinc(II) *meso*-tetrakis(3-carboxyphenyl)porphyrin, while the electrolyte was $I^-/I_3^-$ in 3-methoxypropionitrile. Electron transport in the ZnO-C cells was comparable with that found for colloidal $TiO_2$ films (transport time $\sim$ 10 ms) and was light intensity dependent. Electron transport in solar cells with ZnO-N electrodes was about 2 orders of magnitude faster ($\sim$30 $\mu$s). Thus, the morphology of the working ZnO electrode plays a key role for the electron transport properties.

Highly ordered nanostructures of ZnO,[1] $TiO_2$,[2] and other wide band gap semiconductors are promising alternatives to the mesoporous nanoparticle thin films that are currently used for dye-sensitized solar cells (DSSCs) and other devices. DSSCs prepared from colloidal solutions are characterized by complex interfaces.[3] The possibility to employ a well-defined semiconductor layer morphology in DSSCs is attractive, as it could allow control of the surface functionalization and also improve the fundamental understanding of the interfacial electronic processes that are the basis for solar energy conversion. These are key premises for improving the performance of solar cells.

Over the past few years, ZnO has emerged as the material of choice for the preparation of nanostructured electrodes, especially those based on crystalline, columnar structures generally called nanorods or nanowires.[4] In particular, the directionality of transport of the injected electron through the vertical nanorods is expected to be high. ZnO nanorods have been prepared using various methods, including vapor−liquid−solid processes, chemical vapor deposition, and chemical synthesis through aqueous solutions.[1,5,6] Among them, metal organic vapor deposition (MOCVD) is an excellent growth technique as it leads to well-ordered arrays of ZnO nanorods that are vertically aligned, single-crystalline, and with a low density of defects.[7] Films of MOCVD-grown ZnO nanorods are abbreviated in this paper as ZnO-N to distinguish them from ZnO nanorods grown by other methods. The functionalization of ZnO-N films has

been recently published.[8] The few DSSCs prepared from ZnO nanorods (grown from aqueous solutions) reported to date have exhibited efficiencies similar to those observed for cells prepared from colloidal nanoparticles.[4] While the electron mobility of a nonsensitized ZnO nanorod layer and of single nanorods has been measured using the field-effect transistor technique (1−5 $cm^2 V^{-1} s^{-1}$),[4a,5,9] experimental data on the electron transport in a *working solar cell* with ZnO nanorods sensitized with a dye and in the presence of electrolyte is not available. Determination of the electron transport properties of ZnO nanorod materials in a working solar cell will improve our understanding of these devices and may eventually lead to new designs with improved performance.

We have measured the electron transport properties of a DSSC with the working electrode made of MOCVD-grown ZnO nanorods (ZnO-N) on gold (Figure 1), and we have made a direct comparison with a cell prepared from ZnO mesoporous nanoparticles of similar thickness and sensitized with the same dye. The $\sim$1.8 $\mu$m thick ZnO-N film (nanorod diameter $\sim$ 0.15 $\mu$m) was grown on a 0.1 $\mu$m gold layer deposited on a Si substrate using titanium as the adhesion layer. The zinc oxide layer uniformly covered the gold surface so that gold was not in contact with the electrolyte or the dye. Since the working electrode was not transparent, the cell was illuminated through the conductive glass counter electrode. The dye employed was zinc(II) *meso*-tetrakis(3-carboxyphenyl)porphyrin, **1**,[10] with meta anchoring groups, which is an efficient sensitizer for $TiO_2$ electrodes.[11] Porphyrins are highly promising dyes for DSSCs[11]

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**Figure 1.** Schematic representation of the ZnO-N cell sensitized with **1**. The gold layer is deposited on a silicon substrate. (An enlarged view of the FESEM image of ZnO-N is in the Supporting Information, Figure S1.)

but to date have not been employed for the sensitization of ZnO nanorod cells. A schematic representation of the ZnO-N cell is shown in Figure 1.

A cell prepared from a thin ($\sim$2 $\mu$m) layer of colloidal ZnO (crystal size $\sim$ 15 nm) and sensitized with **1** was prepared for comparison. We will refer to the ZnO film prepared from the colloidal solution as ZnO-C. Experimental details about the preparations of the cells are reported in the Supporting Information. Briefly, the ZnO-N and ZnO-C films were sensitized by immersion in a 0.4 mM EtOH solution of **1**, rinsed, and immediately sealed with the Pt-coated FTO counter electrode. The electrolyte solution (0.05 M I$_2$, 0.10 M LiI, and 0.6 M TBAI in 3-methoxypropionitrile) was introduced in the cell by capillarity. The active electrode area was 0.7 cm$^2$.

The dye-sensitized nanostructured ZnO solar cells gave a good photoresponse, clearly reflecting the characteristic porphyrin absorption spectrum (Figure 2).[12] Quantum efficiencies on the order of 30% were calculated for both ZnO-N and ZnO-C films. Solar cell efficiencies, 0.1% and 0.6% for ZnO-N and ZnO-C, respectively, were modest in comparison to the previously reported[4] nanorod cells. The ZnO layer thickness of the electrodes used in this study (1.8 $\mu$m for ZnO-N film and 2 $\mu$m for ZnO-C) is about 1 order of magnitude less than that used in the previously reported nanorod cells (10 to 17 $\mu$m),[4] and this explains the lower efficiencies.

For further characterization, monochromatic light with a wavelength of 640 nm was used, ensuring a rather homogeneous light absorption profile in the films. The photocurrent density was higher for the ZnO-C cell than for the ZnO-N by a factor 5, which is easily explained by the higher surface area—and consequently larger amount of adsorbed dye—of the ZnO-C film.

A comparison of the measured electron transport times in the two types of ZnO solar cell (ZnO-C and ZnO-N) is shown in Figure 3. Electron transport in the ZnO-C cells was relatively slow ($\sim$10 ms), but becomes faster with increased illumination intensity, and was comparable with that found for colloidal TiO$_2$ films.[13] Interestingly, the photocurrent response time in the ZnO-N cell was about 2 orders of magnitude faster ($\sim$30 $\mu$s). This implies that the electron transport in the ZnO-N film is improved, as expected for the vertical columnar structure.[4a,5] The actual electron transport time in the ZnO-N nanorods may be much faster than the measured 30 $\mu$s, as the response speed of the photocurrent is limited by the *RC* time of the system, where the resistance *R* is determined by the series resistance of the electrodes ($\sim$10 $\Omega$) and the capacitance *C* by the capacity of the electrode/electrolyte interfaces. If the ZnO-N would behave as a perfect single crystal, then a transport time of about 1 $\mu$s is calculated.[14]

The large difference in electron transport time in ZnO-C and ZnO-N can be caused by several factors. First, the large difference in morphology of the films: ZnO-C consists of small, randomly connected nanocrystals, whereas ZnO-N consists of larger, vertically oriented nanorods. The large number of grain boundaries in the ZnO-C case, with associated traps and/or energy barriers, is likely the origin of the slower electron transport. The difference in surface area of the electrodes (ZnO-C has roughness factor that is about 5 times higher than ZnO-N) seems to play a smaller role. Second, the different ZnO growth methods can affect the material quality, possibly resulting in different electron mobilities. The defects in the ZnO-N, prepared by MOCVD, for instance, are expected to be much less compared with that of the ZnO-C samples.[6b] However, both ZnO materials used here are highly crystalline,[6b] and it has been shown that ZnO nanorods prepared by solution-based and gas-phase-based preparation methods display similar electron mobilities.[4a,5] How and whether the preparation method contributes to the large difference in electron transport times will need further investigation.

The charge present in the ZnO-N and ZnO-C films under short-circuit conditions was estimated by switching off the light
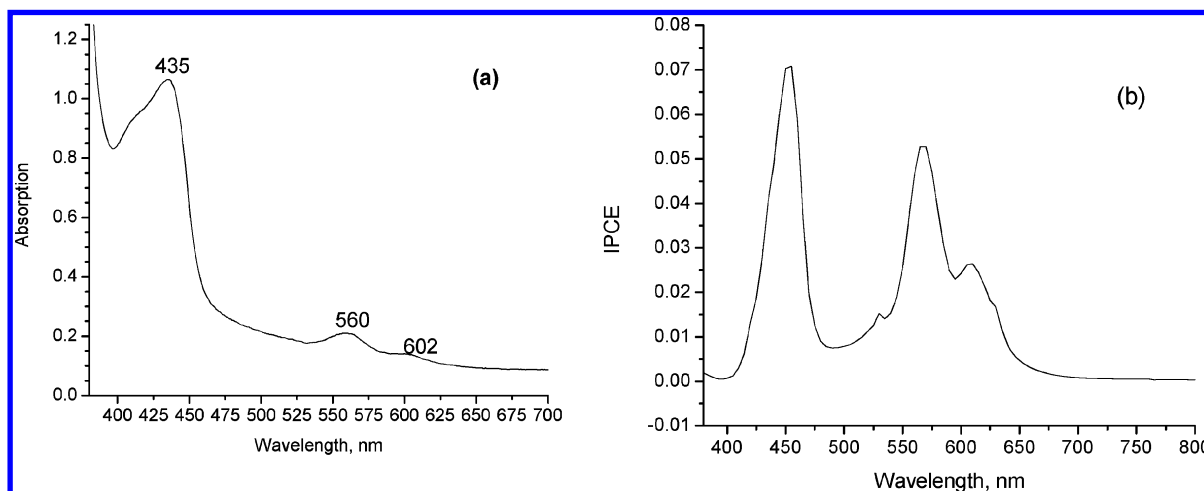


**Figure 2.** (a) Absorption spectrum of **1** bound to ZnO-N/glass. (b) Spectrum of the incident photon-to-current conversion efficiency (IPCE) of the ZnO-N solar cell sensitized with **1**.
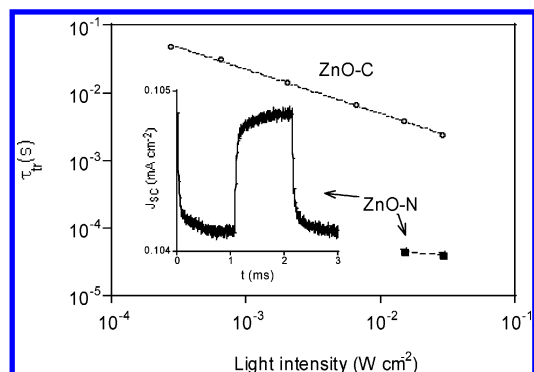
Letters

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**Figure 3.** Electron transport times in DSSCs prepared from ZnO-N (■) and ZnO-C (○) films as function of the light intensity (monochromatic light, 640 nm). Inset (ZnO-N response): Electron transport times were determined from the short-circuit photocurrent response to a small square wave modulation of the light intensity.

and then integrating the decaying current. Under equal light conditions, the charge extracted from the ZnO-C cell exceeded that of the ZnO-N cell by 2 orders of magnitude (see Figure S2 of the Supporting Information). The corresponding average electron concentration in the colloidal film was about one electron per nanocrystal at the highest light intensity.

Additional measurements of the solar cells showed that the lifetime of the electrons injected in the semiconductor, measured under open-circuit conditions, was similar for ZnO-N and ZnO-C (see Figure S3 in the Supporting Information). As lifetimes were more than 1 order of magnitude longer than the transport time at the corresponding light intensities, it can be concluded that electron recombination losses during transport are negligible. The low quantum efficiency must therefore be caused by a poor injection efficiency of the dye molecules, possibly due to the presence of aggregates.[15]

In conclusion, DSSCs prepared from vertically aligned, single-crystalline, MOCVD-grown ZnO nanorod (ZnO-N) electrodes display much faster electron transport than comparable cells with mesoporous ZnO nanoparticle electrodes (ZnO-C) in accordance with data obtained for nonsensitized ZnO nanowires arrays and single, nonsensitized nanowires.[4a,5] The difference can be attributed to the difference in number of grain boundaries that the electron has to pass.

**Supporting Information Available:** Preparation of the ZnO-N and ZnO-C films, binding procedures and solar cells preparation, methods for electron transport measurements, figures of charge and electron lifetime vs light intensity, and IV curves are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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