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Roger Chang  
*CUNY City College*

Kemakorn Ithisuphalap  
*CUNY City College*

Ilona Kretzschmar  
*CUNY City College*

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Impact of particle shape on electron transport and lifetime in zinc oxide nanorod-based dye-sensitized solar cells

Roger Chang, Kemakorn Ithisuphalap, and Ilona Kretzschmar*

Department of Chemical Engineering, City College of the City University of New York, New York, NY 10031, USA

* Correspondence: Email: kretzschmar@ccny.cuny.edu; Tel: 212-650-6769; Fax: 212-650-6660.

Abstract: Owing to its high electron mobility, zinc oxide represents a promising alternative to titanium dioxide as the working electrode material in dye-sensitized solar cells (DSCs). When zinc oxide is grown into 1-D nanowire arrays and incorporated into the working electrode of DSCs, enhanced electron dynamics and even a decoupling of electron transport ($\tau_d$) and electron lifetime ($\tau_n$) have been observed. In this work, DSCs with working electrodes composed of solution-grown, unarrayed ZnO nanorods are investigated. In order to determine whether such devices give rise to similar decoupling, intensity modulated photocurrent and photovoltage spectroscopies are used to measure $\tau_d$ and $\tau_n$, while varying the illumination intensity. In addition, ZnO nanorod-based DSCs are compared with ZnO nanoparticle-based DSCs and nanomaterial shape is shown to affect electron dynamics. Nanorod-based DSCs exhibit shorter electron transport times, longer electron lifetimes, and a higher $\tau_n/\tau_d$ ratio than nanoparticle-based DSCs.

Keywords: DSCs; DSSCs; ZnO; TiO$_2$; shape dependence; surface properties; porosity; interconnectivity; electron mobility

1. Introduction

Since their introduction by O’Regan and Gratzel [1], dye-sensitized solar cells (DSCs) have continuously improved their performance. The champion DSC now boasts an efficiency exceeding 13% [2]. In addition, DSCs have inspired an entire class of perovskite-based devices that have demonstrated unprecedented leaps in power conversion efficiency given the short time they have been studied, improving to 15% efficiency in 2013 and to over 20% more recently [3–6]. DSCs are
an attractive solar technology due to their low production cost, ease of manufacture, and also potential for low light applications. Of the semiconductor materials that are used in DSCs, TiO\textsubscript{2} and ZnO are reported most often \cite{7,8}. TiO\textsubscript{2} and ZnO are similar in that they both have large band gaps \(E_{B,TiO_2,anatase} = 3.2\) eV vs. \(E_{B,ZnO} = 3.3\)–3.4 eV), \cite{1,9,10} with the difference that ZnO has a much higher electron mobility, \(\mu\), than TiO\textsubscript{2} \((\mu_{ZnO} = 10^2\) cm\(^2/V\)-s vs. \(\mu_{TiO_2} = 10^{-5}\) cm\(^2/V\)-s) \cite{11,12}.

Despite the higher electron mobility, studies of DSCs composed of ZnO nanoparticles have shown that their power conversion efficiencies are lower than those of DSCs composed of TiO\textsubscript{2} \cite{13,14,15}. The standard architecture of a DSC calls for a working electrode composed of semiconductor nanoparticles to maximize the surface area available for sensitizer adsorption \cite{1}. For these types of nanoparticle networks, a trap-limited model has been proposed whereby excited photoelectrons must hop from particle to particle in order to exit from the semiconductor network into the collector \cite{16–19}. In this model, electron transport through the nanoparticle network and recombination of the electrons with holes (specifically with oxidized electrolyte molecules) are both governed by trap-limited electron diffusion and are considered to be linked. As a result, the characteristic time constants for electron transport and electron lifetime (before recombination), \(\tau_d\) and \(\tau_n\), respectively, are interdependent \cite{20}. This dependence has been confirmed for ZnO nanoparticle-based DSCs by showing that the \(\tau_d/\tau_n\) ratio is constant over a range of illumination intensities \cite{21} providing one explanation for why the higher electron mobility of ZnO does not lead to improved efficiencies. Interestingly, however, there is evidence that the \(\tau_d/\tau_n\) interdependence can be decoupled when ZnO nanoparticles are replaced by ZnO nanowire arrays \cite{21}.

When ZnO is grown into one-dimensional nanostructures, i.e., ZnO nanowire arrays, and incorporated into DSCs, enhanced electron dynamics have been observed, indicating that the high electron mobility of ZnO is being utilized \cite{22,23,24}. For example, a ZnO nanowire array used as a DSC working electrode shows an enhanced electron transport time compared to a ZnO nanoparticle DSC \((\tau_{d,\text{array}} = 30\) µs vs. \(\tau_{d,\text{NP}} = 10\) ms) \cite{23}. Further, the electron diffusion coefficient, \(D_n\), for ZnO nanowires has been estimated to be orders of magnitude larger \((D_{n,NW} = 0.05–0.5\) cm\(^2/\)s) than that of ZnO nanoparticle films \((D_{n,NP} = 1.7 \times 10^{-4}\) cm\(^2/\)s \cite{25}) based on resistivity, carrier concentration and mobility measurements performed on single, dry ZnO nanowires \cite{24}. Comparison of ZnO nanowire array DSCs and ZnO nanoparticle DSCs by Martinson \textit{et al.} \cite{21} revealed that in the case of the nanoparticle DSC, the \(\tau_d/\tau_n\) ratio remained constant, whereas in the ZnO nanowire array DSC, the \(\tau_d/\tau_n\) ratio decreased dramatically as the photon flux increased. These observations indicate that both the shape of the ZnO material and its interconnectivity strongly affect the way electrons are transported through the DSC electrode. Although ZnO nanowire array DSCs represent a promising route, they suffer from a smaller available surface area for dye loading. Attempts to correct for the reduction in surface area have included packing nanoparticles into the voids between the nanowires or by growing dendritic 1-D structures onto underlying 1-D or 2-D structures \cite{26–29}.

In the present work, we investigate a different strategy by utilizing unarrayed solution-grown ZnO nanorods to maintain a large surface area while simultaneously leveraging the high electron mobility of ZnO. The few reports available in the literature regarding DSCs composed of unarrayed 1-D ZnO nanostructures \cite{30,31,32} focus primarily on synthetic techniques with only one study investigating their electron dynamics using impedance spectroscopy \cite{32}. We seek to understand whether the \(\tau_d/\tau_n\) interdependence can be disentangled in such devices by investigating the electron dynamics of a ZnO nanorod-based DSC over a range of illumination intensities using intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy.
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(IMVS), i.e., photoelectrical techniques that measure electron transport time and electron lifetime values, respectively. Electron diffusion lengths and effective diffusion coefficients of ZnO nanomaterials are also calculated and the results are presented as a function of particle shape. Finally, we compare the performance of DSCs made from ZnO nanoparticles and nanorods under low light and standard solar testing conditions and qualitatively discuss observed differences and similarities in the context of ZnO nanomaterial shape.

2. Materials and Method

2.1. ZnO nanoparticle and nanorod synthesis and characterization

2 mmol of zinc acetate dihydrate (Fisher Scientific, Pittsburgh, PA) are dissolved per 100 ml of ethanol. Upon addition of 2 g of sodium hydroxide, a white precipitate is observed. Subsequently, the solution is continuously stirred at room temperature for 1.5 hours. The aspect ratio of the ZnO product is controlled by varying the growth time. The product is cleaned twice by centrifuging, removing the supernatant and replacing it with fresh ethanol. Next, ethanol is replaced with deionized water and the ZnO product is dispersed, frozen and freeze-dried in a lyophilizer yielding a white ZnO powder that shows the characteristic photoluminescence peak at 380 nm (see Supporting Information, Figure S1). Further characterization of the ZnO nanomaterials is performed using high-resolution transmission electron microscopy (JEOL 2100), X-ray powder diffraction (PANalytical X’Pert Pro with Cu Kα radiation 1.541Å), and high-resolution scanning electron microscopy (FEI Nova NanoSEM). Solution grown nanoparticles (grown for 1 day) and nanorods (grown for 3 weeks) are designated SG-NP and SG-NR3, respectively. Commercial ZnO nanoparticles (Strem-NP) purchased from Strem Chemicals (Newburyport, MA) are used as control.

2.2. DSC assembly and testing

Glass slides (1 cm × 2.5 cm) coated on one side with fluorine tin oxide (TEC-7) purchased from Hartford Glass Company (Hartford City, IN) are cleaned by sonication in isopropanol, followed by acetone and then deionized water. The slides are used as substrates for both the working and counter electrodes.

To construct working electrodes, 20 mg of zinc oxide powder is mixed with 10 µL of Triton-X (Acros) and 5.5 µL of acetic acid (5% solution in water) to form a paste. The paste is applied to FTO coated glass slides via doctor blading to give zinc oxide working electrodes with a thickness of 30 µm and an area of 0.25 cm² (0.5 cm × 0.5 cm). Subsequently, the zinc oxide film is calcined at 400 °C for 30 minutes forming the working electrode of the DSC. Electrodes are then dyed by immersion in an ethanolic 0.5 mM N719 dye (Sigma Aldrich, St. Louis, MO) solution for 30 minutes. The excess dye solution is rinsed off with ethanol and the electrodes are air dried.

Counter electrodes are prepared by first drilling a pair of filling holes into the slides using a drill press. Then, a 10 nm layer of platinum is evaporated onto the conductive side of the slide. Physical vapor deposition (PVD) of platinum wire (Ted Pella) is performed using a Cressington Desktop HV Pump Station 308R-EM and Cressington Evaporation Supply LT750. A Cressington Thickness Monitor MTM-10 is used to monitor the thickness of the platinum film.
A gasket is fabricated using Surlyn tape (300 μm) and sandwiched between the working and counter electrodes. Heat is applied to seal the DSC cell together. Next, the cell is filled with 15.5 μl of redox electrolyte solution consisting of 0.5M lithium iodide and 0.05M iodine in acetonitrile. The fill holes are sealed with Surlyn tape completing the DSC assembly.

Intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) data are obtained by synchronizing two Gamry Reference 600 potentiostats. One potentiostat is used to power an LED (blue light at 470 nm) under current control, with 10% AC current superimposed on a DC current at intensities of 9, 190, and 500 mA. The second potentiostat is used to record the DSC response as the frequency of the input is modulated continuously from $10^{-1}$ to $10^4$ Hz. Linear sweep voltammetry performed with a Gamry Reference 600 potentiostat is used to evaluate cell performance. Low light testing is performed using a compact fluorescent lamp (CFL) bulb at 20,000 lux. DSCs are also tested under standard solar testing condition of AM 1.5 using a Newport 67005 Xenon arc lamp (Oriel Instruments, USA) at a light intensity of 100 mW/cm².

3. Results

In the following section, the ZnO synthesis products (SG-NR3 and SG-NP) and the ZnO control (Strem-NP) are characterized using electron microscopy and X-ray diffraction to confirm the identity and crystallinity of the nanomaterials and to determine particle size and shape. ImageJ software is used to measure d-spacings from TEM micrographs and to evaluate the porosity of the fabricated working electrodes from SEM micrographs. Subsequently, the working electrodes fabricated from each of the three nanomaterials are incorporated into DSCs and tested to determine the effect of particle shape and porosity on electron dynamics using intensity modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS).

3.1. Characterization of ZnO nanomaterials

ZnO nanorods with a controllable aspect ratio are grown using a solution phase process [33]. High resolution (HR) TEM allows characterization of the particle size, particle shape, and crystallinity of the ZnO samples as shown in Figure 1. The top row (Figure 1A-C) shows the size and shape of the particles: Strem-NPs are irregularly shaped and show an average diameter of $d_{\text{avg,Strem-NP}} = 13.8 \pm 3.7$ nm, SG-NR3s have an average diameter of $d_{\text{avg,SG-NR3}} = 11.5 \pm 1.3$ nm and an average length of $l_{\text{avg,SG-NR3}} = 29.9 \pm 6.9$ nm and SG-NPs have an average diameter of $d_{\text{avg,SG-NP}} = 6.1 \pm 1.1$ nm. Lattice fringes evident in Figure 1D-F indicate the single crystalline nature of the commercially available Strem-NP powder as well as of the solution-grown SG-NR3 and SG-NP powders. The d-spacings are measured using ImageJ and are indicated in Figure 1D-F. The d-spacing values of 0.28, 0.26, and 0.25 nm found in the HR-TEM images are in good agreement with the corresponding (100), (002) and (101) facets of crystalline ZnO in the wurtzite configuration.

X-ray powder diffraction is employed to further analyze the crystalline nature of the three ZnO powders used in the study. The diffraction patterns (see Supporting Information) from before calcination (Figure S2) and after calcination (Figure S3) confirm the crystalline nature of the ZnO material by exhibiting typical diffraction peaks that correspond to the (100), (002), (101), (102), (110), (103), and (112) planes of ZnO in the hexagonal wurtzite configuration (JPCDS 00-36-1451) [34]. The Strem-NP sample shows additional peaks indicating the presence of
the corrosion product zinc hydrocarbonate (Zn₄CO₃(OH)₆, JCPDS 00-11-0287), which disappears upon calcination (compare Figures S2 and S3). XRD spectra of calcined samples are taken on the FTO glass substrate resulting in typical FTO peaks at \(2\theta = 26.8, 33.8, 37.9, 51.8, 61.7, \) and 65.8° (JPCDS 04-008-8135) [35]. Upon inspection, spectra of the calcined samples exhibit identical peak positions as the uncalcined samples, but decreased peak widths indicating that the ZnO crystal size increases during heat treatment. For example, for the SG-NP sample, the mean crystallite size of the powder increases from 13.2 ±2.7 nm to 30.4 ±3.1 nm. Potential origins for the increase of the crystallite size during the sintering of individual nanoparticles into a network are neck formation between crystallites and thermally induced Ostwald ripening [36].

![HR-TEM images of ZnO powders used for DSC testing.](image)

**Figure 1.** HR-TEM images of ZnO powders used for DSC testing. (A) commercial nanoparticles (Strem-NP), (B) solution grown nanorods (SG-NR3) and (C) solution-grown nanoparticles (SG-NP). (D)-(F) Zoomed in views of samples depicted in (A)-(C) showing lattice fringes. Insets are FFTs of the corresponding HR-TEM images.

HR-SEM analysis of the ZnO powders after they have been sintered for use as electrodes reveals that each nanomaterial produces a working electrode with a distinct surface porosity (Figure 2). ImageJ analysis shows that the Strem-NP and SG-NR3 have porosities of 21.6 ± 2.0% and 18.9 ± 4.1% respectively, while the SG-NP has the highest porosity at 34.6 ± 3.7%. Enhanced capillary coalescence due to surface tension effects [37] is a likely cause for the tighter nanorod packing observed compared to the nanoparticles. Further, it is known that the different facets of ZnO, particularly the (100) and (010) facets parallel to the long c-axis and the (001) facet perpendicular to
it, possess dissimilar free energies [33]. Since the parallel facets are much more prevalent in the nanorods than in the nanoparticles, the differing free energies might also contribute to the observed divergence in packing behavior. In addition, the presence of the corrosion layer in the Strem-NP sample may lead to enhanced sintering of the Strem-NPs at elevated temperatures. The effect of the varying packing behavior on electron dynamics is highlighted in more detail in the Discussion.

![Figure 2](image.png)

**Figure 2.** HR-SEM images of ZnO working electrodes used for DSC testing. (A) Strem-NP, (B) SG-NR3, and (C) SG-NP. (D)-(F) Zoomed in images of samples depicted in (A)-(C).

### 3.2. IMPS and IMVS characterization of electron dynamics

Intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) are used to investigate the impact of nanoparticle shape on electron dynamics in the DSCs. These two techniques provide information on electron dynamics within the working electrode of the DSC, giving values for the electron transport time ($\tau_d$), the electron lifetime ($\tau_n$), as well as parameters that can be derived from these values. IMPS testing performed at an LED intensity of 500 mA on the SG-NR3 DSCs versus the Strem-NP DSCs shows a clear shift in the imaginary component (blue curve) of the photocurrent response (Table 1 and Figure 3A top and middle). According to the IMPS theory, the frequency at which the minimum in the imaginary component occurs can be used to determine the electron transport time, $\tau_d$, using the expression:
The $f_{\text{min}}$ peak occurs at 25.12 Hz for the Strem-NP DSC, whereas it is observed at 63.10 Hz for the SG-NR3 DSC. The values correspond to electron transport times of 6.3 ms and 2.5 ms respectively. The $f_{\text{min}}$ peak is shifted even higher to 100 Hz for the SG-NP DSC (Figure 3A, bottom), resulting in a $\tau_d$ of 1.6 ms.

**Figure 3.** (A) Intensity modulated photocurrent spectroscopy (IMPS) and (B) intensity modulated photovoltage spectroscopy (IMVS) data at 500 mA showing real (red) and imaginary (blue) components of the photocurrent response for (top) Strem-NP, (middle) SG-NR3, and (bottom) SG-NP DSCs.

IMVS is analogous to IMPS except that in this case, the photovoltage response to a frequency modulated light source is recorded (rather than the photocurrent response) and the peak in the imaginary component is a maximum rather than a minimum. The maximum in the imaginary component of the response provides the electron lifetime, $\tau_n$, using the following expression:

$$\tau_n = (2\pi f_{\text{max}})^{-1}$$
The IMVS results show that the SG-NR3 DSC has an $f_{\text{max}}$ peak at 3.98 Hz corresponding to a $\tau_n$ of 40.0 ms (Table 1, Figure 3B middle). In contrast, higher $f_{\text{max}}$ peak values are measured for both the Strem-NP and SG-NP DSCs resulting in shorter electron lifetimes of $\tau_n = 25.2$ and 20.0 ms, respectively, (Figure 3B top and bottom).

In addition to the IMPS and IMVS results, Table 1 presents values for the effective diffusion coefficient ($D_n$) and the electron diffusion length ($L_n$), which are obtained from $\tau_d$ and $\tau_n$ values using the following relations:

$$\tau_d = \frac{L^2}{D_n}$$

$$L_n = (D_n \tau_n)^{1/2}$$

where $L$ is the thickness of the working electrode and is constant. Values for the ratio of $\tau_n/\tau_d$ are also given in Table 1 for the three DSC types at an LED intensity of 500 mA.

| DSC Type | IMPS | | IMVS | | | | | |
|---------|------|----|------|----|---|---|---|
|         | $f_{\text{min}}$ (Hz) | $\tau_d$ (s) | $f_{\text{max}}$ (Hz) | $\tau_n$ (s) | $D_n$ (cm$^2$/s) | $L_n$ (cm) | $\tau_n/\tau_d$ |
| Strem NP | 25.12 | 0.0063 | 6.31 | 0.0252 | 0.0014286 | 0.0060 | 4.0 |
| SG NR3  | 63.10 | 0.0025 | 3.98 | 0.0400 | 0.0036000 | 0.0120 | 15.9 |
| SG NP   | 100.00 | 0.0016 | 7.94 | 0.0200 | 0.0056250 | 0.0106 | 12.5 |

4. Discussion

Using results of IMPS and IMVS measurements as those shown in the previous section, it is possible to address the intriguing question of whether unarrayed ZnO nanorods allow for the decoupling of $\tau_n$ and $\tau_d$. Additionally, the results reveal differences in electron lifetime, electron transport time, electron diffusivity and electron diffusion length owing to changes in the ZnO nanomaterial shape and working electrode porosity.

In the Introduction, the question is posed whether an elongated nanomaterial shape reduces particle hopping events that limit electron transport through a NP-based DSC working electrode. Other groups have observed markedly enhanced electron transport in ZnO nanowire arrays [21–24]. One group, Martinson et al., even reports a decoupling of $\tau_n$ and $\tau_d$ in these arrays due to $\tau_d$ values that are unaffected by increased illumination [21], indicating that $\tau_d$ can be improved such that the constant $\tau_n/\tau_d$ ratio that characterizes NP-based DSCs breaks down [20]. In these ZnO nanowire arrays, it appears that the elongated shape allows for the high electron mobility of ZnO to be taken advantage of and also significantly reduces the contact points between particles.
In order to determine whether the use of unarrayed ZnO nanorods leads to a similar breakdown of the $\tau_n$ and $\tau_d$ interdependence, IMPS measurements are performed at three illumination intensities (9, 190, and 500 mA) to establish whether $\tau_d$ remains constant as LED intensity increases in the case of the SG-NR3 DSC. In the case of the Stem-NP and SG-NP DSCs, i.e., nanoparticle DSC, $\tau_d$ is expected to decrease as LED intensity increases because as more photoelectrons are generated, deep electron traps present in the ZnO nanoparticles are filled, leaving only shallower traps and thus allowing for faster electron transport. While the same filling of traps is expected to occur in the SG-NR3 DSC, the reduced number of contact points, i.e., potential trap sites, in a nanorod network compared to a nanoparticle network, is expected to result in shorter $\tau_d$ values in the SG-NR3 DSC even at lower LED intensity and subsequently, reduced dependence at higher LED intensities. IMVS measurements are also carried out at the three illumination intensities for all three types of DSCs. As the LED intensity increases, the number of photoelectrons and holes generated simultaneously in the working electrode increases. The increased carrier density is expected to lead to accelerated recombination and a shortened $\tau_n$, in all three DSC types.

Figure 4. Electron lifetimes, $\tau_n$, and transport times, $\tau_d$, as a function of LED intensity (9, 190, and 500 mA) obtained from IMVS and IMPS, respectively. Solid lines denote $\tau_n$, whereas dashed lines denote $\tau_d$. Arrows indicate the magnitude of the $\tau_n/\tau_d$ ratio for each nanomaterial type. Stem-NP (black squares), SG-NR3 (red triangles) and SG-NP (blue circles) DSCs.

In Figure 4, the two NP-based DSCs (black squares and blue circles) show constant $\tau_n/\tau_d$ ratios, in good agreement with the understanding of trap-limited electron transport in NP-based DSCs as $\tau_n$ and $\tau_d$ both decrease with increasing LED intensity [20,21]. Unexpectedly, the $\tau_n/\tau_d$ ratio for the SG-NR3 DSC (red triangles) is also found to be constant indicating that $\tau_n$ and $\tau_d$ in the SG-NR3 DSC are not decoupled. $\tau_n$ decreases with increasing LED intensity as expected, but $\tau_d$ also shows the same inverse dependence. A rationale for the unexpected $\tau_d$ behavior could be that the ZnO nanorods are not long enough to allow electrons to overcome trap-limited transport in the electrodes. With the
given increase in aspect ratio (from 1:1 to ~ 3:1), the SG-NR3 DSC exhibits a reduction in the number of point contacts resulting in the longer \( \tau_n \) and shorter \( \tau_d \) compared to the Strem-NP DSC (Figure 4). However, unlike in a nanowire array, there are still numerous contact points between the nanorods in the SG-NR3 DSC. Further investigation of ZnO nanorods with aspect ratios between the ~ 3:1 investigated here and ~ 30:1 aspect ratio of the nanowire array synthesized by Martinson et al. [21] is required, as well as investigation into how to reduce the frequency of contacts. Nevertheless, the measurements summarized in Figure 4 are instructive because they demonstrate that a change in ZnO nanomaterial shape improves DSC electron dynamics.

Interestingly, the ZnO nanorod DSC exhibits the highest electron lifetimes over the range of intensity values studied when compared to both types of nanoparticle DSCs (see solid lines in Figure 4). Since the SG-NR3 DSC has a longer electron lifetime than either the densely packed Strem-NP DSC or the loosely packed SG-NP DSC, the IMVS results indicate a clear influence of particle shape uncomplicated by packing behavior. \( \tau_n \) is a measure of how long an electron can survive in the working electrode before it recombines with a hole. In the Strem-NP and SG-NP DSCs, each time an electron crosses from one nanoparticle to another, it can potentially recombine with a hole, for example, an oxidized electrolyte molecule. The same holes are present in the SG-NR3 DSC, however, because of the increased length along one axis of the nanorod, electrons can reach the anode while crossing fewer junctions and therefore experience fewer potential recombination events. The longer electron lifetime measured for the SG-NR3 DSC may be a reflection of this lower probability of recombination.

With regard to the electron transport time, \( \tau_d \), the IMPS results show that electrons exit the working electrode of the SG-NR3 DSC more rapidly than that of the Strem-NP DSC. This behavior is observed for a range of intensities as shown in Figure 4 (dashed lines) and indicates that the difference in particle shape (nanorod versus spherical nanoparticle) affects \( \tau_d \). In particular, the high electron mobility of ZnO contributes to the faster \( \tau_d \) in the SG-NR3 DSC compared to Strem-NP DSC because electrons can take advantage of this material property when moving through the 1-D structure of the nanorods, but cannot do so in a nanoparticle-based electrode. Additionally, the IMPS result for the SG-NP DSC suggests that particle packing has an important influence on \( \tau_d \) as well. The SG-NR3 DSC and Strem-NP DSC have similar porosities (Figure 2) and therefore the difference in their electron transport times is attributed to the effect of shape. This argument is further supported by the similar working electrode surface areas available for dye loading calculated for the Strem-NP DSC and the SG-NR3 DSC of \( A_{S, \text{Strem-NP DSC}} = 6.42 \times 10^{16} \text{ nm}^2 \) and \( A_{S, \text{SG-NR3 DSC}} = 6.14 \times 10^{16} \text{ nm}^2 \), respectively (see Supporting Information). Meanwhile, the SG-NP DSC has the shortest \( \tau_d \) of all three DSC types, is also the least densely packed, and has the highest working electrode surface area of \( A_{S, \text{SG-NP DSC}} = 1.72 \times 10^{17} \text{ nm}^2 \) (see Supporting Information). Since the SG-NP DSC has more than twice the working electrode surface area for dye loading compared to the Strem-NP and SG-NR3 DSCs, a shorter \( \tau_d \) is expected due to a higher electron density and the increased filling of shallower traps in the SG-NP DSC. The result for the SG-NP DSC is also in agreement with a trap-limited model of electron transport. Electron transport through a porous nanoparticle network as described by this model proceeds by an electron hopping mechanism that is quite slow due to the vast number of particles an electron must visit in order to reach the anode. If the number of particles is reduced (i.e., lower density particle packing), the electrons will encounter fewer nanoparticles and electron transport times decrease as is observed for the SG-NP DSC. This observation also suggests that a method for decreasing the \( \tau_d \) of the SG-NR3 DSC further is to increase the porosity of the working.
electrode. One idea is to fabricate ZnO nanorods with magnetically addressable capped ends that can be assembled into an ordered porous structure, thereby limiting the number of junctions and decreasing $\tau_d$. The open structure would also be more compatible with solid polymeric electrolytes and viscous electrolytes such as ionic liquids.

An additional conclusion from Figure 4 is that the magnitude of the $\tau_n/\tau_d$ ratio is greatest for the ZnO nanorod DSC compared to the ZnO nanoparticle DSCs. This can be discerned from the length of the arrows connecting the $\tau_n$ and $\tau_d$ values for each type of DSC and the calculated $\tau_n/\tau_d$ ratios are also given in Table 1. The result indicates that the SG-NR3 DSC gives photoelectrons a better chance of percolating through the working electrode before they recombine since the electron lifetime is proportionally longer than the transport time in the nanoparticle DSCs.

As for the calculated electron diffusion coefficients, as expected, $D_n$ is higher for the SG-NR3 DSC than for the Strem-NP DSC, because the effective diffusion coefficient and the measured electron transport time are inversely proportional. Regarding values for $L_n$, the electron diffusion length is greatest for the SG-NR3 DSC. It is twice as long as that for the Strem-NP DSC and slightly longer than that for the SG-NP DSC. Because $L_n$ depends on $\tau_d$, the differences in particle packing that affect $\tau_d$ should also have an effect on $L_n$. However, any decrease in $\tau_d$ due to looser particle packing would be at least partially offset by a decrease in $\tau_n$ as well. This can be seen in the case of the SG-NP DSC (see Table 1). It exhibits the lowest $\tau_d$ (1.6 ms) as well as the lowest $\tau_n$ (20.0 ms), both of which can be explained by its less dense working electrode packing. Due to such packing, an individual nanoparticle has fewer neighboring particles, i.e., fewer contact points. This shortens $\tau_d$ while also exposing the particles in the SG-NP DSC to greater interfacial contact with hole-conducting species in the liquid electrolyte, making recombination more likely and reducing the electron lifetime. Referring to Equations (4) and (5), it can be seen that the effect of low density packing is to increase $D_n$ (since $\tau_d$ and $D_n$ are inversely proportional) but to lower $\tau_n$. In calculating $L_n$, the two values offset each other and the effect of particle packing on $L_n$ is diminished. Therefore the fact that $L_n$ is measured to be highest for the SG-NR3 DSC is significant because it suggests the nanorod shape gives the longest electron diffusion length, regardless of differences in particle packing among the three DSC types. In general, $L_n > L$ is a requirement for a well-functioning DSC. The lowest $L_n$ value obtained, 60 µm for the Strem-NP DSC, is twice the working electrode thickness of $L = 30$ µm. While $L_n > L$ is routinely achieved for a functional DSC, a longer $L_n$ could be of benefit in some types of highly porous DSCs that attempt to accommodate solid state or ionic liquid electrolytes. Nanorod DSCs could be useful for this purpose. They might also be useful in attempts to replace the iodide/triiodide couple in the electrolyte. If the kinetically slow recombination of photoelectrons with triiodide is replaced by a different, faster recombination reaction, $\tau_n$ will likely drop. However, if as seen with the ZnO nanorods, the DSC already exhibits a higher $\tau_n$, perhaps such a system will tolerate faster one-electron redox systems.

Finally, the J-V characteristics of ZnO DSCs with the three nanomaterials at low light and standard solar testing conditions are provided for completeness in Figure 5A and B, respectively. Under low light testing conditions ($P_{in} = 2.9$ mW/cm²), the short circuit density, $J_{SC}$, for the SG-NR3 DSC is $874 \pm 143$ µA/cm² and $933 \pm 116$ µA/cm² for the Strem-NP DSC. For the SG-NP DSC, the $J_{SC}$ is $394 \pm 51$ µA/cm². Meanwhile, under low light, the open circuit voltage, $V_{OC}$, for the SG-NR3 DSC is $467 \pm 8$ mV compared to $387 \pm 10$ mV for the Strem-NP DSC and $381 \pm 9$ mV for the SG-NP DSC. The DSCs are also tested under standard solar testing conditions ($P_{in} = 100$ mW/cm²) and exhibit a $J_{SC}$ of $0.92 \pm 0.18$ mA/cm² for the SG-NR3 DSC, $5.69 \pm 0.22$ mA/cm² for the Strem-NP
DSC, and $2.85 \pm 0.16 \text{ mA/cm}^2$ for the SG-NP DSC. The $V_{OC}$ values are $416 \pm 11 \text{ mV}$ for the SG-NR3 DSC, $435 \pm 11 \text{ mV}$ for the Strem-NP DSC, and $457 \pm 9 \text{ mV}$ for the SG-NP DSC.

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Figure 5. Plots of current density versus voltage for the three DSC types when tested under (A) low-light and (B) standard AM 1.5 solar testing conditions. SG-NR3 (dotted red line), Strem-NP (solid black line), and SG-NP (dashed blue line) DSCs.

A direct quantitative comparison between the J-V curves for the three types of DSC electrodes is difficult, because of variations in actual surface area and light harvesting efficiency [21]. However, several qualitative observations can be made regarding trends in $J_{SC}$ taking into account the estimated surface area available for dye loading and the inter-particle pore size (see Supporting Information). The working electrode surface area for the Strem-NP DSC ($A_{S, Strem-NP DSC} = 6.42 \times 10^{16} \text{ nm}^2$) is slightly larger than that for the SG-NR3 DSC ($A_{S, SG-NR3 DSC} = 6.14 \times 10^{16} \text{ nm}^2$). The electrode surface areas are in good agreement with the measured $J_{SC}$ values because increased dye loading correlates with a larger $J_{SC}$ (see Figure 5A). In contrast, the SG-NP DSC has the largest calculated surface area ($A_{S, SG-NP DSC} = 1.72 \times 10^{17} \text{ nm}^2$) and also the shortest $\tau_d$ as measured by IMPS (see Figure 4), but the lowest $J_{SC}$. A rationale for the inverted trend might be the 5x smaller inter-particle pore size in the SG-NP DSC electrode, which might hinder diffusion of both the N719 dye during impregnation and the electrolyte components (acetonitrile, iodide ions, and triiodide ions) during operation. The molecular/hydrodynamic radii of these species range from 0.1 to 1 nm [38,39,40]. The hindered mass transport of ions might also explain why the shorter $\tau_d$ of the SG-NP DSC (see Figure 4) does not translate into a higher $J_{SC}$ when the SG-NP DSC is under operation. Further, the observed 80 mV upward shift in $V_{OC}$ for the SG-NR3 DSC can be explained by the longer electron lifetime in the SG-NR3 DSC compared to Strem-NP and SG-NP DSCs (see Table 1). Similar shifts in $V_{OC}$ have been reported by other groups for TiO$_2$-based DSCs [41,42]. An increased $V_{OC}$ is an indication of an upward shift in the Fermi level of the DSC semiconductor due to an increase in electron density [43]. In the SG-NR3 DSC the increase in electron density results from the longer electron lifetime. Further, an increase of illumination from low-light to standard AM 1.5 solar testing conditions results in increased current densities as expected (Figure 5B). However, the magnitude of increase shows some
variation among the three DSC types. More studies are underway to identify the origin of these variations.

5. Conclusion

Overall, the results demonstrate that nanoparticle shape is a parameter that affects electron dynamics in ZnO DSC electrodes. We observe that nanorod-based DSCs exhibit shorter electron transport times, longer electron lifetimes and a high $\tau_n/\tau_d$ ratio compared to nanoparticle DSCs. When the $\tau_n/\tau_d$ ratio is measured as a function of increasing illumination intensity, we find that nanorods of ~3:1 aspect ratio do not yet allow electron transport to be decoupled from electron recombination. It is proposed that if the aspect ratio is increased, and porosity is increased so as to reduce the number of point contacts, electrons can overcome trap-limited transport and take advantage of the higher electron mobility associated with ZnO.

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Conflict of Interest

The authors declare no conflicts of interest regarding this paper.

References


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