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## Aspect-Ratio Dependent Electron Transport and Recombination in Dye-Sensitized Solar Cells fabricated with one-dimensional ZnO nanostructures

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### Highlights

- Investigated the aspect ratio dependence on electron transport proerties of ZnO
- Longer ZnO nanords showed better solar cell performance
- Low aspect ratio ZnO exhibit better light scattering effect

### Abstract

Though one-dimensional (1-D) ZnOnanrods are promising transport electron transport material in the photoanode of Dye Sensitized Solar Cells (DSSC), 1-D ZnOnanorod based DSSCs exhibit poor energy conversion efficiencies. In this study, DSSCs were fabricated with 1-D ZnOnanorods having different aspect ratio and the dependence of solar cell performance on aspect ratio of ZnOnanorods was investigated. Photoanodes fabricated with different 1-D ZnOnanorods having aspect ratios of 4.4, 5.4, 5.8, 6.8 and 7.6 showed increasing solar cell performance with the increase of aspect ratio where 2.1 and 4.7% light conversion efficiencies were observed respectively for the lowest and highest aspect ratio of 1-D ZnO nanostructures. We study the electrical and operational differences between DSSC made with ZnO nanostructures with different aspect ratio. Electrochemical impedance spectroscopy (EIS) is used to quantify the aspect ratio depended electron transport properties, charge recombination, life-time and charge diffusion lengths of excited electrons in 1D ZnOnanorods and electron transport properties are correlated to the observed cell performance. In addition, effect of aspect ratio of ZnOnanorods on dye loading amount and light scattering properties were also investigated.

Key words: 1-D ZnO, aspect ratio, dye-sensitized solar cell, electron transport

#### 1. Introduction

In Recent past, nano structures metal oxides such as TiO<sub>2</sub>, SnO<sub>2</sub> and ZnO are received great interest due to their physical, chemical, semiconducting properties, cost effectiveness, simple fabrication procedures and environmental friendliness[1, 2]. The same properties make them much more attractive materials for applications including photonic devices, catalysis, chemical sensors, drug delivery, and energy conversion and storage systems[1-4]. Among these applications, the use of metal oxides as photoanode materials in DSSC is an attractive subject of research and a solar conversion efficiency of 12.3% has been reported for mesoporous TiO<sub>2</sub> nanoparticle based DSSCs is challenging due to the slow electron transport rate in the TiO<sub>2</sub>nanoparticlephotoanode during the electron transport process within the TiO<sub>2</sub> nanoparticle/5]. Other factors that limit the efficiency of TiO<sub>2</sub> nanoparticle based DSSC are the presence of numerous grain boundaries and the inherent higher charge recombination between injected photoelectrons in the trap states of TiO<sub>2</sub> nanoparticles and oxidized dye molecules or with tri-iodide electrolyte[6].

Finding of alternative suitable oxide materials for photoandode materials in DSSC is vital for further improvement of efficiency of solar cells. Among alternative oxides such as ZnO, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, SrTiO<sub>3</sub>, etc, nanostructured ZnO has emerged as the best alternative photoanode material for DSSC due to its wide band gap (3.3 eV), higher electron mobility and electron diffusion coefficient and easy to fabricate different nano/micro structures compared to  $TiO_2$ [7-9]. However, the highest reported efficiency for a DSSC fabricated with ZnOphotoanode and sensitized with Ru dye was found to be 6.6% which is lower than that of TiO<sub>2</sub> based DSSC .Despite higher dye loadings, better charge transport and reduced charge recombination properties of ZnO based photoanode, the solar cell performance of ZnO based photoanode was found to be inferior to that of  $TiO_2$  based photoanode. Several reasons have been attributed to poor solar cell performance of ZnO based photoanode and the foremost reasons are found to be; (a) the chemical instability in ruthenium dye solution. As Ruthenium dyes are not specially designed for ZnO anode, high acidity of the carboxylic acid binding groups of the dyes lead to dissolution of ZnO and precipitation of dye-Zn<sup>2+</sup> complexes and this insulating layer is reported to be hindering the electron injection from the excited dye to the conduction band of ZnO[10]; (b) the slow charge injection from ruthenium dye to ZnO as a result of low dielectric constant and low density of states in the conduction band of ZnO and poor wave function overlapping between dye molecules and ZnO particles[11,

12].Despite its lower cell performance, ZnO can be considered as the best alternative to  $TiO_2$  considering it's higher electron mobility, electron diffusion coefficient and ability to grow/fabricate different nano/micro structures[13, 14].

As a mean of enhancing solar cell performance of ZnO based photoanode, several 1-D ZnO nanostructures have been investigated. Such 1-D ZnO structures are expected to enhance the electron transport by several orders of magnitude faster than percolation through a random polycrystalline ZnO network[15]. The application of 1D ZnO nanostructures in the DSSC fields emerged recently due to the diversity of 1D ZnO nanostrucutres and their optical and electronic properties. Different ZnO nanostructures have been synthesized by various methods for diverse applications[16]. Different ZnO nanostructures such as nanowires[17, 18]nanorods, [19, 20]nanotubes, [21] tetrapods, [22] nanosheets[23]and hierarchical structures [24, 25] have been successfully investigated in ZnO-based DSSCs. The anode fabricated with various ZnO nanostructures have been positively influenced on dye loadings, electron transport properties and diminish charge recombination leading in enhancment in the overall solar cell performance[16].Nevertheless, DSSCs based on 1D ZnO nanostructures have not reached to the goal as expected, even though it shows fast charge transport properties. Such poor performance has been mainly attributed to the insufficient surface area of the 1-D structures for dye adsorption compared with nanoparticles and hierarchical structures and poor light scattering properties of 1-D ZnO structures[26].Interfacial modification of ZnO particles would provide a great way to tackle some of the problems mentioned above and such interfacial modifications such as, lithium ions insertion[27], deposition of metal particles[28] and deposition of a thin layer of TiO<sub>2</sub>[29]have been investigated and found to be effective methods in enhancing the overall solar cell performance of ZnO.In a recent investigation, Zhang et al demonstrated enhanced light scattering while retaining the high dye adsorption by introducing polydispersed aggregates consisting of ZnO nanocrystallites[30]. Considering factors such as surface area and high charge transport properties, constructing of well packed ZnO 1-D structures and hierarchical morphologies based on ZnO 1-D structures could be an effective way to improve the performance of ZnO based DSSCs. In this work, we investigated the aspect ratio depended solar cell performance of ZnO nanorods synthesized by varying the hydrothermal temperatures. Electron transport properties of dye sensitized 1-D ZnO nanorods with different aspect ratio was investigated 1-D ZnO nanorods with EIS measuremnts to understand the aspect ratio depended solar cell performance.

### 2. Methodology

### 2.1 Synthesis of ZnO nanorod

All reagents were analytical grade. In a typical synthesis, 2.00 g of zinc acetylacetonate (Sigma chemicals, AR) was dissolved in a 32 mL of ethanol and the solvent was ultrasonically treated for 5 min and the solvent was transferred in to a 48 mL of Teflon linear autoclave and heated at desired temperatures (100, 120, 140, 160 and 180°C) for 20 h. After the reaction, the autoclave was allowed to cool to room temperature and the white precipitate was separated by centrifuging, followed by several cycles of washing and re-dispersion with ethanol and finally dried in a vacuum oven. The ZnO NRs synthesized at 100, 120, 140, 160 and 180°C were labelled as ZnO NR – 1,ZnO NR – 2, ZnO NR – 3, ZnO NR – 4 and ZnO NR – 5 respectively.

### 2.2 Assembly of DSSC

Doctor-bladed method was used to prepare the ZnOphotoanode on FTO glass (Dyesol, sheet resistance  $8\Omega$ /sq) and ZnO coated FTO glass was sintered at 150 °C for 10 min, followed by treating at 300 °C for 15 min and finally at 450 °C for 30 min. Sintered ZnO photoanodes were soaked in a dye solution containing 0.3 mM N719 dye for 1 hour at room temperature and then washed with ethanol and dried in air. Iodide/triiodide redox couple was used as an electrolyte which consisted of tetrapropylammonium iodide (0.738 g), iodine (0.06 g), ethylene carbonate (3.6 ml) and acetonitrile (1 ml) and Pt was used as counter electrode.

### 2.3 Characterization

The morphologies of the different ZnO nanorods were characterized by scanning electron microscopy using a ZEISS SUPRA 50VP model scanning electron microscopy. UV–vis absorbance spectra are measured by a Shimadzu 2450 UV-vis spectrophotometer. The current-voltage measurements of DSSCswith cell area of 0.25 cm<sup>2</sup> were performed under one sun condition using a solar simulator (ORIEL Sol3A, AM 1.5 global, 100 mWcm<sup>-2</sup>). The intensity of the light was calibrated with a standard Si-reference cell. UV–vis absorbance spectra are measured by a Shimadzu 2450 UV-vis spectrophotometer. The external quantum efficiency (EQE) experiments were performed on a Bentham PVE300 unit with a TMc 300 monochromator based IPCE with a xenon arc lamp. A calibrated type DH Si photodetector was used as a reference. For EIS measurements, ZnO nanorod on FTO with cell area of 0.2 cm<sup>2</sup>was employed andEIS measurements (Zahner Zennium Electrochemical Workstation) were performed under illumination (ORIEL Sol3A, 100mW cm<sup>-2</sup>) while the cell was biased at different voltages. The AC signal was used with amplitude of 10 mV and frequency of 0.1Hz to 1 MHz range. Mott–Schottky analysis was performed in a three-electrode cell. The

ZnO photoanode without dyes were used as the electrode, a Ag/AgCl electrode served as the reference electrode, and platinum wire was used as the counter electrode.

#### 3. Results and Discussion

Our main focus was to investigate the variation of electronic as well as physical properties of 1-D ZnO nanostructures with the variation of aspect ratio of 1-D ZnO nanorods and how these electronic and physical properties affect their solar cell performance. In an earlier publication we reported the synthesis of 1-D ZnO nanorods with aspect ratios of 7.6, 6.8, 5.8, 5.4 and 4.4 setting the hydrothermal temperatures at 100, 120, 140, 160 and 180°C respectively. Figure 1 shows the variation of length and diameter and hence the aspect ratio of ZnO nanorods with the variation of hydrothermal temperature. A clear decrease in aspect ratio is observed with the increse in ZnO hydrothermal temperature.

SEM images of 1-D ZnO nanorods synthesized by hydrothermal method at 100 and  $180^{\circ}$ C having sapect ratios of 7.5 and 4.4 respectivly are shown in Figure 2 for comparison purpose. SEM images shown in Figure 2 clearly demonstrates the formation of cylindrical type 1-D ZnO nanorods with varying lengths and diamters with the variation of the hydrothermal temperature. Additionally, Figure 2b indicates the formation of significant random ZnO nanorod aggregates at high hydrothermal temperatures compared to low temperatures where as in low hydrothermal temperatures, densely packed bundles of nanorods are seen. The cross sectional image of both SEM images showed a cell thickness of ~ 12  $\mu$ m.

The solar cell performances of the photoelectrodes fabricated with ZnO nanords having different aspect ratios were found to be depended highly on the aspect ratio of ZnO naords. Figure 3a and 3b compares the J-V curves and IPCE of DSSCs fabricated with ZnO nanorod anodes having different aspect ratios with the same film thickness and sensitized with N719 respectively. The DSSC performance of these cells are summarized in Table 1. The results presented in Table 1 and Figure 3a clearly demonstrate the increase in  $J_{sc}$ ,  $V_{oc}$  and FF resulting in overall increase in solar cell efficiency with the increase in aspect ratio of ZnO. Higher solar cell efficiencies were noticed for higher aspect ratio ZnO nanorods and 23, 12 and 10% increase in  $J_{sc}$ ,  $V_{oc}$  and FF respectively were observed when the aspect ratio increases from 4.4 to 7.6 for the same thick ZnO nanorod anode films. The incident photon to current conversion efficiency (IPCE) spectra as a function of wavelength for ZnO NR based DSSCs are shown in Figure 3b. Among the solar cells fabricated,ZnO NR with aspect ratio  $\sim$ 7 exhibits a better photoelectrical response, and its IPCE is higher than that of the other

ZnO NR based DSSC over the entire wavelength region of 400-800 nm. IPCE values shown in Figure 3b are also in good agreement with the observed Jsc of ZnO NRs shown in Figure 3a. The maximum peak of IPCE curves for all the ZnO NR based DSSC exhibit at approximately 530 nm in the visible region and vary from approximately 60% to 40%.

It is interesting to note that the DSSCs fabricated with ZnO NR in this investigation showed higher  $V_{OC}$  compared to the  $V_{oc}$  reported for the solar cell fabricated with ZnO nanpartcles and increases monotonically from 0.55 V to 0.63 V when the aspect ratio increases from 4.4 to 7.6. The observed higher  $V_{oc}$  for 1-D ZnO NR is found to be correlated with the back-electron transfer rates of different aspect ratio of ZnO nanorods. It is known that the large resistance to the back-electron transfer from the injected electrons to the  $I_3^-$  in the electrolyte led to higher  $V_{oc}$  in DSSC due to accumulation of electron in the conduction band (CB).Though, the dark current measurement in DSSC cannot be related directly to the back electron transfer process due to difference in potential distribution across the electrode in dark and under light, a comparison of dark current between the investigated cells can provide useful information regarding the back electron transfer process. The back electron transfer from injected electrons and the  $I_3^-$  in the electrolyte of ZnO nanorods with different aspect ratio was investigated by dark IV measurements.

Figure 4shows the dark current-voltage characteristics of the DSSCs of ZnO NR film with having different aspect ratio with the applied bias from 0 to +0.75 V. The onset of the dark current for the ZnO NR with aspect ratio 4.4 occurs at a bias about +0.40 V, with a subsequent dramatic increase of dark current with the increase of potential. In contrast, when the aspect ratio increases from 4.4 to 7.6, the onset potential shifted to +0.50 V, hence the dark current for the high aspect ratio ZnO NR films were noticeably smaller than that of low aspect ratio ZnO NRs. The increase of the onset potential and the reduction of the dark current clearly demonstrated the decrease in back electron transfer with the increase of aspect ratio of ZnO NRs and hence enhanced V<sub>oc</sub> for higher aspect ratio ZnO nanorods can be justified. On the other hand, it is expected to have enhanced charge transport properties in ZnO nanorods due to 1-D nature of ZnO nanorods, minimizing the charge recombination. This type of diminished charge recombination in high-aspect 1-D ZnO nanorods will increase the electron density in ZnO nanorods shifting its onset potential toward a higher forward bias (negative shift of Fermi level) could also result in enhanced V<sub>oc</sub> values.

The dependence of FF with the variation of aspect ratio of ZnO NRs is similar to that of the dependence of  $V_{oc}$  on aspect ratio of 1-D ZnO NRs. Normally FF is associated with the resistance of the electron transport medium where decrease (increase) in resistance results in increase (decrease) in FF due to better electron transport and interconnectivity between particles[31].As given in Table 1, FF increases from 50.7 to 59.4% when the aspect ratio increases from 4.4 to 7.6 indicating enhanced electron transport properties of longer ZnO NRs.

Likewise the dependence of Voc and FF with the variation of aspect ratio of ZnO NRs, Jsc is also found to increase with the increase of aspect ratio of ZnO NRs. As given in Table 1,  $J_{sc}$  is as well found to be increased with the increase of aspect ratio of ZnO nanorods. It is known that the current density of a DSSC largely depends on the amount of adsorbed dye onto the nanostruttres in the photoanode. The adsorbed dye amounts on different ZnO photoanode is given in Table 1 which were calculated by desorbing the adsorbed dye on 1-D ZnO nanostructures. Dye loading amounts presented in Table 1 indicates the increase in dye loading amounts as the aspect ratio of ZnO nanorods increases and likewise J<sub>sc</sub> is also found to increase with the increase of aspect ratio. Higher dye adsorption of ZnO nanord synthesied at lower hydrothermal temperatures is due to high aspect ratio, high surface area resulting in higher dye adsorption compared to low aspect ratio, low surface area of ZnO nanords synthesied at higher hydrothermal temperatures [32]. Additionally, by SEM analysis, it was demonstrated the formation of well defined 1-D ZnO nanostructures at lower hydrothermal temperatrues while aggregates and short ZnO 1-D structures were observed at higher hydrothermal temperatures. Formation of well-packed ZnO 1-D structures results in yielding higher amounts of ZnO nanostructures in the photoandode and hence enhanced dye loadings in high aspect ratio 1-D ZnO nanorod photoanodes could be one of the reasons for higher Jsc for 120  $^{0}$ C hydrothermal systification of 1-D nanorods than that of 180  $^{0}$ C hydrothermal synthesized ZnO nanorods.

On the other hand, UV-vis diffuse reflectance spectra results of different aspect ratio ZnO NR films shown in Figure 5 indicate enhanced light scattering ability in the 400–800 nm region for ZnO NR synthesized at higher hydrothermal temperatures than that of lower hydrothermal temperatures. Nanorods are known to scatter light efficiencity and as a result of the higher light scattering capabilities, an enhanced photocurrent can be expected due to maximization of the light harvesting efficiency[33].As expalined before, ZnO synthesised at higher hydrothermal temperatures having low aspect ratio ZnO NR showed enehnced light

scattering effect compared to high aspect ratio ZnO NRs. Despite higher light scattering properties, photoanode films fabricated with low-aspect ratio ZnO nanorods showed lower photocurrent than that of higher aspect ratio nanorods indicating that the dye loading amount rather than light scattering is a significant factor for enhanced  $J_{sc}$ .

The above results clearly demonstrate the enhancement of solar cell performance of 1-D ZnO NRs with the increase of the aspect ratio and the possible factors that contribute to enahnced solar cell performanc could be due to several factors such as increase in dye loading amount, decrease in charge recombination, increase in charge transport properties, negative shift in flat band potentials and enhance light scattering effect or synergic effects of these properties. To assess the variation of charge transport and recombination with the variation of aspect ratio and their effect on solar cell performance, we quantify the chracteristic conductivity and capacitance of the photoanodes with different aspect ratio ZnO NR via EIS method. By EIS analysis, electron transport in an oxide film, recombination property at oxide/electrolyte interface, charge transfer at counter electrode/ electrolyte interface, and electron diffusion in an electrolyte can be investigated[34]. Furthermore, in the transmission line model, the charge transport mechanism in ZnO network is characterized by the chemical capacitance  $C_{\mu}$ , the electron transport resistance  $R_w$ , and the charge transfer resistance  $R_k$ , since these parameters directly related to the electron lifetime ( $\tau_n$ ), electron diffusion coefficient (D<sub>n</sub>), and diffusion length (L<sub>n</sub>)[35].

Figure 6 a, b shows the Nyquist plots of a DSSC fabricated with ZnO nanorods having aspect ratio 7.6 (highest solar cell performance) at different applied bias potential under 1 sun illumination and fitted according to the equivalent circuit derived from transmission line model of DSSCs. The Nyquist plots exhibit only two semicircles, where the semicircle at high-frequency  $(10^6 - 10^3 \text{ Hz})$  is associated to the redox reaction  $\Gamma/I_3^-$  at the Pt/electrolyte interface ( $R_{pt}$ ), whereas the larger circle at mid-frequency  $(1 - 0.01 \text{ Hz})^-$  region is assigned to the electron transport ( $R_w$ ) in the ZnO NR network and the electron transfer at the oxide/electrolyte interface ( $R_k$ ) for the charge transfer processes occurring at the ZnO NR/dye/electrolyte interfaces. The charge transport resistance ( $R_w$ ) is overlapped with  $R_k$  in the semicircle at the mid-frequency region due to the characteristic of  $R_k \gg R_w$ [36].However, under reduced bias voltage from the open circuit condition,  $R_w$  becomes larger due to low electron concentration in conduction band of an oxide and can be distinguished from  $R_k$ , as shown in Figure 6b. The potential dependences of the transmission line parameters of Rk, Rt

and Cm were extracted from the EIS fits. Figure 7 shows the variation of  $R_k$ ,  $R_w$ ,  $C_\mu$  and  $\tau_n$  with the applied voltage for solar cells fabricated with ZnO nanorods having aspect ratios of 7.6, 5.8 and 4.4 under illumination and the calculated  $R_k$ ,  $R_w$ ,  $C_\mu$  and  $\tau_n$  at an applied potential bias at Voc under 1 sun illumination are given in the Table 2.

As shown in Figure 7-a, the semilogarithmic plot of the recombination resistance  $(R_k)$  vs bias potential indicates the decrease of  $R_k$  with the increase of forward bias for all ZnO nanords. The potential dependence of  $R_k$  which was determined in terms of the Buttler-Vollmer transfer factorwas found to be the same for all three ZnO nanorods despite having different aspect ratio.[37]However, it is clearly seen higher  $R_k$  values for high-aspect ratio ZnO nanrods than the low aspect ratio ZnO nanaorods. A larger charge recombination resistance is a feature generally necessary for good performance of DSSC.[38] The higher charge transfer resistance for high aspect ratio ZnO nanorods implies that the higher fill factor and open circuit potential. The dependence of  $R_k$  on the aspect ratio can be understood by considering the ZnO preparation conditions. As explained earlier, for the synthesis of high and low aspect ratio ZnO NRs, low and high hydrothermal temperatures were employed respectively. It is known the formation of oxygen vacancies when oxides are formed at high temperatures [39] and these oxygen vacancies may trap the conduction band electrons and act as recombination centers for the oxidized species in an electrolyte through the interface. As such, as shown in Table 2, for the ZnO NRs having low aspect ratio formed at higher hydrothermal temperatures could expect to have lower Rk and hence lower FF as well as Voc and hence observed FF, Voc for the photoelectrode fabricated with low aspect ratio ZnO NRs can be justified.

The dependence of the macroscopic charge transport resistance ( $R_w$ ) on aspect ratio of ZnO nanorods is shown in figure 7b. Compared to low-aspect ratio ZnO nanords, the high aspect ratio ZnO nanorods showed lower  $R_w$  at any given equal applied potential which will be a beneficial factor for high performance solar cells. The transport resistance was decreased with the increase of aspect ratio of ZnO NRs indicating that the electron transport along the ZnO NR is facilitated for the NRs having longer length and higher diameter ZnO NRs. The higher  $R_w$  for the low aspect ratio ZnO NRs could be due to formation of aggregates of shorter ZnO 1-D nanords (Figure 1 c,e) resulting in poor electron transport through the 1-D ZnO nanostructures. Formation of aggregates of ZnO nanorods was clearly observed with ZnO nanorods synthesized prepared at higher hydrothermal temperatures and

these shorter nanorods aggregates are unfavorable for the movement of electrons to through the ZnO NR network. The observed higher Rw of the low aspect ratio ZnO NRs could be explained in terms of mean free path. For the electrodes prepared with high and low aspect ratio ZnO NRs havaing same film thicknees, the electrons have to pass through different number of boundaries for the same traveling distance depending on the NR lengths as shown schem 1. As such, electron in low aspect ratio ZnO NRs (shorter NRs) meet more boundries than high aspect ratio ZnO NRs (longer NRs) resulting in large Rw. Furthermore as the crystallite size of different ZnO nanostrucutres synthesized by differnt hydrothermal temperatures found to be the same having ~ 20 nm large ZnO crystallites, a variation of crystalline properties cannot be the major contribution for the observed variation of Rw with the hydrothermal temperatures.

The other important parameter of photovoltaic operation is the cpacitance behavior of photoelectrode at forward bias voltage. The capaciatance of the photoelectrodes prepared with the different aspect ratio ZnO NRs are shown in Figure 7c. As shown in Figure 7c, the chemical capacitance of all three ZnO nanorods having aspect ratio 7.6, 5.8 and 4.4 is exponentially increased with the increase of the bias voltage and the capicatnace was found to increase with the increase of aspect ratio of ZnO NR. The increase in C<sub>µ</sub> with the increase of forward could be attributed to increase in electron density (n) of the ZnO nanostructures due to dye injection raising the quasi-Fermi level (EF) under illumination. Since  $dE_F = -qdV$ , where q is the elementary charge, the C<sub>µ</sub> can be explained by the relationship of voltage to carrier density in EIS by the form (1) and the exponential increase in C<sub>µ</sub> with the increase of forward could analyze using the following model (2).[39]

$$C_{\mu} = q\left(\frac{dn}{dV}\right)(1)$$

$$C_{\mu} = Co_{,\mu} exp\left(-\alpha \frac{qV}{k_BT}\right)$$
 (2)

where,  $C_a$  is the pre-factor,  $k_B$  is the Boltzmann constant, *T* is the temperature (300 K), *e* is the elementary charge, *V* is the applied potential and  $\alpha$  is a coefficient describing an exponential distribution of trap states below the conduction band edge ( $\alpha < 1$ ). As explained earlier, the  $C_{\mu}$  of the device fabricated with high aspect ratio ZnO nanorods is higher than that of the low aspect ratio ZnO nanords, indicating higher electron concentration in high aspect ratio ZnO NRs. A higher capacitance indicates a better electrical communication between the quasi-Fermi level in the semiconductor and the conducting substrate as a result

of better interconnection of ZnO nanorods yielding facile electron transport minimizing the electron– hole recombination. The smaller slope ( $\alpha$ ) of  $C_{\mu}$  for the low aspect ratio ZnO NRs indicated a broader distribution of the density of trap states (DOS) in low aspect ratio ZnO NRs.<sup>38</sup> The broader distribution of trap states in low aspect ratio ZnO NRs may results in enhanced charge recombination as well as positive shift in flat-band potential leading to lower Voc of the device fabricated with low aspect ratio ZnO NRs and hence observed lower Voc for lower aspect ratio ZnO NRs can be further justified.

The other important parameters of photovoltaic operation are the electron lifetime  $(\tau_n)$ , diffusion coefficient (D<sub>n</sub>) and diffusion length (L<sub>n</sub>) which can be derived from measured Rk, Rw and Cµ by EIS measurements. The  $\tau_n$ , D<sub>n</sub>, and L<sub>n</sub> under illumination are plotted against applied bias voltage and given in Figure 7d, Figure 8a and b respectively. As shown in Figure 7d,  $\tau_n$  ( $\tau_n = R_{ct}C_{\mu}$ ) decreases exponentially with the increase of the applied voltage for all the ZnO NRs. However the electron lifetime observed for high aspect ratio ZnO nanords is several times larger than that of lower aspect ratio ZnO nanostructures.

The electron diffusion coefficient  $(D_n)$  was calculated by following equation (3) whereas, *L* is film thickness of the ZnO NR photoanode.

$$D_n = \frac{L^2}{R_w C_\mu} \tag{3}$$

The highest  $D_n$  is observed for ZnO NRs with higher aspect ratio and the  $D_n$  values exponentially increase with increase the bias voltage (figure 8a). Table 02, further shows that the ZnO NR DSSC – 1 and ZnO NR DSSC – 2 have high  $D_n$  value which will favor for the better electron transport for long distance with less hindrance. On the other hand, the electron effective diffusion length,  $L_n$  (defined as the mean distance a photoelectron will travel before recombine) in the photoanodes convince the competition between transport and recombination of electrons which can be expressed as in equation (4).

$$Ln = \sqrt{D_n} \tau_n \tag{4}$$

 $L_n$  is an important parameter in DSSCs since diffusion is dominated as an electron transport process through the nanostructured semiconductor photoanode.Furthermore, it is used as a measurement of charge collection efficiency in DSSCs.[40]If  $L_n$  is greater than the nanostructured semiconductor layer thickness (*L*), then can be expected high charge collection efficiency.[40]The nanorods aggregates synthesis at low temperature has higher  $L_n$  than the high temperature synthesis nanorods (Figure 8b and Table 2). This observation implies that charge transport and charge collection are better for high aspect ratio ZnO NRs

synthesised at low temperature than that of the low aspect ratio ZnO NRs nanorods synthesised at high temperatures. Under the working condition of DSSCs (at Voc), it is found that the  $L_n$  is much higher than the ZnO NR layer thickness (Table 2). This implies that thicker photoanode films would be expected much more performance however, voltage loss connected with increasing L, would limit the optimum film thickness of photoanode.

The charge collection efficiency ( $\eta_{CC}$ ) is an important parameter in determining the performance of DSSCs based on composite electrodes containing nanoparticles and 1-D structures and has been used to quantify the improvement of Jsc. The charge collection efficiency can be estimated from the relationship of ( $\eta_{CC}=(1-\tau d/\tau n, \tau d=\tau n/(Rk/Rw)$ ) where  $\tau n$  and  $\tau d$  are electron lifetime and diffusion time respectively. The calculated  $\eta_{CC}$  were 90, 80 and 75% for ZnO NRs having aspect ratio of 7.6, 5.8 and 4.4 respectively indicating the enahnement of charge collection efficiency for higher asepect ratio ZnO NRs. As mentioned earlier, improvement in charge collection efficiencies will result in an enhancement of the short circuit current for high aspect ratio ZnO NRs than low aspect ratio ZnO NRs and can be justified the superior solar cell performance of high aspect ratio ZnO NR based photoelectrds. Considering all the cases of ZnO NR aggregates, ZnO NR – 1 and 2 photoanodes have the high  $D_n$  and higher  $L_n$  which favor for the electron transport (Table 02). As a result, the ZnO NR DSSC – 2 showed a remarkable increase of the short circuit current density with compared to other nanorod aggregates.

#### 4. Conclusions

In summary, different aspect ratio ZnO NRs were synthesized by changing the hydrothermal temperature. The solar cell perfomance was highly depended on morphological nature and the aspect ratio of ZnO NRs. High aspect ratio ZnO NRs formed at low hydrothermal temperatures exhibit superior electron transport properties than low aspect ratio ZnO NRs due to the advantage of structural improvement of ZnO NRs. Additionaly, high aspect, one-dimensional ZnO NRs could provide a direct path for carrier transport, resulting in small electron transport resistance, long electron diffusion length and diffusion coefficient while reducing the charge recombination. Overll charge collection is higher for high aspect ratio ZnO NRs than low aspect ZnO NRs resulting in efficient solar cell performance for DSSC based on hish aspect ZnO NRs.

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### Tables

Table 1. Photovo at one sun illumin	Itaic paramete nation.	rs of the DSSCs	fabricated with o	different aspect r	atio ZnO NRs
DSSC	ZnO NR - 1	ZnO NR - 2	ZnO NR - 3	ZnO NR - 4	ZnO NR – 5
V <sub>oc</sub> (mV)	626.8	602	574.2	560.4	553.8
J <sub>sc</sub> (mA/cm <sup>-2</sup> ) Fill Factor (%) Efficiency (%)	10.74 59.49 4.00	12.96 59 4.60	11.77 56.33 3.81	8.70 54.67 2.66	7.52 50.71 2.11
Adsorbed Dye Amount (mol/cm <sup>2</sup> ×10 <sup>-8</sup> )	5.038	5.781	5.478	3.084	2.607
ZnO NRs synthe - 2, ZnO NR - 3,	sized at 100, 1 ZnO NR – 4 a	20, 140, 160 an nd  ZnO NR – 5	id 180 °C were la respectively.	abelled as ZnO N	IR – 1 <u>, </u> ZnO NR

Solar Cells	$R_k (\Omega.cm^2)$	$R_w \left(\Omega.cm^2\right)$	$C_{\mu}$ ( $\mu$ F/cm <sup>2</sup> )	$\tau_n (ms)$	D <sub>n</sub> (cm <sup>2</sup> .S <sup>-1</sup> ) X
ZnO NR-1	7.14	0.16	817.5	5.83	10.74
ZnO NR-2	7.49	0.15	839.5	6.29	11.37
ZnO NR-3	8.58	0.28	603.3	5.17	8.51
ZnO NR-4	8.69	0.36	480.7	4.17	8.25
ZnO NR -5	9.06	0.44	400.7	3.63	8.10
ZnO NRs synth – 2, ZnO NR – 3	nesized at 100, 1 3, ZnO NR – 4 a	20, 140, 160 ar nd  ZnO NR – 5	d 180 °C were la respectively.	abelled as Z	2nO NR – 1 <u>, </u> Zn
ZnO NRs synth - 2, ZnO NR - 3	nesized at 100, 1 3, ZnO NR – 4 a	20, 140, 160 ar nd ZnO NR – 5	d 180 °C were la respectively.	abelled as Z	nO NR – 1 <u>, </u> Zn
ZnO NRs synth - 2, ZnO NR - 3	nesized at 100, 1 3, ZnO NR – 4 a	20, 140, 160 ar nd ZnO NR – 5	d 180 °C were la respectively.	abelled as Z	nO NR – 1 <u>, </u> Zn
ZnO NRs synth - 2, ZnO NR - 3	nesized at 100, 1 3, ZnO NR – 4 a	20, 140, 160 ar nd ZnO NR – 5	d 180 °C were la	abelled as Z	nO NR – 1 <u>, Z</u> n
ZnO NRs synth - 2, ZnO NR - 3	nesized at 100, 1 3, ZnO NR – 4 a	20, 140, 160 ar <u>nd ZnO NR – 5</u>	d 180 °C were la	ibelled as Z	nO NR – 1 <u>, Z</u> n

### Figures



Figure 1. Variation of the aspect ratio of ZnO NR with the variation of hydrothermal temperature.



Figure 2. Surface SEM images of (a) ZnO NR - 1 and (b) ZnO NR - 5



Figure 3. (a) J-V curves and (b) IPCE spectra of ZnO NR based DSSCs at 1 sun illumination.



Figure 4. Dark J-V characteristics of ZnO NR based DSSCs.



Figure 5 . Diffuse reflectance of bare ZnO NR prepared on Fto glass substrate



Figure 6. (a) Nyquist Plot of ZnO NR-1 based DSSC at different bias voltages under 1 sun illumination and (b) enlarged Nyquist plot of the same in high frequency region.



Figure 7. (a) Interfacial charge recombination resistance ( $R_k$ ), (b) electron transport resistance ( $R_w$ ), (c) chemical capacitance ( $C_m$ ) and (d) electron lifetime ( $t_n$ ) of different ZnO NRs.



Figure 8. (a) Electron diffusion coefficient and (b) electron diffusion length of different ZnO NRs.



**Scheme 1.**Schematic diagram of possible electron pathways in (a) high aspect and (b) low aspect ratio ZnO NRs.

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