Low temperature carving of ZnO nanorods into nanotubes for dye-sensitized solar cell application

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High aspect ratio zinc oxide (ZnO) nanotubes (NT) were synthesized based on a two-steps approach. In the first step, ZnO nanorod (NR) arrays were prepared by chemical bath deposition from an aqueous of zinc nitrate. In the second step, the cores of ZnO NRs were carved selectively in a KCl solution, resulting in the formation of a tubular structure. The influence of KCI concentration, temperature, and immersion time on the ZnO NT formation process was completely characterized and investigated. 12.5 μm NRs and NTs have been utilized to manufacture dye-sensitized solar cells (DSSCs) and as a result, conversion efficiencies of 1.06% and 2.87% were obtained, respectively. Electrochemical impedance spectroscopy measurements have demonstrated that the NTs could acquire a higher electron lifetime compared to NRs which causes a faster electron collection. The overall improvement in NT-based DSSC performance demonstrates a new approach to enhance the efficiency of dye-sensitized solar cells.

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1. Introduction

Dye-sensitized solar cells (DSSC) have been increasingly investigated as a candidate for conventional inorganic solid solar cells. TiO₂ and ZnO are commonly regarded as the most promising electrode materials for DSSCs due to their wide band gaps, which are suitable for interfacial electron transport. Regarding solid state physics, ZnO-based DSSCs should perform almost equally well as corresponding TiO₂-based DSSCs [1,2]. Compared to TiO₂, ZnO as an electrode has even more advantages including much easier morphology control, better electron mobility and thin film crystallization at lower temperature, which is useful in flexible-type DSSCs based on plastic substrates [3–5]. On the other hand, DSSCs based on zinc oxide (ZnO) nanostructures, have a limited solar energy conversion efficiency (η) (less than 7%) [6–9].

ZnO is a promising wide direct bandgap semiconductor (3.3 eV) with a huge excitonic binding energy of 60 meV at room temperature [10]. During the last decade, it has attracted much attention to become a candidate in many electrical and optical applications due to its unique properties. However, its extremely weak hole transport characteristics have obstructed the performance of ZnO junction-based devices [11]. ZnO has been widely proposed for transparent electronic, optoelectronic and electrochemical devices such as gas sensors [12], solar cells [13–15] and light emitting diodes [16–19]. This material has a rich family of nanostructures in different shapes and sizes. NRs and NTs are the most important nanostructures because of their single crystal hexagonal wurtzite structure. There are several methods to synthesize ZnO nanostructures [20–24]. Among these methods, aqueous chemical growth (ACG) approach is the most favorable and economical one which in addition to its high yield, is less hazardous and compatible with various substrates [25].

There are several reports on the growth and carving of these nanostructures; however, the present study focuses extensively on carving the NRs to NTs. We have used indium doped tin oxide (ITO) glass substrates to fabricate ZnO NT arrays. First of all, ZnO NR arrays were synthesized in an aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine. In the second step, the polar surface of hexagonal ZnO NRs was selectively etched in a KCl solution. The effects of KCI concentration, etching time, and temperature during the second step have been investigated, and the grown materials were utilized to fabricate the dye-sensitized solar cells. The ZnO nanotube absorption effect, electron life time, electron transport time, effective electron diffusion coefficient and electron transport resistance are predicted empirically from the electrochemical impedance spectroscopy for the first time which are indeed in agreement with other methods.

2. Materials and methods

2.1. Synthesis of ZnO NT arrays on ITO glass substrate

Indium doped tin oxide (ITO) glasses were used as the substrates for the growth of ZnO NRs. Aluminum doped zinc oxide (AZO) seed layer was sputtered on the ITO glass substrate by radio frequency sputtering. The growth solution contained zinc...
nitrile hexahydrate (Zn(NO₃)₂·6H₂O, Merck, 25 mmol), hexamethylenetetramine ((CH₂)₆N₄, Merck, 12.5 mmol) and 5–7 mM polyethylenimine (PEI) in deionized (DI) water. The one dimensional NRs were grown hydrothermally by dipping the substrates upside down into the solution. The growth process was performed at 90 °C and led to NRs with lengths of 12.5 μm which could be observed in cross-sectional SEM pictures. In order to achieve magnificant optical properties, a post-growth carving process was performed on the NRs. To carve these NRs to NTs, the substrates were placed upside down in aqueous solution of potassium chloride (KCl). The experiment was systematically designed for different etching times, temperatures and KCl concentrations to achieve the optimized process. For complete conversion to NTs, these variables must all be optimized with respect to the dimensions of the original ZnO NRs. The morphology of the prepared ZnO NTs thin film electrodes were observed by field emission scanning electron microscopy (FESEM, Hitachi S-4700) and transmission electron microscopy (TEM, JEM-2010-JEOL, Japan). X-ray diffraction (XRD) measurement was performed to explore crystalline structure of ZnO NTs by Philips Xpert, with Cu Kα radiation (λ = 0.15418 nm). UV-visible absorption spectra were performed on a Cary 500 spectrophotometer. To investigate optical properties, photoluminescence (PL) measurements were carried out at the ambient temperature by Cary Eclipse fluorescence spectrophotometer with a He–Cd laser of 325 nm wavelength as the excitation source.

2.2. Fabrication of ZnO-based DSSC

The ZnO NRs and NTs were used as photoanodes in DSSCs with 12.5 μm thickness and an area of about 0.25 cm². Before assembling the solar cell, the NT and NR photoanodes were annealed in a (Zn(NO₃)₂·6H₂O, Merck (0.2 mol)) aqueous solution for 5 min and then placed in a furnace to anneal at 450 °C for 30 min. Annealed ZnO electrodes were sensitized in an ethanol solution (0.2 mmol) of N719 dye (ruthenium (2, 2’-bipyridyl-4, 4’-dicarboxylate) 2(NCS) 2, Dyesol, Australia) for 1 h at 60 °C. The excess unanchored dyes were rinsed using absolute ethanol and dried in air, then covered with platinum as the counter electrode. The internal space of the cell was filled with liquid electrolyte (tetrabutyl-ammonium iodide (0.6 mol), LiI (0.5 mol), l₂ (50 mmol), 4-tertbutylpyridine (0.5 mol) in acetonitrile) dissolved in acetonitrile by capillary action. The effect of ZnO NRs and NTs over DSSC functionality was then measured and compared.

The density–voltage (J-V) curves were collected using a simulated sunlight (luzchem-IVIUM) at intensity of 100 mW/cm² under irradiation of AM1/5. Electrochemical impedance analysis on the cells, under standard irradiation, was carried out using luzchem-IVIUM in an open-circuit voltage of cells. Impedance measurement of cells was recorded in a frequency range from 0.01 Hz to 0.1 MHz with ac amplitude of 10 mV. The Z-view modelling program was used to model and fit the spectra data by inserting a built-in extended element (DX type11 – Bisquert #2) in the equivalent circuit, which allows modelling of the transmission line.

3. Results and discussions

The density, size and morphology of the ZnO NRs and NTs were evaluated with field emission scanning electron microscope (FESEM).

The impact of the KCl concentration was studied for samples on which 12.5 μm long NRs were grown using the ACG method. As it is illustrated in Fig. 1(a)–(d), hexagonal-shaped ZnO NRs were grown uniformly on a large area which is suitable for conducting the carving experiment. In the carving process, different concentrations of the KCl solution (2, 3, 4 and 5 M) at 90 °C were used, for 5 h, to etch the NRs.

Fig. 1(a)–(d) demonstrates the NTs after the carving process in each one of the etching solutions. As illustrated in Fig. 1(d), the NRs in the 5 M KCl solution were almost washed off the substrate and only small areas of NTs were left. It is worth mentioning here that the SEM pictures on samples, which were etched in 3 and 4 M solutions, were almost similar.

Fig. 2 is the XRD analysis of these samples. The strong peak in all samples for (002) planes displays the perfect orientation of the NT along the c-axis perpendicular to the substrate. The theta–2theta curve of the sample etched in 5 M solution shows a relatively strong (100) peak which relates to some flipped over NTs on the substrate that we captured by FESEM. The other interesting feature in this figure is that when one compares the peak intensity of a specific non-polar plane of the NTs; e.g. (103) from bottom-up (2M:193, 3M:164, 4M:137, 5M:104); a slight decreasing trend is observed. This can be elucidated by the fact that, as the NRs continuously carve and (002) the peak intensity weakens, the height of the tubes also decreases. To form these NTs in this alkali solution, the following reaction occurs: [26]

\[
\text{KCl} + \text{H}_2\text{O} \rightarrow \text{KOH}^- + \text{HCl}
\]

(1)

\[
\text{ZnO} + 2\text{OH}^- \rightarrow \text{ZnO}_2^{2-} + \text{H}_2
\]

(2)

![Fig. 1. SEM pictures from samples carved in (a) 2, (b) 3, (c) 4 and (d) 5 M KCl solutions.](image)
Because there is no other assistant reagent in the chemical solution for carving the NRs, the preferential etching happens. The (002) polar planes, where the etching process is favored, are metastable and acquire higher surface energy. These surfaces are located at the most defected part of the rods which is the circumference of the central $c$-axis. This leads to the carving process of the NRs to NTs in this solution. It can be seen in Fig. 1(a) that even 2 M KCl solution is enough for the tube conversion.

The process temperature is another important parameter which must be optimized. Fig. 3(a)–(d) shows the morphology of the samples when the process temperature varies (75, 80, 85 and 90 °C). As discussed earlier, 2 M KCl solution was chosen for this experiment. Samples were situated in the solution for 5 h.

The inner and outer walls of the tubes are almost perfect in all samples in this figure; however, Fig. 4 can give us valuable information about the progress of the process inside the tubes. The (002) peak decreases as we increase the temperature of the solution. Nonetheless, opposite to what we achieved in Fig. 2, here in Fig. 4 the intensity of the non-polar planes are increasing; e.g. (102) plane intensity is 106, 146 and 222 for 75, 85 and 90 °C, respectively. This means that even though the NT conversion is happening, we do not observe any shrinkage in the length of the tubes. The length began to shrink at 95 °C. Therefore, 90 °C was selected in the last series of experiments for optimizing the carving time.

The last parameter for determining the final optimized carving process is the carving time.

Fig. 5(a)–(d) displays the result of the etching time variation on samples in 2 M KCl solution at 90 °C. After 3 h of carving, the polar (002) planes are still visible in FESEM images which means that

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![Fig. 2. XRD of the ZnO NTs carved in 2, 3, 4 and 5 M KCl solutions.](image1)

![Fig. 3. SEM pictures from samples carved in 2 M solution at (a) 75, (b) 80, (c) 85 and (d) 90 °C.](image2)

![Fig. 4. XRD of the ZnO NTs carved in 2 M solution at 75, 85 and 90 °C.](image3)
the process must continue for a longer time (see Fig. 5(a)–(b)). After 7 h, not only the polar planes but also the non-polar planes are etched and we see an uneven top surface for the walls. This can also be viewed in Fig. 6 in which the peak intensity for (102) and (103) planes decreases dominantly when etching time passes 5 h.

Up to 5 h, the non-polar faces’ intensities have a very slow decreasing rate; however, as it is shown, after 7 h the walls are etched and the intensity decreases dominantly. All this leads to the conclusion that the best choice of NTs for the DSSC manufacturing is the one fabricated in 2 M KCl solution at 90 °C for 5 h.

Further morphological characterization of the ZnO NRs and NTs were performed by TEM images. Fig. 7(a) displays a typical TEM image of the ZnO NRs, which clearly indicates the rod-like morphology of the obtained ZnO sample. The accompanying SAED pattern (see the inset in this figure) shows that the ZnO NR was a single crystal with a hexagonal wurtzite structure. Fig. 7(b) presents the general picture of an individual NT with 1.2 μm in length. The TEM images demonstrate that the shapes of the rod and tube are similar, which makes it difficult to identify them. However, there is a color difference between the edge and the center at the end of the NT structure which is due to the hollow shape of the tube. The color of the center is brighter because the NT is hollow, as also reported by Zhang et al. [27]. As shown in the inset of Fig. 7(b), the ZnO NT has also a single-crystal wurtzite structure. Fig. 7(c) and (d) are the cross-sectional pictures of the final ZnO NRs and NTs. It can be seen the lengths of the nanostructures were remained unchanged after conversion (12.5 μm).

Fig. 8 compares the current density–voltage (J–V) characteristic of DSSCs fabricated using aligned ZnO NRs and NTs photoanodes. The corresponding J–V characteristics were measured under 100 mW/cm² light intensity (1.5AM) and summarized in Table 1. During the photocurrent measurements, the cell efficiency (η) is expressed by the following equation:

\[
FF = \frac{V_{opt}I_{opt}}{V_{oc}I_{sc}}
\]

\[
\eta = \frac{(FF \times |I_{sc}| \times V_{oc})}{P_{in}}
\]

where \(P_{in}\) is the power of incident white light, \(FF\) is fill factor, \(V_{opt}\) and \(I_{opt}\) are voltage and current density for maximum output power, and \(V_{oc}\) and \(I_{sc}\) are open circuit photovoltage and short circuit photocurrent, respectively. Comparing the open circuit voltage, short circuit photocurrent, fill factor and power conversion efficiencies, it can be determined that the morphology of ZnO photoanodes have a profound impact on the performances of DSSCs. DSSCs fabricated with aligned ZnO NTs photoanode have achieved a high solar-to-electricity conversion efficiency (η) of 2.87% with a high short circuit current (\(I_{sc}\)) of 8.83 mA/cm², open circuit voltage (\(V_{oc}\)) of 0.6 V, and fill factor (FF) of 0.54.
However, DSSC fabricated with aligned ZnO NRs photoanode exhibits a relatively low $\eta$ of 1.06% with $J_{sc}$ of 4.17 mA/cm$^2$, $V_{oc}$ of 0.49 V and FF of 0.51. The ZnO nanowire and nanotube DSSCs used in this study were not as efficient as typical nanoparticle DSSCs due to their lower surface area and thus, lower light harvesting efficiency.

The aligned ZnO NTs photoanode has appreciably enhanced the conversion efficiency by three times with significantly improved $J_{sc}$, $V_{oc}$ and FF. The enhanced photovoltaic performances and the improved $J_{sc}$ are mainly related to the improved light harvesting efficiency. Dye desorption experiments were used to study dye adsorption on the surface of ZnO nanowires and nanotube. After the nanowire and nanotube substrates were dyed, they were immersed in 5 ml of 1 M aqueous NaOH solution to remove the dye. Fig. 9 shows the optical absorption spectra of NaOH solutions containing dye desorbed from ZnO nanowire and nanotube. The

### Table 1

<table>
<thead>
<tr>
<th>DSSC</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>Fill factor</th>
<th>$\eta$ (%)</th>
</tr>
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<tbody>
<tr>
<td>ZnO NTs</td>
<td>8.83</td>
<td>0.6</td>
<td>0.54</td>
<td>2.87</td>
</tr>
<tr>
<td>ZnO NRs</td>
<td>4.17</td>
<td>0.49</td>
<td>0.51</td>
<td>1.06</td>
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</table>

Fig. 9. Absorption curves for aqueous NaOH solutions containing dye desorbed from ZnO nanotube and nanowire photoelectrode.
concentration of desorbed dye determined by UV–Vis spectroscopy was used to calculate the amount of dye in the sensitized samples. The results reveal that absorbance of the ZnO nanotube is higher than that of ZnO nanowire. The high absorbance of the photoelectrode indicates that greater amount of increasing the surface profile of the photoelectrode by carving ZnO nanowire to favor high dye loadings.

This is occurred due to a few reasons: higher surface contact area of the NTs with dye compared to NRs, higher dye absorption due to the light resonance in NT structures and also partial absorption of light by NTs.

The higher absorption of light by the NTs compared to the NRs can be seen in Fig. 10. This figure displays the photoluminescence (PL) spectra of the NRs in contrast with NTs carved at different intervals. An intensive sharp UV emission at ~390 nm is attributed to the free exciton emission from the wide band gap of ZnO structures. A broader green emission at ~618 nm is related to the recombination of electrons in single occupied oxygen vacancies in ZnO nanomaterials [28]. All of the samples in this figure have a wide peak of absorption in the visible range which is definitely one of the reasons that gives the ZnO NRs/NTs a high potential for this application. However, inserting intentional defects in the crystal structure (or surface energy levels in the band structure) through the carving process will amplify this peak which means higher absorption in the visible range. The unusual decrease in the intensity of this peak for the sample which was being carved for 7 h is due to the fact that the long carving time decreased the length of the tubes significantly.

Thus, ZnO NTs present a reasonably high performance charge collection and transition to the electrolyte layer. This performance measured here on DSSCs with photoanode using aligned ZnO NTs is significantly higher than the previously reported values [29,30].

For a detailed investigation of the transport properties of ZnO NTs and NRs, the impedance measurements were carried out under the illumination of AM1.5 100 mW/cm$^2$, applying a 10 mV ac small signal over the frequency range of $10^{-2}$–$10^5$ Hz using a potentiostat and a frequency response analyzer. This analysis determines the correlation between the electrical and structural properties of the material. The impedance spectrum of ZnO NTs and NRs is shown in Fig. 11. This spectrum shows only a semi-circle that in intermediate frequency can be attributed to the grain boundary effect. To extract the recombination and transport behavior, we have fitted the spectra with the help of the equivalent circuit of the transmission-line model [31,32].

The electron transport resistance ($R_t$) in the nanostructure is strongly dependant on the crystallinity of the material. The charge transfer resistance ($R_{ns}$) is related to the recombination of an electron with electrolyte. The electron lifetime ($\tau_n$), electron transport time ($\tau_d$), the effective electron diffusion coefficient ($D_{eff}$) and the first-order reaction rate constant for electrons being lost ($K_{en}$) in ZnO NRs- and ZnO NTs-based DSSCs are calculated from the impedance analyzes and listed in Table 2. The Nyquist plots (Fig. 11) show that the radius of the right semi-circle of the NT-based device is larger compared to that made using the NRs. The larger semi-circle indicates an increase in the charge transfer resistance and therefore, a decreased electron lifetime. The lifetime $\tau_n$ can be calculated using the equation $\tau_n = 1/(2\pi K_{en})$, where $K_{en}$ is the peak frequency, which for the NTs and NRs were respectively 0.38 and 0.23 Hz at $V_{oc}$. These frequencies correspond to a $\tau_d$ of 0.061 s and 0.036 s, respectively, i.e., the $\tau_d$ of the NT-based devices is two times larger than that of the NR-based devices. The longer $\tau_n$ of the device fabricated using the NT-like morphology indicates more effective suppression of the back reaction between electrons in its conduction band and $\Gamma^{-3}$ ions in the electrolyte. The increased $\tau_d$ is thought to be another source of high $J_{sc}$ and $\eta$ of the device fabricated using the NT-like morphology. As mentioned in Table 2, the steady state electron density ($n_i$) in ZnO NT DSSCs is one order of magnitude larger than that in ZnO NRs DSSC. Table 2 also compares the charge collection time ($\tau_d$) and the charge lifetime ($\tau_n$) for these devices. According to this table, $\tau_d$ is two orders of magnitude faster than $\tau_n$ in DSSC based on ZnO NT. The faster electron collection helps the accumulation of electrons in the conduction band of ZnO NT, leading to a rise in electron density (chemical potential) of the ZnO, and an increase in $V_{oc}$. Moreover, this faster electron collection limits the reverse electron transfer. Hence, more electrons can reach the collecting electrode which explains an enhanced $J_{sc}$ in NT DSSC compared to the NR one, as represented in Table 1. It is worth mentioning that effective diffusion coefficients ($D_{en}$) in ZnO NTs-based DSSC are also larger than that of ZnO NRs-based DSSC.

As represented in Table 2, the electron recombination resistance $R_{rc}$ in the ZnO-NTs DSSC is larger than that in ZnO NRs, whereas, the electron transport resistance $R_t$ in ZnO-NT is smaller than that in ZnO-NR. The smaller $R_{rc}$ in ZnO NR, which indicates the occurrence of more abundant electron interfacial recombination, is consistent with the observation of lower FF in the cell. In addition, smaller $R_{rc}$, in the ZnO NRs results in lower effective diffusion coefficient, which influences the $J_{sc}$ of the ZnO-NR DSSC as well. Further examination of the impedance results also showed that the recombination rate of electron and electrolyte ($K_{en}$) in the NT cells is smaller than that in the NR cells.

**Fig. 10.** Photoluminescence (PL) spectra of the ZnO NTs carved in 2 M KCl solution at 90 °C for 0, 3, 5 and 7 h.

**Fig. 11.** Nyquist plots of the DSSCs based on ZnO NR and ZnO NT arrays electrodes, performed under illumination at applied bias of $V_{oc}$.
The summary of the electron transport properties in ZnO NT and ZnO NR photoanodes which were determined by impedance analysis. The cell areas are 0.25 cm².

<table>
<thead>
<tr>
<th>DSSC</th>
<th>$D_{el}$ (cm² s⁻¹)</th>
<th>$K_{el}$ (s⁻¹)</th>
<th>$\tau_e$ (s)</th>
<th>$\tau_n$ (s)</th>
<th>$R_s$ (Ω)</th>
<th>$R_t$ (Ω)</th>
<th>$n_{fr}$ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT</td>
<td>$8.0 \times 10^{-3}$</td>
<td>16.4</td>
<td>$6.10 \times 10^{-2}$</td>
<td>$7.9 \times 10^{-4}$</td>
<td>209.5</td>
<td>2.7</td>
<td>$1.02 \times 10^{10}$</td>
</tr>
<tr>
<td>NR</td>
<td>$4.59 \times 10^{-3}$</td>
<td>28.1</td>
<td>$3.6 \times 10^{-2}$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>143.77</td>
<td>5.5</td>
<td>$2.0 \times 10^{18}$</td>
</tr>
</tbody>
</table>

4. Conclusions

Large scale arrays of highly oriented ZnO NTs with high intentional defects and surface states have been fabricated and characterized. The DSSCs made of these 12.5 µm NRs and NTs resulted in conversion efficiencies of 1.06% and 2.87%, respectively. A detailed investigation of the transport properties of ZnO NTs and NRs using impedance spectrum of ZnO took place to clearly determine the correlation between the electrical and structural properties of these structures. According to this study, twofold electron lifetime electron accompanied by half electron transport time for ZnO NT devices compared to NR ones, is their twofold electron transport properties which finally causes a lower FF in these cells.

References