CHAPTER-VII

Hydrothermal Growth of ZnO Nanowire and Nanoneedle Arrays with Flower Structure on ZnO-TiO$_2$ Seed Layer for DSSC Applications
7.1 Outline

ZnO nanowire arrays (NWAs) and nanoneedle arrays (NNAs) were hydrothermally grown on the spin coated ZnO-TiO$_2$ seeded FTO substrates by varying the growth parameters such as solution concentrations and growth times, respectively. XRD patterns and Raman spectra confirm the hexagonal structure of ZnO nanostructures grown along the c-axis direction and crystallinity of the films increases with an increase in the solution concentrations and growth times. The ZnO thin films display NWAs and NNAs grown for 3 and 5 h respectively. The NNAs show better light absorption and reflectance with a high dye loading than that of the NWAs. The efficiency of DSSCs based on NWAs and NNAs is 0.91 and 1.47 %, respectively. The DSSC based on NNAs photoanode shows a less electron recombination compared to DSSC based on NWAs photoanode.

The work discussed in this chapter has been published in

7.2 Introduction

Numerous research groups have devoted much time to synthesize different novel structures such as nanoparticle (zero dimensional) (Memarian et al., 2011), nanorod or nanowire (Law et al., 2005), nanotube (one dimensional) (Martinson et al., 2007), nanosheet (two dimensional) (Hosono et al., 2005) and microsphere particle (three dimensional) (Zhu et al., 2012). The efficiency of DSSC depends on morphology of the photoanode (Liu et al., 2013). The photoanode should possess high electron mobility, charge collection, charge separation, surface area and light scattering ability. In this case, the nanoparticle based DSSC has a large surface area to more dye loading. Although it has high surface area, the efficiency of the DSSC is low due to the presence of a large number of grain boundaries, which significantly affect electron mobility. The poor electron mobility leads to recombination between back electron transfer and either oxidized dye molecules or oxidized species in the electrolyte (Kang et al., 2015). In order to minimize these types of recombinations, some researchers have synthesized one dimensional (1D) nanostructures such as nanowires and nanorods which offer a direct pathway to the injected electron to reach FTO conductive substrate. The high electron mobility of 1D nanostructure has inhibited the recombination between back electron transfer and either oxidized dye molecules or oxidized species in the electrolyte. 1D nanowire based DSSC has achieved a low efficiency compared to the nanoparticles based DSSC. This is due to the deficiency of surface area to dye loading, instability, poor coverage of nanowire on FTO substrate which causes recombination between injected or collected electrons from the uncovered FTO substrate and the oxidized electrolyte species or oxidized dye molecules (Kang et al., 2015). To prevent these types of recombinations, Wang et al., introduced the TiO₂ blocking layer between FTO substrate and
ZnO seed layer. Eventhough, they used the blocking as well as the seed layer, the efficiency of the DSSC is low due to the deficiency of surface area for high dye loading (Wang et al., 2009). In the previous chapter, the ZnO nanowire arrays have been vertically grown on a uniform surface of ZnO-TiO₂ seeded FTO substrate and obtained an efficiency of 0.84 % (Marimuthu et al., 2016a). To further enhance the conversion efficiency, some of the researchers have employed the scattering layer to improve light absorption through multiple scattering of incident light within the photoanode and they have significantly increased the efficiency of DSSCs (Chou et al., 2007; Kim et al., 2012; Qu et al., 2014).

In the present work, the ZnO-TiO₂ seed layers with some agglomerated grains were coated on FTO substrates by employing sol-gel spin coating technique. It is followed by the 1D nanostructures which were hydrothermally grown on seed layer coated FTO glass substrates. By changing the Zn(NO₃)₂ concentration and growth time, the dense and the upright nanowire arrays (NWAs) and the nanoneedle arrays (NNAs) with flower like structures were grown to increase light scattering ability for a high light absorption. The structural, morphological, vibrational and optical properties of nanostructures were investigated. Finally, the DSSCs were constructed by using optimized NWAs and NNAs nanostructures and they were studied through current density-voltage curves and electrochemical impedance spectra.

7.3 Experimental details

7.3.1 Photoanodes preparation

ZnO nanostructures were grown via a two-step process. In the first step, ZnO-TiO₂ seed layers were prepared onto FTO conductive substrates by employing spin coated technique. The 0.3 M of zinc acetate dihydrate (90 %) and titanium oxide powder (10 %) was
dissolved and dispersed in isopropyl alcohol. It is followed by 0.3 M of monoethanolamine which was added as a stabilizer. The solution was continuously stirred at 60 °C for 2 h to get the sol. ZnO-TiO₂ thin film was coated at 3000 rotations per minute (RPM) for 20 sec. The coated film was eventually annealed at 450 °C for 1 h. Before the seed layer deposition, the FTO substrates were ultrasonically rinsed with acetone and deionized water for 10 min separately. Thereafter, the rinsed FTO substrates were baked at 100 °C in the air for 10 min. In the second step, the nanostructures were grown on ZnO-TiO₂ seed layers by employing hydrothermal technique (Marimuthu et al., 2016b). An aqueous growth solution containing zinc nitrate hexahydrate (0.01 M), 0.1 % of polyvinyl alcohol (0.01 M) and hexamethylenetetramine (0.01 M) was dissolved in deionized water. The viscosity of the solution was found to be 1.31 Pa.s using Oswald viscometer. The ZnO-TiO₂ seed layer is immersed into a bottle containing the solution at 45° angle to avoid any unwanted precipitation from top of the solution on the growing ZnO nanostructures. The temperature of growth solution is maintained at 80 °C. In order to grow the well defined nanostructures, the concentrations and growth times are varied about 5-50 mM and 3-5 h respectively. The grown ZnO nanostructures are eventually rinsed with ethanol and deionized water. Afterwards, they are baked at 100 °C for 30 min in air atmosphere.

7.3.2 DSSCs construction

The grown ZnO NWAs and NNAs films are soaked into 0.3 mM of N719 dye solution prepared in ethanol for 3 h in a dark room. Thereafter, the dye loaded photoanode films are rinsed with ethanol to remove unbounded dye molecules. The Pt electrodes are spin coated on FTO substrates at 500 RPM for 30 sec by using a 5 mM solution of chloroplatinic acid in isopropyl alcohol, followed by coated films baked at 100 °C for 10 min. Once again
the procedure is repeated. Finally, the pre-heated Pt electrodes are annealed at 400 °C for 1 h. The dye loaded ZnO nanostructured photoanodes and Pt electrodes are sandwiched between Surlyn spacer. The active area of the cells is fixed about 0.20 cm². A liquid electrolyte containing 0.6 M 1-methyl-3-propylimidazolium iodide, 0.1 M lithium iodide, 0.05 M iodide and 0.5 M tert-butylpyridine was filled into the active area by pouring a few drops through the holes on the Pt electrode. Finally, the holes are sealed with Surlyn film.

7.4. Results and Discussion

7.4.1 Preparation of ZnO seed layer using spin coating

7.4.1.1 Structural analysis

Figure 7.1 shows the XRD pattern of the ZnO-TiO₂ seed layer.

Figure 7.1 illustrates the XRD pattern of ZnO-TiO₂ seed layer prepared by employing sol-gel spin coating technique annealed at 450 °C. The diffraction peaks are indicated through a star symbol corresponding to FTO substrate. All the diffraction peaks are indexed with the hexagonal wurtzite structure (except peak indexed by a black dot symbol), which is
in good agreement with the International Center for Diffraction Data (ICDD) card no. 36-1451. The peaks (100), (002), (101) and (103) correspond to ZnO. The peak (101) is indicated by the black dot symbol, which is well in accordance with anatase phase of TiO$_2$ and ICDD card no. 89-4921.

7.4.1.2 Morphological analysis

Figure 7.2 shows the FE-SEM image of the ZnO-TiO$_2$ seed layer.

Figure 7.2 presents the FE-SEM image of ZnO-TiO$_2$ seed layer, which shows a uniform distribution of agglomerated TiO$_2$ nanoparticles over the surface of FTO substrate. The size of the agglomerated TiO$_2$ is varied between 1.56 µm and 8.62 µm. The agglomeration contains a large number of TiO$_2$ nanoparticles whose size are varied from 18 to 38 nm as shown in Fig. 7.2. ZnO nanoparticles are coated on agglomerated TiO$_2$ particles, which act as a nucleation center to grow the dimensional nanostructures. A few nanorods are found in some places which are grown horizontal to the surface of FTO substrate. The width and the length of the nanorods are found to be in the range of 407-711 nm and 3.14-8.26 µm respectively.
7.4.2 Hydrothermal growth of one dimensional nanostructures

7.4.2.1 Growth mechanism

ZnO nanostructures are hydrothermally grown based on following reactions (Tian et al., 2011; Zhu et al., 2013).

\[
\text{Zn(NO}_3\text{)}_2 (s) \rightarrow \text{Zn}^{2+} (aq) + 2\text{NO}_3^- (aq) \quad (7.1)
\]
\[
\text{Zinc nitrate} \quad \text{Zinc (II) + Nitrate}
\]

\[
(\text{CH}_2\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 4\text{NH}_3 + 6\text{HCHO} \quad (7.2)
\]
\[
\text{HMTA + Water} \quad \text{Ammonia + Formaldehyde}
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} \rightarrow \text{NH}_4^+ + \text{OH}^- \quad (7.3)
\]
\[
\text{Ammonia + Water} \quad \text{Ammonium hydroxide} \quad \text{Ammonium + Hydroxide}
\]

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 (s) \rightarrow \text{ZnO (s)} + \text{H}_2\text{O} \quad (7.4)
\]
\[
\text{Zinc (II) + Hydroxide} \quad \text{Zinc hydroxide} \quad \text{Zinc oxide + Water}
\]

Zinc nitrate (Zn(NO$_3$)$_2$) salt dissociates into Zn$^{2+}$ and NO$_3^-$ ions in deionized water (reaction 7.1). Hexamethylenetetramine (CH$_2$N$_4$) reacts with water (H$_2$O) to give formaldehyde (HCHO) and ammonia (NH$_3$), respectively, and it acts as a pH buffer to provide controllable supply of OH$^-$ ions through slow decomposition. Further, the NH$_3$ reacts with H$_2$O to form the ammonium hydroxide (NH$_4$OH), which gives OH$^-$ ions (reaction 7.2&7.3). These OH$^-$ ions combines with Zn$^{2+}$ ion to form zinc hydroxide (Zn(OH)$_2$). Eventually, the Zn(OH)$_2$ thermally dehydrates into ZnO (reaction 7.4).

7.4.2.2 Effect of concentration

7.4.2.2.1 Structural analysis

XRD patterns of ZnO nanostructures grown with different concentrations at a constant temperature of 80 °C are shown in Fig. 7.3. The diffraction peaks are indexed by a star symbol corresponding to F doped SnO$_2$ substrates, all other peaks except peak indicated
by a black dot symbol can be indexed to hexagonal wurtzite structure and are in good concordance with ICDD card no. 36-1451.

Figure 7.3 shows the XRD patterns of ZnO nanostructures grown with different Zn(NO$_3$)$_2$ concentrations of (a) 5 mM, (b) 10 mM and (c) 50 mM. The prominent diffraction peaks at angle 31.68°, 34.34° and 36.16° correspond to (100), (002) and (101) planes respectively. The weak peak (indicated by black dot symbol) appeared at 25.7° is due to the presence of TiO$_2$ anatase phase in seed layer for nanostructure grown at a concentration of 10 mM, which very well coincided with ICDD card no. 89-4921. When the concentration of growth aqueous precursor is increased from 10 to 50 mM, the intensity of diffraction peaks also increased which means that the crystallinity of the nanostructure increased at higher concentration. In addition, the intensity of (002) plane increased with respect to concentration which implies that the crystalline is grown along the c-axis to the surface of the substrate (Marimuthu et al., 2016a). The other diffraction peaks reveal that the crystalline is grown at random orientation or at their preferential orientation.
7.4.2.2.2 Morphological analysis

Figure 7.4. FE-SEM images of the ZnO nanostructures grown with different concentrations of (a&a1) 5 mM, (b&b1) 10 mM and (c&c1) 50 mM.
The surface morphologies of ZnO nanostructures grown at different Zn\(^{2+}\) concentrations are shown in Fig. 7.4. Figs. 7.4(a&a1) show nanowires grown at a concentration of 5 mM (Zn\(^{2+}\)). It can clearly be seen that some of the nanowires are agglomerated and found to be less dense as shown in Fig. 7.4(a1). The diameter and the length of the nanowires are varied in the range between 30-111 nm and 300-485 nm, respectively. Further, the concentration of Zn\(^{2+}\) is raised to 10 mM, nanowire arrays (NWAs) with the hexagonal structures are vertically and densely grown with diameter of 61-103 nm (the insert image of Fig. 7.4(b), which is good concurrence with (002) plane in XRD result. The NWAs can be favored for high electron mobility. A few flowers like structures appeared as shown in Fig. 7.4(b) and they are composed of a large number of nanowires which are grown at different orientations as shown in Fig. 7.4(b1). The random orientation of nanowires is confirmed by the presence of other satellite planes (100), (101), (102), (110), (103) and (112) in the XRD pattern. Flower consisting of randomly oriented nanowire can be acted as a light scattering center to absorb a number of photons (Chou et al., 2007). The diameter and the length of NWAs are changed in the range of 42-47 nm and 202-504 nm respectively. As the concentration of Zn\(^{2+}\) is further increased to 50 mM, SEM images of Fig. 7.4(c& c1) show similar structure, but the significant changes occurred in diameter of NWAs in the range between 123 and 382 nm as shown in Fig. 7.4 (c). The increased diameter of the NWAs decreases the surface area of the film. In addition, a few nanotubes are randomly grown whose diameters are varied between 0.7 and 1.2 µm.

7.4.2.2.3 Raman spectra analysis

Figure 7.5 shows the Raman spectra of 1D nanostructures grown at different precursor concentrations. It is the best tool to study the crystal phase, crystallinity and defects
of the materials. Raman peak observed at 636 cm\(^{-1}\) corresponds to \(E_g\) mode, which is ascribed to the tetrahedral anatase phase of TiO\(_2\) \((\text{Marimuthu et al., 2016a})\). Raman peaks appeared at 332, 437 and 580 cm\(^{-1}\) owing to \(E_{2L}\)-\(E_{2H}\), \(E_2\)(high), and \(E_1(\text{LO})\) mode, respectively.

**Figure 7.5** shows the Raman spectra of the ZnO nanostructures grown at different concentrations of (a) 5 mM, (b) 10 mM and (c) 50 mM. The small peak centered at 332 cm\(^{-1}\) is assigned to second order non-polar mode of Raman scattering. The peak at 580 cm\(^{-1}\) is found due to the presence of oxygen vacancies (or) Zn interstitials. The high intensive peak around at 437 cm\(^{-1}\) is attributed to hexagonal wurtzite structure and non-polar optical mode of ZnO, which is due to heavy vibration of an oxygen atom. The intensity of \(E_2\)(high) mode is significantly enhanced as concentration of the growth solution increased from 5 to 50 mM as shown in Fig. 7.5. This is an indication of the improved crystalline nature of the grown nanostructures which is in accordance with XRD.
results (Jung et al., 2012). According to Raman selection rule, the absence of $A_1$(TO) and $E_1$(TO) modes represents that ZnO nanostructures are perpendicularly grown on seed layer coated FTO substrate (Lupan et al., 2010a). This observed result is also confirmed through the presence of high intensity (002) plane in XRD pattern as shown in Fig. 7.3. The Raman peak appeared in the range of 1050-1200 cm$^{-1}$ is due to the multi-phonon process (Kim et al., 2011). It can be observed that the crystallinity of nanostructures increased with increase in the solution concentration.

### 7.4.2.2.4 Photoluminescence spectra analysis

**Figure 7.6** shows the PL spectra of pure TiO$_2$ NPs, and the ZnO nanostructures grown at different concentrations of (a) 5 mM, (b) 10 mM and (c) 50 mM.
Photoluminescence (PL) spectra of pure TiO$_2$ NPs and ZnO nanostructures grown at different Zn(NO$_3$)$_2$ concentrations are recorded in the range of 370-560 nm under an excitation wavelength of 325 nm and the same are shown in Fig. 7.6. The PL emission peaks at 411, 435 and 460 nm are observed for pure TiO$_2$ NPs as shown in Fig. 6 (pure TiO$_2$ NPs). The PL emission peak observed at 411 nm (3.02 eV) is attributed to self-trapped excitons localized in TiO$_6$ octahedral structure (Zhang et al., 2014). The emission peaks at 435 nm (2.85 eV) and 460 nm (270 eV) are observed due to oxygen vacancies with two trapped electrons in TiO$_2$ (Abazovic et al., 2006; Zhang et al., 2014). When the ZnO nanostructures are grown on a ZnO-TiO$_2$ seed layer at 5 mM Zn(NO$_3$)$_2$, the PL peaks at 379, 391, 491 and 520 nm additionally appeared. The peaks at 379 nm (3.27 eV) and 391 nm (3.16 eV) are assigned to near band edge emission due to free exciton recombination by exciton-exciton collision as well as radiative recombination of an electron in the conduction band and a hole in the valence band (Panigrahy et al., 2010; Zhu et al., 2014b). It can be noticed from Fig. 7.6(a) that the various emission peaks in UV region are due to different shapes of ZnO nanostructures (Djurisic et al., 2006). The peaks at 491 nm (2.53 eV) and 520 nm (2.38 eV) are due to energy difference between singly ionized oxygen vacancy (V$_O$) and top of the valence band (Shakti et al., 2014). An increase in intensity of emission peak at 411 nm (3.01 eV) may be the superposition of violet emission peak of ZnO due to electrons transition from the bottom of conduction band to energy level of zinc vacancy (V$_{Zn}$) (Panigrahy et al., 2010). When ZnO NWAs are grown at 10 mM Zn(NO$_3$)$_2$, the intensity of the UV emissions is significantly increased due to increasing the excitons. A new blue emission peak at 444 nm (2.79 eV) is observed due to the electrons transition from the interstitial zinc (Zn$_i$) to the top of the valence band (Chen et al., 2013). The increase in ZnO related peaks and decrease in
TiO$_2$ related peaks indicate the increase in growth rate of ZnO NWAs. When there is a further increase in the concentration of Zn(NO$_3$)$_2$ to 50 mM, the emission peaks related ZnO considerably increased with decrease in emission peaks related to TiO$_2$, which is due to increase in growth rate of ZnO. From the PL spectra, it is observed that the near band edge emission peaks of ZnO nanostructures are increased with an increase in the concentration of Zn(NO$_3$)$_2$ due to increase in growth rate.

7.4.2.3 Effect of growth time

7.4.2.3.1 Structural analysis

Figure 7.7 exhibits the XRD patterns of ZnO nanostructures grown at a concentration of 10 mM at 80 °C for different growth times (b) 3 h and (d) 5 h.

Figure 7.7 shows the XRD patterns of nanostructures grown at a constant temperature of 80 °C for different growth times. All the diffraction peaks (except peaks indicated by black dot and star symbol) are indexed to hexagonal wurtzite structure and are also in good agreement with ICDD card no. 36-1451. The small peak observed at 25.7 is due to the presence of TiO$_2$ anatase phase. As the growth time increased from 3 to 5 h, the intensity of
the (002) plane remarkably increased as shown in Fig. 7.7. It confirms that the crystallinity of the nanostructures improved in proportion to the growth time. From this XRD result, it can be confirmed that the crystalline nature of nanostructure grown for 5 h is higher than the nanostructure grown for 3 h.

7.4.2.3.2 Morphological analysis

Figure 7.8 shows the FE-SEM images of ZnO nanostructures grown at a concentration of 10 mM at 80 °C for different growth times (b&b1) 3 h and (d&d1) 5 h.

Figure 7.8 presents the SEM images of nanostructures grown at a concentration of 10 mM at 80 °C for different growth times. Fig. 7.8(b&b1) show NWAs grown for 3 h, and the explanation of NWAs is elaborately given in the effect of concentration. Fig. 7.8(d&d1) displays a nanoneedle arrays (NNAs) like structure grown for 5 h at 80 °C. The flowers like
structures are observed at a few places in the prepared thin film as shown in Fig. 7.8(d). On the other hand, the NNAs are vertically and densely grown along the c-axis to ZnO-TiO$_2$ seeded substrate, which is well consent with high intensity (002) plane in XRD pattern. The flower like structure is composed of a large number of nanoneedles, which are attached at one big grain, and a few nanoneedles are combined to form a bigger one as shown in the insert of Fig. 7.8(d1). The nanoneedles show the length, diameter of the tip and base in the range of 600-830, 40-70 and 60-160 nm, respectively. The flower like structures having nanoneedles act as light scattering center for high light absorption. From this observation, when the growth time of the nanostructures is increased from 3 to 5 h, the morphological change occurred from NWAs to NNAs.

7.4.2.3.3 Raman spectra analysis

![Figure 7.9](image)

**Figure 7.9** exhibits the Raman spectra of ZnO nanostructures grown at a concentration of 10 mM at 80 °C for different growth times (b) 3 h and (d) 5 h.

Raman spectra of Fig. 7.9 display $E_{2L}$-$E_{2H}$, $E_2$(high) and $E_{1l}$(LO) modes corresponding to the hexagonal wurtzite structure of ZnO. The $E_g$ mode is observed due to tetrahedral
anatase phase of TiO$_2$. As the growth time is extended from 3 to 5 h, the intensity of E$_2$(high) mode notably increased as shown in the inset of Fig. 7.9. It can be confirmed that the crystallinity of NNAs notably enhanced compared to NWAs structures. This is good in accordance with the XRD result (Jung et al., 2012). It can be confirmed that the crystallinity of the nanostructures get increased in proportion to growth time.

### 7.4.2.3.4 Photoluminescence spectra analysis

Figure 7.10 shows the PL spectra of ZnO nanostructures grown at a concentration of 10 mM at 80 °C for different growth times (b) 3 h and (d) 5 h.

Figure 7.10 shows the PL spectra of ZnO nanostructures grown for different growth times carried out in the wavelength range of 370-560 nm. When the growth time is increased from 3 h to 5 h, the emission peaks related ZnO nanostructures increased while the emission peaks related TiO$_2$ decreased as shown in Figs. 7.10(b&d), which is due to increase in the growth rate of ZnO nanostructures. Especially, the intensity of UV emission peaks obviously increased due to increase in the exciton recombination. It can be observed that the growth time increases with the growth rate of ZnO nanostructures.
7.4.2.4 UV-Visible spectra analysis

![Graph](image)

**Figure 7.11** illustrates the UV-Vis reflectance and absorption spectra of (b) NWAs and (d) NNAs.

The reflectance and the absorption spectra of NWAs and NNAs are carried out in the wavelength range of 300-700 nm and the same are shown in Fig. 7.11. The reflectance of ZnO NNAs is significantly increased compared to ZnO NWAs. The increased reflectance indicates the NNAs nanostructure having a higher light scattering ability than the NWAs which extend the light travelling path length within the photoanode by multiple scattering of incident light (*Kang et al.*, 2015). Thereby, the light absorbance of NNAs is notably higher than the NWAs nanostructure as shown in Fig. 7.11. It can be seen that NNAs have a good light absorption which can increase the photo to current conversion efficiency.

In order to find out the dye loading of nanostructures, both NWAs and NNAs photoanodes were soaked into 5 mM of eosin yellow dye solution for 3 h. Thereafter, the dye absorbed photoanodes were rinsed with ethanol to remove abundant dye molecules. Dye molecules were detached by dipping the photoanode in 10.5 pH of KOH solution for 24 h.
Figure 7.12 exhibits the UV-Vis absorption spectra of dye detached from (b) NWAs and (d) NNAs.

Figure 7.12 displays the UV-Vis absorption spectra of dye solution. The absorption peak is observed at 515 nm due to a specific interaction of chromophores in eosin yellow dye (Yoshida et al. 2000). No other impurity peaks are observed for KOH solution in the spectra. It is illustrated that dye detached from NNAs photoanode shows a better dye absorbance than the NWAs photoanode. It obviously indicates that NNAs have a large internal surface area for high dye loading. In general, the high dye loaded photoanode harvests a large number of photons from incident light, which may generate more photocurrent.

7.4.2.5 J-V Characterization

In order to study the light harvesting efficiency, the optimized ZnO NWAs and NNAs nanostructures are used as a photoanode for DSSCs. Fig. 7.13 presents current density versus voltage (J-V) curves of NWAs and NNAs respectively. The measured and the calculated parameters such as open circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$), fill factor (FF) and efficiency ($\eta$) are shown in Table 7.1.
Figure 7.13 presents the J-V curves of DSSCs based on (b) NWAs and (d) NNAs. The $V_{oc}$ and $J_{sc}$ of the DSSC based on NWAs are about 656 mV and 3.51 mA with a FF of 0.38. The photo to current conversion efficiency is about 0.91 %. As compared to the DSSC based on NWAs, the DSSC based on NNAs exhibits a high $J_{sc}$ of 5.70 mA with a slight low $V_{oc}$ of 617 mV. The increased $J_{sc}$ from 3.51 to 5.70 mA mainly depends on the increased internal surface area and superior light scattering effect of NNAs. The increased $J_{sc}$ may be the reason for increase in film thickness from 3.68 to 4.47 µm for NWAs and NNAs respectively. The $\eta$ of NNAs is around 1.47 %, which is higher than the NWAs. The slightly decreased $V_{oc}$ of NNAs from 686 to 617 mV depends on energy difference between quasi Fermi band edge and reduction potential of $I^-/I^-_3$ redox couple in the electrolyte (Zhu et al., 2013). However, the FF of the NNAs is significantly increased from 0.38 to 0.42, which may be ascribed to reduction of electron recombination at NNAs/dye/electrolyte interface (Jiang et al., 2007). This study reveals that DSSC based on NNAs shows high $J_{sc}$, FF and $\eta$. The obtained $\eta$ is higher than the previously reported values (Rahman et al., 2015).
Table 7.1 displays the Photovoltaic parameters of the DSSCs based on NWAs and NNAs.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>( V_{oc} ) (mV)</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>( FF )</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>686</td>
<td>3.51</td>
<td>0.38</td>
<td>0.91</td>
</tr>
<tr>
<td>D</td>
<td>617</td>
<td>5.70</td>
<td>0.42</td>
<td>1.47</td>
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7.4.2.6 Electrochemical impedance spectra analysis

![EIS spectra of DSSCs based on (b) NWAs and (d) NNAs.](image)

**Figure 7.14.** EIS spectra of DSSCs based on (b) NWAs and (d) NNAs.

Electrochemical impedance spectroscopy (EIS) spectra were carried out to investigate the kinetics of charge transfer processes at electrode/electrolyte interface for DSSCs based on NWAs and NNAs photoanode under dark condition in the frequency range of 500 kHz to 0.1 Hz by applying an AC signal of 400 mV open circuit voltage. Fig. 7.14 shows the Nyquist plots of DSSCs which are fitted with an equivalent circuit by using Z SimpWin software, and the circuit is shown in the insert of Fig. 7.14. The two peaks are observed in Nyquist plots.
the first one, the peak is appeared at higher frequency region in the range of 500-1 kHz as shown in Fig. 7.14 which is attributed to charge transfer resistance ($R_{ct}$) between Pt electrode and electrolyte interface. The second peak is observed at the middle frequency region in between 1000 and 1 Hz, which is due to charge transfer recombination resistance ($R_{rec}$) between injected electrons and oxidized dye molecules or oxidized species of $\Gamma^- / I_3^-$ in the electrolyte (Guo et al., 2014). The $R_{rec}$ of the NWAs (633.3 Ω) is lower than the NNAs (954.5 Ω), which is ascribed to large number of recombination that take place at dye loaded photoanode and electrolyte interface in NWAs based DSSC (Wu et al., 2007). The increased $R_{rec}$ value can increase the FF of DSSC based on NNAs photoanode which is in good concurrence with $J-V$ results.

### 7.5 Conclusions

ZnO-TiO$_2$ thin films were spin coated on FTO substrates as a blocking as well as seed layer, and NWAs and NNAs were hydrothermally grown on ZnO-TiO$_2$ seed layers. The crystal structure, morphology, vibrational, luminescence and optical properties of nanostructures were evaluated by means of XRD, FE-SEM, Raman, PL and UV-Vis spectroscopy respectively. The results show that the grown nanostructures were hexagonal wurtzite structure oriented along perpendicular direction to ZnO-TiO$_2$ seed layer with NWAs and NNAs like morphologies. The NNAs structure shows better light scattering ability and dye loading than NWAs structure. The NNAs based on DSSC exhibited best photovoltaic conversion efficiency of 1.47 %. EIS results revealed that DSSC based on NNAs photoanode had a higher $R_{rec}$ than the DSSC based on NWAs photoanode.