CHAPTER-IV

Influence of Hexamethylenetetramine on Electrochemically Synthesized One-Dimensional ZnO Nanostructured Thin Films for DSSC Applications
4.1 Outline

ZnO thin films were synthesized on FTO glass substrates by pyrolyzing the electrodeposited zinc hydroxide chloride hydrate thin films. The effect of HMTA concentrations on structural, morphological, vibrational and optical properties was investigated. The ZnO growth orientation is transferred from (101) to (002) plane as the HMTA concentrations get increased from 0 to 9 mM. The well-defined hexagonal nanorods and nanoneedle structures are observed for ZnO thin films deposited in absence and presence of HMTA. The increase in intensity of $E_2$(high) vibrational mode, near band edge emission and UV absorption confirms the ZnO nanoneedles synthesized in the solution containing 9 mM HMTA having better crystallinity, lesser atomic defects and higher dye loading respectively. The DSSC fabricated based on nanoneedles synthesized in the solution containing 9 mM HMTA exhibits an efficiency of 1.02 % with less charge recombination at ZnO nanoneedle/dye/electrolyte interfaces.
4.2 Introduction

Synthesis of diverse morphologies of metal oxides such as titanium oxide (TiO\(_2\)), zinc oxide (ZnO) and tin oxide (SnO\(_2\)) nanostructures are interestingly investigated in the field of energy harvesting devices to reduce fossil fuel demand for a few decades (Zhao et al., 2014). Among these TiO\(_2\), ZnO and SnO\(_2\) semiconductors, ZnO is a versatile material due to an easy synthesis of different morphologies and has a large exciton binding energy of 60 meV with a band gap of 3.37 eV (Mahmood et al., 2013). These superior properties are employed to be used in dye-sensitized solar cell (DSSC) (Marimuthu et al., 2015a). ZnO has been synthesized in a variety of shapes such as zero dimensional (0D) (nanoparticles) (Rashid et al., 2014), one dimensional (1D) (nanowires, nanotubes, nanorods, nanopillars) (Lee et al., 2007; Marimuthu et al., 2016a; Henni et al., 2016), two dimensional (2D) (nanosheets, nanowalls, nanoplatelets) (Pradhan and Leung, 2008b) and three dimensional (3D) (microspheres) (Kang et al., 2015). Among these nanostructures, 1D nanostructures have a better electrical property that is used to reduce the recombination between back transfer electrons and the oxidized dye molecules or electrolyte species in DSSCs (Marimuthu et al., 2016a). They have been synthesized with the help of physical and chemical deposition routes, including sputtering (Bortoleto et al., 2015), thermal evaporation (Calestani et al., 2011), chemical vapor deposition (Nicolay et al., 2012), pulsed laser deposition (Tsoutsouva et al., 2011), chemical bath deposition (Nayeri et al., 2013), hydrothermal (Gao and Nagai, 2006) and electrochemical deposition (Pradhan and Leung, 2008b). Among the different deposition routes, the electrochemical deposition has emerged as an alternative to physical deposition routes due to its low cost instrument, and low temperature enough to crystallization (Marimuthu et al., 2015a). Morphologies of electrochemical deposition of 1D
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nanostructure have been controlled by changing the solution concentration, deposition potential, bath temperature and deposition time (Illy et al., 2011). Pradhan and his team reported that, as the concentration of Zn(NO)_3 is more than 0.01 M, the formation of 2D is more possible, whereas the 1D nanostructures are formed as the concentration of Zn(NO)_3 which is less than 0.01 M. The dehydration of Zn(OH)_2 into ZnO should be faster than the formation of Zn(OH)_2 for the growth of 1D nanostructures (Pradhan and Leung, 2008b). At the same time, the use of low concentration is a drawback to produce a large number of OH^- ions, thereby the ZnO growth rate decreases. To increase the growth rate, the solution containing ammonium nitrate favors in generating a large number of OH^- ions by the electroreduction of more NO_3^- ions into NO_2^- ions (Tang et al., 2011). 1D nanostructure has been synthesized with the help of hydrothermal technique in an aqueous solution containing an equimolar concentration of Zn(NO_3)_2 and hexamethylenetetramine (HMTA) that acts as a pH buffer as well as a complexing agent which gradually supplies OH^- ions (Chen et al., 2012b). In the previous chapter-I, the DSSC consisting of ZnO with metallic Zn exhibited less fill factor due to the increase in recombination between the back transfer electrons and either the oxidized dye molecules or electrolyte species.

Here, in order to eliminate the metallic Zn phase, various concentrations of HMTA such as 0, 3, 6 and 9 mM respectively were added in the deposition solutions. The effect of HMTA on structural, morphological, vibrational and optical properties was studied with the help of XRD, SEM, Raman and PL spectroscopy respectively. The amount of dye loading was estimated from UV-Visible absorption spectra. For comparison purpose, J-V curves and EIS spectra were recorded for DSSCs based on nanorods and nanoneedles photoanodes films synthesized in the solutions containing 0 and 9 mM HMTA respectively.
### 4.3 Experimental details

#### 4.3.1 Photoanodes preparation

ZnO thin films were potentiostatically deposited on FTO substrates by three electrode system using EG&G Princeton Applied Research model 362 potentiostat/galvanostat instrument in an aqueous solution containing 0.01 M Zn(NO$_3$)$_2$.6H$_2$O as a Zn source and 0.1 M KCl as a supporting electrolyte dissolved in deionized water. The FTO substrate was used as a working electrode with a sheet resistance of 15 Ω. Platinum and silver/silver chloride electrodes were served as a counter electrode and a reference electrode, respectively. Before the FTO substrates are used for ZnO electrodeposition, they were cleaned with isopropanol and acetone in ultrasonic bath for 10 min each. Finally, The FTO substrates were rinsed with deionized water to remove the dust. The distance between the working and the counter electrode was fixed around 3 cm. The deposition solution was saturated by bubbling the molecular oxygen slowly on the whole deposition process with a constant stirring of 300 rotation per minute (RPM) by using a magnetic stirrer. The ZnO thin film was deposited at a constant deposition potential of $-1.3$ V at 70 °C bath temperature for 10 min. In order to study the effect of HMTA on the deposition of metallic Zn in ZnO thin films, the HMTA concentration is varied in the range of 0-9 mM in the deposition solutions. Finally, the deposited ZnO thin films were rinsed with deionized water and dried at 100 °C for 1 h before thin films are subjected to further characterizations.

#### 4.3.2 DSSCs construction

For comparison purpose, the ZnO nanorods and nanoneedles films synthesized in the solutions containing 0 and 9 mM HMTA respectively were used as the photoanodes. The nanostructured films were sensitized by immersing them in 0.3 mM N719 ethanolic dye
solution for 3 h. Thereafter, they were rinsed with ethanol to eliminate the unbounded dye molecules. Platinum (Pt) was coated on FTO substrate from previous report (Marimuthu et al., 2017a). A solution containing 5 mM chloroplatinic acid in isopropanol was spun on the ultrasonically cleaned FTO substrate at a RPM of 500 for 30 sec. Subsequently, the coated Pt films were barked at 100 °C for 10 min. The same procedure was repeated once again. Finally, the films were annealed at 400 °C for 1 h. DSSC was assembled by sandwiching the ZnO photoanode and Pt counter electrode between a Surlyn film. An 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 poured into an active area of 0.20 cm² through holes on counter electrode.

4.4 Results and discussion

4.4.1 Structural analysis

Figure 4.1 shows the XRD patterns of ZnO, Zn and Zn₅(OH)₆Cl₂·H₂O nanostructures synthesized on the FTO substrate in solutions containing various concentrations of HMTA at a constant deposition potential of −1.3 V at 70 °C. The diffraction peaks are marked by a star symbol corresponding to FTO substrate in Fig. 4.1&4.2. Fig. 4.1(a) displays a set of diffraction peaks of nanostructure synthesized in solution containing 0 mM HMTA corresponding to ZnO except the peak which appeared at 43.7° as shown in Fig. 4.1(a). The prominent diffraction peaks (100), (002) and (101) clearly matched with the hexagonal wurtzite structure of ZnO and in good accordance with international centre for diffraction data (ICDD) card no. 89-0510. The peak appeared at 43.7° corresponds to (101) plane of metallic Zn and is well indexed with ICDD card no. 04-0831. When the ZnO film is synthesized in the solution containing 3 mM HMTA, a new (100) diffraction peak (marked
by the black dot symbol) appeared for zinc hydroxide chloride hydrate (Zn$_5$(OH)$_8$Cl$_2$.H$_2$O) as shown in Fig. 4.1(b). The observed new peak is consistent with ICDD card no. 07-0155.

![XRD patterns](image)

**Figure 4.1** shows the XRD patterns of ZnO, Zn and Zn$_5$(OH)$_8$Cl$_2$.H$_2$O nanostructures synthesized in the solutions containing various concentrations of HMTA (a) 0 mM, (b) 3 mM, (c) 6 mM and (d) 9 mM.

At the same time, the intensity of the metallic Zn peak significantly decreased as illustrated in Fig. 4.1(b). When the HMTA concentration increased about 6 mM in the solution, the peak which appeared for metallic Zn almost disappeared while the intensity of the Zn$_5$(OH)$_8$Cl$_2$.H$_2$O discernibly increased compared to the films synthesized in solutions containing 0 and 3 mM HMTA respectively as shown in Fig. 4.1(c). Further by increasing the HMTA concentration to 9 mM, the intensity of (100) peak of Zn$_5$(OH)$_8$Cl$_2$.H$_2$O visibly increased with disappearance of metallic Zn as shown in Fig. 4.1(d). The increase in
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Intensities of the Zn$_5$(OH)$_8$Cl$_2$.H$_2$O reveals that the nanostructured film synthesized in the solution containing 9 mM HMTA has a good crystalline nature.

Figure 4.2 shows the XRD patterns of ZnO films synthesized in solutions containing various concentrations of HMTA annealed at 450 °C for 1 h. All the diffraction peaks are well indexed to the hexagonal wurtzite structure of ZnO and are in good agreement with ICDD card no. 89-0510. One can observe from Fig. 4.1 and 4.2 that after the nanostructured films had annealed at 450 °C, the Zn$_5$(OH)$_8$Cl$_2$.H$_2$O phase is completely converted into ZnO through solid state transformation of crystal structure according to reaction given below (reaction 4.1) (Xu et al., 2010b; Illy et al., 2010).

$$\text{Zn}_5\text{(OH)}_8\text{Cl}_2\cdot\text{H}_2\text{O} \rightarrow 5\text{ZnO} + 4\text{H}_2\text{O} \uparrow + 2\text{HCl} \uparrow$$  \hspace{1cm} (4.1)

Zinc hydroxide chloride hydrate $\rightarrow$ Zinc oxide + water + Hydrochloric acid

Figure 4.2. XRD patterns of ZnO films annealed at 450 °C synthesized in the solutions containing various concentrations of HMTA (a) 0 mM, (b) 3 mM, (c) 6 mM and (d) 9 mM.
Figure 4.2(a) shows a high intense (101) diffraction peak, which is due to preferential or parallel growth of ZnO to the surface of the substrate. When ZnO is synthesized in the solution containing 3 mM HMTA, the intensity of the (002) peak is increased compared to the reference pattern. The increased intensity of (002) peak indicates that the crystallite begins to grow along the c-axis or is in perpendicular direction to the surface of the FTO substrate (Fig. 4.2(b)) (Marimuthu et al., 2016a). By increasing the HMTA concentrations to 6 and 9 mM respectively, the intensity of the (002) peak is continuously increased and is found to be singular most intense with decreasing the intensity of (100) and (101) peaks as shown in Fig. 4.2(c&d). These increased (002) and decreased (101) peak intensities revealed that the crystallites are highly oriented along the (0001) direction. Fig. 4.2(b-d) shows the intensity of (002) peak which considerably increases with an increase in the HMTA concentrations, which confirms in increasing the crystalline nature of ZnO (Marimuthu et al., 2017a). It can be inferred that the ZnO nanostructure synthesized in the solution containing 9 mM HMTA has an excellent crystalline nature with (0001) growth orientation.

4.4.2 Morphological analysis

Figure 4.3 shows the SEM images of ZnO thin films synthesized in solutions containing various concentrations of HMTA. The nanorods with well-defined hexagonal structures are observed as the film is synthesized in the solution containing 0 mM HMTA. The size of the nanorods has to be varied approximately 176-124 nm and 252-378 nm in width and length respectively (Fig. 4.3(a)). The nanorods are oriented at a lateral growth orientation that is in good accordance with a high intensity (101) diffraction peak in the XRD pattern as illustrated in Fig 4.2(a). When the film is synthesized in the solution containing 3 mM HMTA, the morphology of the film gets changed from nanorods to nanoneedles that are
uniform and vertically covered on the surface of the FTO substrate as shown in Fig. 4.3(b). They are approximately 100-200 nm and 360-400 nm in width and length respectively. Further by increasing the HMTA concentration to 6 mM, the nanoneedles densely grow on the surface of the FTO substrate. The size of the nanoneedles is approximately 140-200 and 400-440 nm in width and length, respectively. A few flowers like structures are observed in some places, which consist of nanoneedles as the petals on them as displayed in Fig. 4.3(c).

Figure 4.3 shows the SEM images of the ZnO films annealed at 450 °C synthesized in the solutions containing various concentrations of HMTA (a) 0 mM, (b) 3 mM, (c) 6 mM and (d) 9 mM.

When the film is synthesized in the solution containing 9 mM HMTA, it can be observed that the flower consists of orderly arranged nanoneedles as presented in Fig. 4.3(d) and insert of
Fig. 4.3(d). The width and the length of nanoneedles are approximately 180-240 nm and 500-600 nm, respectively. When the HMTA concentrations are increased from 0 to 9 mM, the vertical growth of ZnO nanostructures is significantly increased which is in good agreement by increasing the intensity of the (002) peak in XRD results. When the film is synthesized in the solution containing 0 mM HMTA, the ZnO growth takes place due to increase in the interfacial pH by electroreduction of nitrate and molecular oxygen. But, when the films are synthesized in solutions containing various concentrations of HMTA, the ZnO growth is possible in two ways such as electrochemical and hydrothermal. The solution containing Zn(NO$_3$)$_2$ and HMTA could be employed for ZnO growth on seeded substrate through a low temperature hydrothermal method in elsewhere (Tian et al., 2011). In this work, it can be supposed that the ZnO is primarily synthesized by electrochemical followed by hydrothermal growth which takes place secondarily by taking the primary ZnO as the seeds for further ZnO growth. Hence the density of nanoneedles growth significantly increases with an increase in the HMTA concentrations which increase the surface area of the films.

4.4.3 Growth mechanism

The ZnO growth is possible in two ways, (i) electrochemical growth and (ii) hydrothermal growth.

\[
\text{Zn(NO}_3\text{)}_2 (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{NO}_3^- (\text{aq}) \tag{4.2}
\]
Zinc nitrate \hspace{1cm} zinc (II) + Nitrate

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \tag{4.3}
\]
Oxygen + Water + Electron \hspace{1cm} Hydroxide

\[
\text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^- \tag{4.4}
\]
Nitrate + Water + Electron \hspace{1cm} Nitrite + Hydroxide

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 (\text{s}) \rightarrow \text{ZnO} + \text{H}_2\text{O} \tag{4.5}
\]
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\[
\begin{align*}
\text{Zinc (II) + Hydroxide} & \quad \text{Zinc hydroxide} \quad \text{Zinc oxide + Water} \\
\text{Zn}^{2+} + 2e^- & \rightarrow \text{Zn} \\
\text{Zinc (II) + electron} & \quad \text{Zinc} \\
(CH_2)_6N_4 + 6H_2O & \rightarrow 4NH_3 + 6HCHO \\
\text{HMTA + Water} & \quad \text{Ammonia + Formaldehyde} \\
NH_3 + H_2O & \rightarrow NH_4^+ + OH^- \rightarrow NH_3OH \\
\text{Ammonia + Water} & \quad \text{Ammonium + Hydroxide} \quad \text{Ammonium hydroxide} \\
\text{KCl} & \rightarrow K^+ + Cl^- \\
\text{Potassium chloride} & \quad \text{Potassium + Chloride} \\
\text{Zn}^{2+} + 4(NH_3) + 2H_2O & \rightarrow [\text{Zn(NH}_3)_4(\text{OH}_2)_2]^{2+} + \text{Cl}^- \\
\text{Zinc (II) + Ammonia + Water} & \quad \text{Tetra amine diaqueous zinc (II) + Chloride} \\
& \rightarrow [\text{Zn(Cl)(NH}_3)_4(\text{OH}_2)]^+ \\
& \quad \text{Tetra amine monoaqueous chloro zinc (II)} \\
\text{Zn(OH)}_2 (aq) + Cl^- + 3H_2O & \rightarrow [\text{Zn(OH)}_2\text{Cl(OH}_2)_3]^- \\
\text{Zinc hydroxide + Chloride + Water} & \quad \text{Triaqueous dihydroxy chloro zincate (II)}
\end{align*}
\]

\( \text{Zn(NO}_3)_2 \text{ dissociates into zinc (II) (Zn}^{2+} \text{) ions and nitrate (NO}_3^- \text{) ions in deionized water (reaction 4.2). When the ZnO nanorods are synthesized in the solution containing 0 mM HMTA, the ZnO growth takes place only on the basis of the electrochemical technique. Here, molecular oxygen (O}_2 \text{) and nitrate (NO}_3^- \text{) reduce to form the hydroxide (OH}^- \text{) ions that increase the pH value at FTO/electrolyte interface (reaction 4.3&4.4) and produces a zinc hydroxide (Zn(OH)}_2 \text{) white precipitate on the surface of FTO substrate (reaction 4.5) (Elias et al., 2008). The Zn(OH)}_2 \text{ subsequently dehydrates into ZnO at an appropriate temperature of 70 °C or above (Pradhan and Leung, 2008a). When the deposition potential is more negative, the metallic zinc growth is also possible along with ZnO by reason of over deposition potential (reaction 4.6) (Elias et al., 2008). When the ZnO nanoneedles are} \)
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synthesized in solutions containing 3-9 mM HMTA, the ZnO growth takes place on the basis of both electrochemical as well as hydrothermal techniques. Herein HMTA ((CH₂)₆N₄) is not only used as a pH buffer, but it also serves as a complexing agent (Greene et al., 2006). HMTA thermally decomposes with water (H₂O) to form formaldehyde (HCHO) and ammonia (NH₃) (reaction 4.7). The NH₃ subsequently reacts with H₂O to form the ammonium hydroxide (NH₄OH) (reaction 4.8) that reacts with Zn²⁺ ions to give the Zn(OH)₂ which thermally dehydrates into ZnO (reaction 4.5). The potassium chloride dissociates into potassium and chloride (reaction 4.9). The electrochemical growth of ZnO may serve as the seed to grow ZnO for hydrothermal growth. These seeds enhanced the ZnO nanoneedles growth density. In hydrothermal process, when the HMTA concentration increases from 3 to 9 mM, the concentration of NH₃ also increases. These increased NH₃ concentrations lead to form both Zn(OH)₂ and tetra amine diaqueous zinc (II) [Zn(NH₃)₄(OH₂)₂]²⁺ which reacts with chloride (Cl⁻) ions to form tetra amine monoaqueous chloro zinc (II) [Zn(Cl)(NH₃)₄(OH₂)]⁺ ions (reaction 4.10) (Gao and Nagai, 2006). In electrochemical process, when the pH increases at working electrode/electrolyte interface by increasing the HMTA concentrations as well as electroreduction of O₂ and NO₃⁻, the Zn(OH)₂ formation also increases. When the formation of Zn(OH)₂ is higher than their dehydration, the higher electro negativity of Cl⁻ ion absorbs on the Zn(OH)₂ to form triaqueous dihydroxy chloro zinicate (II) [Zn(OH)₂Cl(OH₂)₃]⁻ ion on FTO substrate (reaction 4.11) (Pradhan and Leung, 2008b). [Zn(OH)₂Cl(OH₂)₃]⁻ ions electrostatically absorb [Zn(Cl)(NH₃)₄(OH₂)]⁺ ions on (0001) plane orientation. These absorptions may be the reasons for vertical growth of 1D nanostructure as shown in Fig. 4.3(b-d).
4.4.4 Raman spectra analysis

Figure 4.4 shows the Raman spectra of ZnO films annealed at 450 °C are synthesized in solutions containing various concentrations of HMTA (a) 0 mM, (b) 3 mM, (c) 6 mM and (d) 9 mM.

Figure 4.4 shows the micro Raman spectra of ZnO nanostructures synthesized in solutions containing various concentrations of HMTA. It is very sensitive tool to analyze the crystal structure, crystal perfection and atomic defects (Pradhan et al., 2009). The hexagonal wurtzite structured ZnO is in C6v space group. According to group theory, there are eight Raman modes, in which two are in acoustic modes and the remaining six are in optical modes. Generally, ZnO is formed by covalent and ionic bonds, which lead to coulomb electrostatic force between them (Zn-O). This electrostatic force causes in splitting of the A1 and E1 into transverse and longitudinal optical modes (Panigrahy et al., 2010). These A1 and E1 modes are Raman and infrared active, whereas E2 mode is Raman active only. The B1 is in...
silent mode (Raman inactive). In $A_1$ and $E_1$ modes, the atoms are displaced parallel and perpendicular to the c-axis (Lupan et al., 2010a). Fig. 4.4(a) displays three Raman peaks at 437, 583 and 1120 cm$^{-1}$ respectively. The first order Raman peak which appeared at 437 cm$^{-1}$ is attributed to $E_2$(high) mode due to vibration of oxygen atom. The presence of $E_2$(high) mode confirms the hexagonal wurtzite structure of electrodeposited ZnO films. The second order Raman peak located at 583 cm$^{-1}$ is assigned to $E_1$(LO) mode, which appeared due to the presence of oxygen vacancy or zinc interstitial (Lupan et al., 2011). The peak observed at 1120 cm$^{-1}$ is due to second order multi phonon mode arising from zone boundary centre (Illy et al., 2010). The intensity of $E_2$(high) mode considerably increased with an increase in HMTA concentrations in the range from 3 to 9 mM as shown in Fig. 4.4. The increase in intensity of the $E_2$(high) mode indicates the improvement in crystalline nature of ZnO nanostructure as ZnO film is synthesized in the solution containing a higher concentration of 9 mM HMTA. These results bear ample testimony to the XRD results. When the incident light is perpendicular to the surface of the ZnO, $A_1$(TO) and $E_1$(TO) modes are absent while the remaining modes are present. It can be confirmed from the absence of $A_1$(TO) and $E_1$(TO) modes that the electrodeposited ZnO nanostructures grow along the c-axis or are perpendicular to the surface of the FTO substrate.

**4.4.5 Photoluminescence spectra analysis**

Figure 4.5 shows the PL spectra of ZnO films performed to study the defects as well as crystal quality of the films (Djurisic and Leung, 2006). A near band edge emission peak is found in UV region at around 393 nm on account of either a free exciton recombination or a recombination between an electron in conduction band and a hole in valence band (Panigrahy et al., 2010). The deep level emission peaks are observed in the visible region.
due to defects presented in the materials in the wavelength region of 400-550 nm (Shakti et al., 2014). The violet emission peak is centered at 406 nm that is related to an electron transition from the conduction band to the Zn vacancy.

**Figure 4.5** shows the PL spectra of ZnO films annealed at 450 °C synthesized in solutions containing various concentrations of HMTA (a) 0 mM, (b) 3 mM, (c) 6 mM and (d) 9 mM. An emission peak observed at 442 nm in blue region is assigned to an electron transition from conduction band to the Zn interstitial (Chen et al., 2013). The green emission peaks appeared at 490 and 520 nm that are due to electrons transition from singly ionized oxygen to photoexcited hole (Pradhan et al., 2009). The UV emission peak of the film synthesized in solution containing 3 mM HMTA is found to slightly shift towards lower wavelength region.
from 393 to 391 nm, which indicates the decrease in the native defects in the film. When the films are synthesized in the solutions containing 6 and 9 mM HMTA respectively, the UV emission peak is further shifted from 391 to 389 nm indicating that the films are synthesized in solutions containing higher HMTA concentrations having less native defects. The intensity of the UV emission peak also increased with an increase in the HMTA concentrations from 0 to 9 mM which indicates the decrease in non-radiative recombination centre. The crystal quality of the films synthesized in solutions containing various concentrations of HMTA is estimated from intensity ratio of UV to visible (I_{UV/Vis}) emission (Marimuthu et al., 2016a). The I_{UV/Vis} ratio is estimated to be 0.93, 1.22, 1.36 and 1.43 for films synthesized in solutions containing 0, 3, 6 and 9 mM HMTA, respectively. It is confirmed that the film synthesized in the solution containing 9 mM HMTA exhibits a high crystal quality with less atomic defects.

### 4.4.6 Film thickness

![Graph showing film thickness vs. HMTA concentration]  

**Figure 4.6** shows the thickness of the films annealed at 450 °C synthesized in the solutions containing various concentrations of HMTA (a) 0.0 mM, (b) 3 mM, (c) 6 mM and (d) 9 mM.
Figure 4.6 shows the thickness of the films synthesized in solutions containing various concentrations of HMTA. The thickness of the film is found to be 5.65 µm, as the film is synthesized in solution containing 0 mM HMTA. Thickness of the film is significantly decreased to be 3.68 µm, as the HMTA concentration is about 3 mM. It might be the reduction of metallic Zn deposition. When there is a further increase in HMTA concentration to 6 and 9 mM respectively, the thickness of the films continuously increased to 3.94 and 4.47 µm. The increase in thickness of the films might be due to increase in the hydrothermal growth rate as well as c-axis growth of ZnO. When the HMTA concentrations are increased from 3 to 9 mM, the OH⁻ ion concentrations are increased, which leads to an increase the growth rate. On the other hand, the ZnO growth rate along the c-axis is five times faster than the lateral growth (Pradhan and Leung, 2008b).

4.4.7 UV-Visible spectra analysis

![UV absorption spectra](image)

**Figure 4.7.** UV absorption spectra of dye desorbed from thin films synthesized in solutions containing various concentrations of HMTA (a) 0.0 mM, (b) 3 mM, (c) 6 mM and (d) 9 mM.
In order to find out the better dye loading, dye absorption spectra were recorded in the wavelength range of 400-600 nm. The synthesized nanostructured ZnO thin films were dipped in an ethanolic dye solution consisting of 5 mM eosin yellow for 3 h. Afterwards, the dye loaded ZnO films were gently rinsed with ethanol to remove the unanchored dye molecules. Subsequently, the rinsed dye loaded films were immersed in KOH solution at a pH value of 10.5. Fig. 4.7 shows the absorption spectra of dye desorbed from nanostructured ZnO films synthesized in solutions containing various concentrations of HMTA. The strong absorption peak appeared at 516 nm and it is attributed to a specific interaction among the chromophores of the dye molecules (Yoshida et al., 2000). The dye absorbance decreased as the nanoneedles are synthesized in a solution containing 3 mM HMTA, which indicates that the nanoneedle films having less surface area are compared with the film synthesized in the solution containing 0 mM HMTA. It may be due to reduction of film thickness. When there is a further increase in the HMTA concentrations from 3 to 9 mM, the dye absorbances significantly increased due to increase in the surface area as shown in Fig. 4.7(b-d). Such increased dye absorbance captures a large number of incident photons. As a result, photon to current conversion may increase in DSSC fabricated based on nanoneedles photoanode synthesized in solution containing 9 mM HMTA.

4.4.8 J-V characterization

Current density-voltage (J-V) curves of DSSCs based on nanorods and nanoneedles synthesized in the solutions containing 0 and 9 mM HMTA respectively are shown in Fig. 4.8. The measured and the calculated photovoltaic parameters including short circuit current density (J_sc), open circuit voltage (V_oc), fill factor (FF) and efficiency (η) are summarized in Table 4.1. The $V_{oc}$ and $J_{sc}$ of the DSSC based on nanorods photoanode are 406 mV and
2.41 mA respectively. The η is about 0.36 with FF of 0.37. The $J_{sc}$ is dependent on a number of electrons injected and collected on FTO substrate through ZnO semiconductor nanorods films and the recombination between the injected electrons and either oxidized dye molecules or electrolyte species or surface defects (Zhang et al., 2008).

![Figure 4.8. J-V curves of DSSCs based on (a) nanorods and (d) nanoneedles.](image)

These properties highly depend on crystallinity of nanostructures, facial pathway to electron transfer, and surface defects (Chen et al., 2012a; Wu et al., 2013). The $V_{oc}$ is generally related to the energy difference between redox potential of electrolyte and quasi Fermi level of the semiconductor (Zhu et al., 2013). The $V_{oc}$, $J_{sc}$, FF and η of the DSSC based on nanoneedles photoanode are significantly increased to be 655 mV, 3.91 mA, 0.40 and 1.02 % respectively. The increased $V_{oc}$ is assigned to either increase in the conduction band edge of the ZnO or decrease in the interfacial recombination between collected electrons and oxidized electrolyte species due to increase in the ZnO growth density (Li et al., 2012). The
$J_{sc}$ of the DSSC based on nanoneedles photoanode is considerably higher than the DSSC based on nanorods photoanode, which may be due to higher dye loading and less surface defects of nanoneedles photoanode. The higher dye loading increases the injected electrons due to absorbance of a large number of photons, which diffuse through ZnO nanoneedles with less recombination to reach the FTO substrate. The results are in good concurrence with dye loading and PL results. It could be noted that the DSSC based on nanoneedles photoanode synthesized in the solution containing 9 mM HMTA show a better performance than another DSSC.

Table 4.1. Photovoltaic parameters such as $V_{oc}$, $J_{sc}$, $FF$ and $\eta$ of DSSCs based on nanorods and nanoneedles.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>406</td>
<td>2.41</td>
<td>0.37</td>
<td>0.36</td>
</tr>
<tr>
<td>d</td>
<td>655</td>
<td>3.91</td>
<td>0.40</td>
<td>1.02</td>
</tr>
</tbody>
</table>

4.4.9 Electrochemical impedance spectra analysis

The DSSCs based on nanorods and nanoneedles photoanodes were expected to carry out electrochemical impedance spectroscopy (EIS) spectra to investigate the electron kinetics at electrode/electrolyte interfaces at an applied AC voltage of 10 mV under light luminescence of 100 mW in the frequency range of 100 kHz-0.1 Hz. Fig. 4.9 shows the Nyquist plots of the DSSCs. There are three peaks which appeared in Nyquist plots. The peaks appear at the higher frequency region (100-1 kHz), middle frequency region (1 kHz-1 Hz) and lower frequency region (1-0.1 Hz) that are due to charge transfer resistance ($R_{ct}$) between Pt electrode and electrolyte interface, charge transfer recombination
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resistance ($R_{rec}$) between dye loaded ZnO and electrolyte interface, and $I^-/I_3^-$ ions diffusion resistance ($W_z$), respectively (Tain et al., 2011).

Figure 4.9 shows the EIS spectra of DSSCs based on (a) nanorods and (d) nanoneedles.

The Nyquist plots are fitted with the help of Z SimpWin software to extract the charge transfer recombination resistance ($R_{rec}$) of DSSCs by using an appropriate equivalent circuit. The fitted equivalent circuit is shown in Fig. 4.9. The DSSC based on nanoneedles photoanode has a higher $R_{rec}$ value of 4249 $\Omega$ than the DSSC based on nanorods photoanode (830 $\Omega$). The increased $R_{rec}$ value reveals that the DSSC based on nanoneedles photoanode has a less charge recombination either between the injected electron and the surface defects of nanorods, or between dye loaded photoanode and electrolyte interface (Nayeri et al., 2015). The decrease in charge recombination may increase the photovoltaic parameters, which are in good agreement with $J-V$ results.
4.5 Conclusions

ZnO nanostructures were successfully synthesized on FTO substrates through electrochemical deposition in solutions containing various concentrations of HMTA. The increase in HMTA concentrations from 0 to 9 mM not only increased the zinc hydroxide chloride hydrate growth, but also decreased the metallic Zn deposition. After the films are annealed at 450 °C, the ZnO nanorods film are synthesized in the solution containing 9 mM HMTA had (002) plane growth orientation, a better crystallinity, crystal quality and dye absorbance than other films. The ZnO synthesized in solutions containing 0 and 9 mM HMTA showed the nanorods and nanoneedles with a higher growth respectively. The DSSC based on nanoneedles photoanode had a better photon conversion efficiency of 1.02 %, which is more than two times higher than the DSSC based on nanorods photoanode. The increased $R_{\text{rec}}$ indicated that the DSSC based on nanoneedles photoanodes have a less electron recombination.