CHAPTER-VIII

Chemical fabrication of ZnO hierarchical structure on ZnO-TiO$_2$ seeded FTO substrate for DSSC Applications
8.1 Outline

A novel hierarchical microstructured ZnO thin films consisting of microspheres and nanorods were deposited on zinc oxide-titanium oxide (ZnO-TiO$_2$) seeded FTO substrate by applying a two step chemical techniques. At first, microsphere was electrochemically deposited in the solution containing tri-sodium citrate. It is followed by the nanorods which were hydrothermally synthesized on an optimized microsphere. SEM displays the hexagonal morphologies of microstructure and nanostructure on microstructure respectively. The suppression of ZnO growth along the (0001) orientation is noticed due to electrostatic absorption of citrate ions. The appearance of high intensity XRD peaks, Raman E$_2$(high) mode and UV emission confirms the hierarchical structure possessing a higher crystalline nature with lesser atomic defects. The hierarchical structure has high dye absorption, light absorption, scattering ability and charge transfer recombination resistance. The efficiency ($\eta$) of DSSCs consisting microsphere and hierarchical structures is found to be 3.13 and 4.64 %, respectively.
8.2 Introduction

Fabrication of diverse morphologies such as zero dimensional (0D) (nanoparticles), one dimensional (1D) (nanorods, nanowires, nanopillars, nanoneedles and nanotubes), two dimensional (2D) (nanowalls, platelets and nanosheets), and three dimensional (3D) (microspheres) significantly altered the efficiency of DSSCs, which are simply obtained by varying solution concentrations, capping agent concentrations, bath temperatures and deposition times (Marimuthu et al., 2018). The 1D nanostructures offer a direct pathway for rapid collection of photogenerated electrons in FTO substrate (Zhu et al., 2013). Hence, it reduces back electron transfer due to electron trapping as well as detrapping at a large number of grain boundaries among nanoparticles (Chung et al., 2010). Even though, the recombination between back electron transfer and oxidized dye molecules as well as oxidized electrolyte species is reduced by using 1D nanostructures instead of 0D nanostructure, the conversion efficiency is still low owing to scarcity of surface area for high dye molecule absorption and recombination between collected electrons and oxidized electrolyte species (Xu and Gao, 2012; Marimuthu et al., 2018). To avoid this type of recombination, a thin layer of blocking layer has been employed. As a result, the slight increment in conversion efficiency has been observed (Alberti et al., 2014). The achievement of higher conversion efficiencies not only depend on dye loading but also on crystallinity, crystal structure, light absorption due to scattering effect and recombination rate between injected electron and back electron transfer (Chen et al., 2012a; Hosni et al., 2014). Zhu et al., have synthesized nanorod-nanosheet (NR-NS) hierarchical ZnO architectures by hydrothermal technique in a solution containing sodium citrate and observed a slight increment in conversion efficiency by increasing both surface area as well as light scattering effects (Zhu et al., 2013). They
have synthesized the lateral growth of 2D structure on the vertical growth of ZnO to avoid the loss of incident light transmission among the vertical growth of 1D ZnO nanostructures. The use of microstructures not only increases the light scattering effect but also decreases the surface area for dye loading (Chen et al., 2012a). To enhance the surface area as well as light scattering effect, the microspheres containing aggregated nanoparticles synthesized by way of solvothermal technique have been used in DSSC. Thereby the drastic improvement in conversion efficiency has been obtained. Herein, the primary nanoparticles provide a large surface area for high dye loading and secondary spheres endow a higher light scattering effect (Chou et al., 2007).

In the present work, an attempt has been made to suppress the collected electron recombination, to increase the light scattering effect and reduce back electron transfer, the blocking layer, microspheres and nanorods were synthesized as a building block ZnO hierarchical structure by employing spin coating, electrochemical and hydrothermal techniques respectively. The microspheres were electrochemically deposited on the blocking layer by varying the deposition potential in a solution containing trisodium citrate. After wards, the nanorods were hydrothermally grown over the microspheres. The synthesized microsphere and hierarchical ZnO structures were characterized by using XRD, SEM, micro Raman, PL and UV-Vis spectroscopy. J-V and EIS analysis were carried out for DSSCs containing microsphere and hierarchical structure respectively.

8.3 Experimental Details

8.3.1 Photoanodes preparation

The ZnO-TiO_{2} seed layers were coated on FTO substrates from earlier report and presented in chapter-VI (Marimuthu et al., 2016a). ZnO thin films were electrochemically
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... deposited on ZnO-TiO$_2$ seed layers by a conventional three electrode system. The ZnO-TiO$_2$ seed coated FTO substrate served as a working electrode. Platinum and Ag/AgCl electrodes were served the counter and reference electrodes, respectively. The deposition solution was consisted of 10 mM zinc nitrate hexahydrate, 0.1 M KCl, 9 mM hexamethylenetetramine and 2 mg tri-sodium citrate in deionized water. The molecular oxygen was slowly aerated into the deposition solution during whole deposition process at a constant stirring of 300 RPM. The distance between working and counter electrodes was fixed around 3 cm. The electrodeposition of ZnO thin films was carried out at a constant potential of $-1.1$ V at a bath temperature of 70 °C for 30 min. In order to synthesize the three dimensional microstructures, the deposition potential was varied in the range from $-1.1$ to $-1.3$ V. Eventually, the deposited thin films were rinsed with deionized water before they were subject to further grow as one dimensional nanostructures.

One dimensional ZnO nanostructure was grown on an optimized microstructured ZnO thin film (Film deposited at $-1.3$ V) by employing hydrothermal technique (Marimuthu et al., 2016a). A growth solution consisted of 10 mM zinc nitrate hexahydrate and 10 mM hexamethylenetetramine in 150 ml deionized water. To grow the 1D nanostructure, the optimized thin film was soaked into the growth solution. In order to avoid the reacted precipitation fall on the growth surface, the face of the films was inclinedly placed at an angle of 45° towards the bottom of the bottle. The 1D nanostructure was grown at 90 °C for 5 h. Finally, the grown 1D nanostructured thin film was rinsed with deionized water and dried at 100 °C for 1 h.
8.3.2 DSSCs construction

The optimized microsphere and hierarchical ZnO structured films were soaked in 0.3 mM N719 ethanolic dye solution at room temperature for 3 h. Thereafter, the dye absorbed ZnO thin films were gently rinsed with ethanol to remove unanchored dye molecules. Finally, the dye absorbed thin films were used as the photoanodes. Platinum counter electrodes were coated on FTO glass substrates by applying spin coating technique from the previous report (Marimuthu et al., 2016a). A solution containing 5 mM chloroplatinic acid in isopropanol was spun on the FTO substrates at a RPM of 500 for 30 sec. Afterwards, the coated films were pre-heated at 100 °C for 10 min. Once again the coating procedure was repeated to get the necessary thickness. The coated films were subsequently annealed at 400 °C for 1 h. Finally, they were used as the counter electrodes. DSSC was assembled by sandwiching the photoanode and counter electrode between Surlyn spacer. An electrolyte containing 0.1 M lithium iodide, 0.6 M 1-methyl-3-propylimidazolium iodide, 0.05 M iodide and 0.5 M tert-butylpyridine was poured into an active area of 0.20 cm² through the holes on counter electrode in DSSC. After wards, the holes were closed by Surlyn spacer.

8.4 Results and Discussion

8.4.1 Structural analysis

X-ray diffraction (XRD) patterns of ZnO thin films deposited at various deposition potentials are shown in Figs. 8.1(a,b&c). The diffraction peaks are indicated by a star symbol corresponding to FTO glass substrate. Fig. 8.1(a) shows the XRD pattern of ZnO thin film deposited at −1.1 V. The predominant diffraction peaks (100), (002) and (101) are well indexed to hexagonal wurtzite structure of ZnO. This is in good agreement with international centre for diffraction data (ICDD) card no. 89-0510. A small (100) peak is observed (hash
symbol) corresponding to anatase phase of TiO$_2$ which appeared in the seed layer in good accordance with ICDD cord no. 89-4921.

**Figure 8.1** displays the XRD patterns of ZnO films deposited at various deposition potentials (a) –1.1 V, (b) –1.2 V, (c) –1.3 V and (d) hydrothermal growth of ZnO on electrodeposited ZnO at –1.3 V.

When the film is deposited at a constant potential of –1.2 V, the intensity of ZnO peaks significantly increased with decrease in the FTO peak intensities, which indicate that the growth of ZnO increases with respect to deposition potential. When there is further increase in the deposition potential to –1.3 V, the intensity of ZnO diffraction peaks notably increased. The increase in intensity is due to increase in the growth rate as well as crystallinity of ZnO. From close observation, it can be seen from Fig. 8.1(a,b&c) that as the deposition potential increases from –1.1 to –1.3 V, the intensity of (100) peak of ZnO continuously increases due to increase in lateral growth of ZnO crystallites to the surface of
ZnO-TiO$_2$ seeded substrate. It confirms that the film deposited at $-1.3$ V has a good crystalline nature. Figure 8.1(d) shows the XRD pattern of ZnO film hydrothermally grown on ZnO film electrodeposited at $-1.3$ V. The intensity of all diffraction peaks of ZnO is considerably increased with the disappearance of TiO$_2$ diffraction peak compared to other films which indicate that hydrothermal growth increases the crystallinity and the growth density of ZnO film (Lin et al., 2015). It can confirm that the hydrothermal growth of ZnO has a better crystallinity than other films.

8.4.2 Morphological analysis

The morphologies of ZnO films deposited at various deposition potentials are observed by scanning electron microscope (SEM) and are shown in Fig. 8.2(a-c). Fig. 8.2(a&a1) presents a SEM image of ZnO film deposited at $-1.1$ V. The hexagonal ZnO platelets are vertically aligned with a low growth density on the surface of ZnO-TiO$_2$ seeded FTO substrate. It can be confirmed that the platelets are grown along the lateral growth orientation to the surface of the seeded FTO substrate, which is consistent with high intensity (101) peak in XRD pattern. The lateral growth takes place due to suppression of higher energy Zn$^{2+}$ (0001) growth orientation ((002) plane) by absorbing the citrate ions (Zhu et al., 2014c). The thickness and the width of platelets are varied in the range of 266-600 nm and 0.93-1.99 µm respectively. When there is a further increase in the deposition potential to $-1.2$ V, the density of the platelets considerably increased with a uniform distribution on the surface of seeded FTO substrate as shown in Fig. 8.2(b). It can be seen from Fig. 8.2(b1) that the platelets are grown as a layer by layer. Some of the platelets are agglomerated as a bigger one. It may be due to increase in ZnO growth rate with an increase in deposition potential.
Figure 8.2. SEM images of ZnO films deposited at various deposition potentials (a,a1) –1.1 V, (b,b1) –1.2 V, (c,c1) –1.3 V, and (d,d1) hydrothermal growth of ZnO on microsphere.
The size of the platelets is varied between 1.4-3.4 μm and 0.4-1 μm in width and thickness respectively. When the deposition potential is increased to –1.3 V, the morphology of the film dramatically changed from platelets to microsphere structures that completely masked the entire surface of the seeded substrate (Fig. 8.2(c)). A few nanoneedles are grown in microspheres as displayed in Fig. 8.2(c1). The size of the microspheres is varied between 2.34 μm and 4.36 μm. It can be understood from Fig. 8.2(a-c) that as the deposition potential increased from –1.1 to –1.3 V, the size of the ZnO morphologies notably increased due to increase in growth rate with respect to deposition potentials. The continuous increase in intensity of the (100) peak confirms the increase in crystallinity as well as lateral growth.

Figure 8.2(d&d1) shows the SEM images of hydrothermally grown microsphere-nanorod (MS-NR) hierarchical structure. After hydrothermal growth, the microspheres are completely covered by 1D nanorods. It can be seen from the insert of Fig. 8.2(d) that the well-defined hexagonal ZnO nanorods are grown as a flower structure. The length and the width of nanorods are in the range of 0.9-1.2 μm and 90-300 nm respectively. A few flowers are formed by interlacing the bottom of some nanorods. The magnified SEM images of Fig. 8.2(d1) depict that microspheres are fully covered by nanorods. The nanorods are uniformly grown on microsphere and are noticed obviously.

8.4.3 Growth mechanism

In electrochemical deposition, zinc nitrate (Zn(NO₃)₂) dissociates into zinc (Zn²⁺) and nitrate (NO₃⁻) in deionized water (reaction 8.1). ZnO formation takes place in terms of electroreductions of (NO₃⁻) and molecular oxygen (O₂) into hydroxide (OH⁻) at the working electrode/electrolyte interface (reactions 8.2&8.3) (Shinagawa and Izaki, 2014).

\[
\begin{align*}
\text{Zn(NO}_3\text{)}_2 (aq) & \rightarrow \text{Zn}^{2+} (aq) + 2\text{NO}_3^- (aq) \\
\text{Zinc nitrate} & \rightarrow \text{Zinc (II) + Nitrate}
\end{align*}
\]
O₂ + 2H₂O + 4e⁻ → 4OH⁻ (8.2)
Oxygen + Water + Electron → Hydroxide

NO₃⁻ + H₂O + 2e⁻ → NO₂⁻ + 2OH⁻ (8.3)
Nitrate + Water + Electron → Nitrite + Hydroxide

Na₃C₆H₅O₇ → 3Na⁺ + C₆H₅O₇⁻ (8.4)
Tri-sodium citrate → Sodium (I) + Citrate

Zn²⁺ + 4(C₆H₅O₇)³⁻ → [Zn(C₆H₅O₇)₄]¹⁰⁻ (8.5)
Zinc (II) + Citrate → Tetra citrate zincate (II)

(CH₂)₆N₄ + 6H₂O → 4NH₃ + 6HCHO (8.6)
HMTA + Water → Ammonia + Formaldehyde

NH₃ + H₂O → NH₄⁺ + OH⁻ (8.7)
Ammonia + Water → Ammonium + Hydroxide

Zn²⁺ + 2OH⁻ → Zn(OH)₂ (s) → ZnO + H₂O (8.8)
Zinc (II) + Hydroxide → Zinc hydroxide → Zinc oxide + Water

The increase in OH⁻ ions combines with Zn²⁺ ion to form zinc hydroxide (Zn(OH)₂), which subsequently dehydrates into zinc oxide (ZnO) at an appropriate temperature of 70 °C (Zoolfakar et al., 2013). Trisodium citrate (Na₃C₆H₅O₇) dissociates into sodium (Na⁺) and citrate (C₆H₅O₇⁻) ions (reaction 8.4). Subsequently, the C₆H₅O₇⁻ complexes with Zn²⁺ to form tetra citrate zincate (II) ([Zn(C₆H₅O₇)₄]¹⁰⁻) ions (reaction 8.5). Based on SEM images, a possible growth mechanism is proposed. Fig. 8.3(a) presents a different growth orientation of ZnO. When the electrodeposition is carried out at −1.1 V, the platelet structure is formed on account of an absorption of [Zn(C₆H₅O₇)₄]¹⁰⁻ on the fast growth orientation of (0001) plane as shown in Fig. 8.3(b), which takes place owing to Coulombic attractive force between polar plane of Zn²⁺ and [Zn(C₆H₅O₇)₄]¹⁰⁻ (Palumbo et al., 2009). As a result, the growth of ZnO slows down in c-axis growth orientation (Zhu et al., 2014c). Thus, the growth takes place in
other orientations. As a consequence, the 2D structure is formed. When there is a further increase in the deposition potential to $-1.2$ V, small changes occurred in platelet structure grown as layer by layer, which may be due to increase in growth rate and increase in deposition potential. The 3D microsphere is formed as the deposition potential is prolonged about $-1.3$ V. It could further increase the growth rate of the ZnO.

Figure 8.3 shows the schematic diagram of (a) ZnO growth orientations, (b) formation of ZnO microstructures at different deposition potentials, and (c) hydrothermal growth of 1D structure on microsphere.

In hydrothermal technique, ZnO nanorod growth takes place along the $(0001)$ orientation owing to high surface energy of $(0001)$ plane as displayed in Fig. 8.3(c) (Zhu et al., 2014a). $(\text{CH}_2)_{6} \text{N}_4$ (HMTA) thermally reacts with $\text{H}_2\text{O}$ to form formaldehyde ($\text{HCHO}$) and ammonia ($\text{NH}_3$) (reaction 8.6). The $\text{NH}_3$ reacts with $\text{H}_2\text{O}$ to form ammonium hydroxide ($\text{NH}_4\text{OH}$) that reacts with $\text{Zn}^{2+}$ to give $\text{Zn(OH)}_2$ which thermally gets converted into ZnO (reactions 8.7&8.8) (Marimuthu et al., 2017a). According to the above proposed growth mechanism, the 1D nanostructure had been hydrothermally grown on the ZnO-TiO$_2$ seeded
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FTO substrate in a solution containing equal molar concentration of zinc nitrate and HMTA (Marimuthu et al., 2016a). It also confirms the formation of 1D nanostructure on microspheres along the (0001) orientation as shown in SEM images (Fig. 8.2(d &e)).

8.4.4 Raman spectra analysis

![Raman spectra](image)

**Figure 8.4** shows the Raman spectra of ZnO (c) microsphere (d) hierarchical structures.

Raman spectra were recorded to study the crystallinity, vibrational properties and defects presented in optimized microsphere and hierarchical structures. ZnO, which is $C_{6v}$ space group, is formed by ionic and covalent bonds due to electrostatic interaction between Zn and O atom. This electrostatic interaction causes a split in $A_1$ and $E_1$ modes into longitudinal optical (LO) mode and transverse optical (TO) mode. According to Raman selection rule, ZnO has six optical modes ($A_1+2B_1+E_1+2E_2$) (Panigrahy et al., 2010). Herein, $A_1$ and $E_1$ modes are Raman and infrared active. On the other hand, $E_2$ mode is only Raman active. Fig. 8.4 shows the Raman spectra of microspheres and hierarchical structures. The second order Raman peak observed at 336 cm$^{-1}$ is ascribed to $E_{2L-2H}$ mode that appeared due to multi phonon scattering (Inguanta et al., 2013). Raman peak observed at 437 cm$^{-1}$ is
attributed to $E_2$(high) mode, which is due to vibration of the oxygen atom. The presence of $E_2$(high) mode confirms the hexagonal wurtzite structure of ZnO (Marimuthu et al., 2018). The second order Raman peak at 580 cm$^{-1}$ is assigned to $E_1$(LO) mode that appeared owing to zinc or oxygen defects (Kim et al., 2011). The peak appeared in the range of 1000-1200 cm$^{-1}$ is due to second order multi phonon mode presented from the zone boundary center (Marimuthu et al., 2017a). The intensity of $E_2$(high) mode of the hierarchical structured film is significantly increased after hydrothermal growth, indicating that the hierarchical structures are better crystalline in nature than the microsphere, which is in good agreement with XRD results (Marimuthu et al., 2018). It can be observed from this study that hierarchical structure has the best crystallinity.

8.4.5 Photoluminescence spectra analysis

The luminescence properties of microsphere and hierarchical structures were investigated through photoluminescence (PL) spectroscopy recorded under an excitation wavelength of 325 nm in the wavelength range of 350-510 nm. Figs. 8.5(c&d) present the four emission peaks of microsphere at 378, 408, 444 and 492 nm. The high intensity UV emission peak at 378 nm (3.28 eV) is attributed to the near band edge emission of radioactive recombination among the electrons in conduction band and holes in the valence band as well as free exciton-exciton recombination (Li et al., 2007; Panigrahy et al., 2010). The visible emission peaks are assigned to deep level emission in the presence of various defects presented in ZnO (Park et al., 2009). The violet emission peak is appeared at 408 nm which is due to the interstitial zinc (Sheini et al., 2010). The blue emission peak is observed at 444 nm (2.79 eV) due to an electron transition from zinc vacancy to valence band (Chen et al., 2013). The green emission peak is noticed at 492 nm (2.50 eV) because of an electron
transition from singly ionized oxygen vacancy to valence band. When the nanorods are grown on the microsphere, the intensity of UV emission of hierarchical structure significantly increased compared to the microsphere structure, which indicates an increase in radiative emission with decrease in non-radiative centre (Marimuthu et al., 2018). It can be seen that the hierarchical structure has a better crystal quality.

Figure 8.5 illustrates the PL spectra of (c) microsphere and (d) hierarchical structure.

8.4.6 UV-Visible spectra analysis

The reflectance and the absorption spectra were recorded to study light scattering and light absorption of microsphere and hierarchical structures in the wavelength range of 350-700 nm and are shown in Fig. 8.6. Fig. 8.6 shows a better light reflectance in the range of 400-700 nm. The reflectance of hierarchical structure is a much higher than that of the microsphere. Typically, the microsphere has a good light scattering property (Chou et al.,
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2007). The increased reflectance indicates that the hierarchical structure containing microsphere and nanorods shows a high light scattering ability compared to microsphere (Zhu et al., 2013).

![Graph showing UV-Vis reflectance and absorption spectra](image)

**Figure 8.6** shows the UV-Vis reflectance and absorption spectra of (c) microsphere and (d) hierarchical structures.

The increase in light scattering ability of the film increases the light traveling pathway within the film through multi light scattering. It could be observed from the SEM images of Fig. 8.2(c&d) that the growth of nanorods significantly reduces the voids in the hierarchical structured film, which may be the reason for higher light scattering. Optical absorption spectra show an intrinsic absorption peak below 385 nm, which is attributed to electron transition from valence band to conduction band (Zhang et al., 2008). The hierarchical structured film shows a high optical absorbance compared to the microsphere, which may be due to the higher light scattering ability of hierarchical structure, and change in the film thickness from 9.83 µm (microsphere) to 11.90 µm (hierarchical). As a result, the optical
absorption slightly increased. It can be concluded that the hierarchical structure has high light absorption and light scattering ability.

Figure 8.7 exhibits the UV dye absorption spectra of dye desorbed from (c) microsphere and (d) hierarchical structures.

Dye absorption spectra of dye desorbed from microsphere and hierarchical structures were carried out to investigate the dye loading of films in the wavelength range from 400-700 nm. The optimized microsphere and the hierarchical structures were immersed into an ethanolic solution containing 5 mM eosin yellow dye molecules for 3 h. Afterwards, the dye anchored microsphere and hierarchical structures were well rinsed with ethanol to remove the unbounded dye molecules. Subsequently, the rinsed photoanodes were dipped into an alkaline solution of potassium hydroxide (KOH) at a pH value of 10.5 for 3 h to desorb dye molecules from microsphere and hierarchical structures. Fig. 8.7 displays the absorption spectra of dye solutions desorbed from microsphere and hierarchical structures. The high intensive absorption peak which appeared is centered at 516 nm and is attributed to the interaction among chromophores in dye molecules (Yoshida et al., 2000). It can be
observed that the absorbance of dye molecules in hierarchical structure is significantly higher than the microsphere structure, indicating that the hierarchical structure has a large internal surface for high dye loading. The increase in light scattering ability, optical absorption and dye loading of hierarchical structure containing microsphere and nanorods can notably increase short circuit current by absorbing the number of photons (Kim et al., 2012).

8.4.7 J-V characterization

![J-V curves of DSSCs](image)

Figure 8.8 exhibits the J-V curves of DSSCs consisting of (c) microsphere and (d) hierarchical structures.

Current density-voltage (J-V) curves for DSSCs consisting of microsphere and hierarchical structures were carried out under a light illumination of 100 mW from Xeon lamp and are shown in Fig. 8.8. The measured and the calculated parameters such as open circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$), fill factor ($FF$) and photo conversion efficiency ($\eta$) are summarized in Table 8.1. The DSSC containing microsphere is exhibited a $J_{sc}$ of 12.27 mA and a $V_{oc}$ of 671 mV. The $\eta$ of the DSSC is estimated about 3.13 % with a
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$FF$ of 0.38. The $J_{sc}$ is directly related to charge injection efficiency from the excited dye molecules to the conduction band of the semiconductor, the charge collection efficiency from semiconductor to FTO conductive substrate and light harvesting efficiency associated with light scattering as well as dye loading (Zhang et al., 2008). The $V_{oc}$ of DSSC is mainly related to potential energy difference between quasi Fermi level and redox potential of electrolyte, and recombination between the collected electrons and the oxidized electrolyte species (Shin et al., 2014). The DSSC containing hierarchical structure is obtained a $J_{sc}$ of 15.95 mA, which is notably higher than the DSSC consisting of microsphere. The increased $J_{sc}$ may be attributed to higher light scattering ability of hierarchical structure that increases the light travelling path length within the photoanode by multiple light scattering (Chou et al., 2007). The increase in surface area is one of the reasons for increasing the $J_{sc}$. The increased surface area of photoanode absorbs a large number of dye molecules that absorb multiple scattered photons, which significantly increase the $J_{sc}$. The $V_{oc}$ of the DSSC is slightly increased by 39 mV from 671 to 710 mV. This increased $V_{oc}$ may be associated with either increasing the Fermi level of semiconductor or the inhibition of interfacial recombination (Li et al., 2012). The $FF$ is slightly increased from 0.38 to 0.41, which is attributed to reduction of recombination at the semiconductor/electrolyte interface, and recombination between injected electrons and surface defects of semiconductor (Wang et al., 2010). By increasing the $J_{sc}$, $V_{oc}$ and $FF$, the $\eta$ of the DSSC containing hierarchical structure is considerably increased from 3.13 to 4.64 %. The obtained $\eta$ is significantly high compared to the previous reports (Marimuthu and Anandhan, 2017b; Marimuthu et al., 2016a, 2017a, 2018). It can confirm that the DSSC containing hierarchical structure exhibits highest photo conversion efficiency.
Table 8.1 shows the Photovoltaic parameters of the DSSCs consisting of microsphere and hierarchical structure.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>( V_{oc} ) (mV)</th>
<th>( J_{sc} ) (mAcm(^{-2}))</th>
<th>( FF )</th>
<th>( \eta ) (%)</th>
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<tr>
<td>c</td>
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<td>0.38</td>
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<td>710</td>
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<td>0.41</td>
<td>4.64</td>
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8.4.8 Electrochemical impedance spectra analysis

Figure 8.9 shows the EIS spectra of Nyquist plots of DSSCs containing (c) microsphere, (d), hierarchical structures, and (e) \( R_{\text{rec}} \) value of DSSCs containing microsphere and hierarchical structures with respect to different biasing voltages.
Electrochemical impedance spectroscopy (EIS) spectra were carried for DSSCs containing microsphere and hierarchical structures to investigate the electron kinetics at electrode/electrolyte interfaces under dark condition by applying different AC biasing voltages in the frequency range of 100 kHz-0.1 Hz. Figs. 8.9(c&d) displays the Nyquist plots of DSSCs containing microsphere and hierarchical structures with respect to different AC biasing voltages. Generally, the Nyquist plot of DSSC exhibits three frequency regions, namely the higher frequency region from 100 kHz to 1000 Hz, middle frequency region from 1000 Hz to 1 Hz and low frequency region from 1 Hz to 0.1 Hz is attributed to charge transfer resistance at Pt/electrolyte interface, charge transfer recombination resistance at ZnO/dye/electrolyte interface and Warburg or ion diffusion resistance in electrolyte, respectively (Kim et al., 2012). The Nyquist plots are fitted with a suitable equivalent circuit by using Z SimpWin software as displayed in Fig. 8.9(e). The equivalent circuit contains resistances and capacitances. Here, $R_s$ is the sheet resistance, $R_{ct}$ and $C_{pt}$ are charge transfer resistance and double layer capacitance respectively at the Pt electrode/electrolyte interface. $R_{rec}$ is the charge transfer recombination resistance at ZnO/dye/electrolyte interface. $CPE$ is the constant phase element. $W_z$ is the diffusion resistance of $I^-/I_3^-$ redox ions (Marimuthu et al., 2017a). In the present work, three semicircles were observed. Out of the three semicircles, the middle frequency region is only considered to study the charge transfer recombination resistance ($R_{rec}$) to describe electron kinetics at ZnO/dye/electrolyte interface. The Nyquist plot DSSC containing hierarchal structure shows a large diameter of semicircle compared to DSSC containing microsphere in the middle frequency region, which indicates that the DSSC having a higher $R_{rec}$ value exhibits a lesser charge recombination at the ZnO/dye/electrolyte interface (Shi et al., 2013b). This decreased charge recombination may
be attributed to an increase in crystalline nature of the hierarchical structure after the hydrothermal growth. Fig. 8.9(c) shows the $R_{\text{rec}}$ values of the DSSCs consisting of microsphere and hierarchical structure with respect to biasing voltages. The $R_{\text{rec}}$ values get decreased as the biasing potentials are increased which is due to reduction in potential barrier to charge injection at ZnO/dye/electrolyte interface. In all biasing voltages, the DSSC containing hierarchical structure has highest $R_{\text{rec}}$ value. This higher $R_{\text{rec}}$ indicates that a lesser number of defect densities in hierarchical structures acted as recombination centre compared to another DSSC (Musselman, et al., 2011). It can be found that the DSSC containing hierarchical structure has best photo conversion efficiency with a less charge recombination.

### 8.5 Conclusions

Microsphere and hierarchical structures were successfully synthesized by employing a two step electrochemical and hydrothermal techniques. They acted as a light scattering center to increase light harvesting ability through multiple light scattering. The hexagonal wurtzite structure of microstructure was oriented along lateral growth direction due to absorption of citrate ion on (0001) growth orientation. SEM images displayed an increase in the microstructure size as well as growth density with an increase in deposition potentials. The nanorods were grown at different growth directions on microstructure. Raman and PL results manifested that the hierarchical structure possessed a better crystallinity with lesser atomic defects than the microsphere. The hierarchical structure had higher dye loading, light absorption and scattering ability. The efficiency of DSSCs is found to be 3.13 and 4.64 % for microsphere and hierarchical structure photoanodes, respectively. The DSSC containing hierarchical structure exhibited a higher charge transfer recombination resistance compared to DSSC containing microsphere.