CHAPTER-II

Materials Introduction, Review of literature, Scope of the present work, Materials for DSSC fabrication, Experimental flowcharts, Material characterizations and Contents of the thesis
2.1 Materials introduction

2.1.1 General introduction of ZnO

The ZnO can be classified as wurtzite, zinc blende and rock salt crystal structures. The ZnO crystal structures are presented in Fig. 2.1. In these structures, an anion (O\textsuperscript{2−}) is surrounded by four cations (Zn\textsuperscript{2+}) in tetrahedral coordination, and vice-versa. It has sp\textsuperscript{3} hybrid covalent bonding. These compounds are both ionic as well as covalent bonds in nature. However, large difference in electronegativity of O\textsuperscript{2−}=3.44 and Zn\textsuperscript{2+}=1.65 leads to strong ionic bonding in ZnO. The ZnO, which is II-IV group semiconductor, has a wide band gap as well as ionicity at the ionic and covalent semiconductor boundary.

Figure 2.1: Crystal structure of ZnO (a) wurtzite (b) zinc blende and (c) rock salt.
Among the different crystal structures, ZnO wurtzite phase is thermodynamically the most stable state under atmospheric conditions. On the other hand, zinc blende is in metastable phase and is only stable on cubic substrate like GaN. The rock salt phase is more stable at relatively high pressures. The phase transition of ZnO takes place from thermally stabled wurtzite phase to rock salt phase at a high pressure of 10 GPa. At the time phase transition, the volume is reduced by 17%. This volume reduction is due to attenuation of lattice dimensions which lead to interionic coulomb interaction. The ZnO wurtzite structure forms hexagonal unit cell arrangement in three dimension, which has two lattice parameters such as \(a\) and \(c\) in the ratio of \(c/a=1.633\) with a density of 5.605 g/cm\(^3\). The lattice parameter of wurtzite may deviate due to free charge, stress, temperature and impurities. The difference in electronegativities of the two constituents can be correlated by \(c/a\) ratio.

Yakov Frenkel introduced the term exciton in crystals in 1936 (Frenkel et al., 1936). It may define that an electron-hole pair is bounded by Coulomb attractive force, which is called the exciton. When the group velocity of an electron and a hole is equal, the exciton is formed. The material having small dielectric constant has a strong Coulomb interaction between electron and hole and it results in a small radius called Frenkel exciton. On the other hand, the semiconductor material generally has a large dielectric constant. Hence, the electric field reduces Coulomb interaction between electron and hole resulting in large radius than the lattice space called Wannier exciton. The energy required to ionize the electron-hole couple is equal to binding energy. In semiconductor, the exciton is used for light emission at low temperature (thermal energy of exciton is \(kT \leq B.E.\)), which replaces a electron-hole pair recombination at a high temperature. Hence, ZnO possesses a higher free exciton binding energy of 60 meV at room temperature (Ma et al., 2001; Hauschild et al., 2006). The
exciton binding energy provides stability against thermal separation of excitons. The optical properties of semiconductor are related to both intrinsic and extrinsic effects. In intrinsic effect, the optical transition takes place between an electron in the conduction band and a hole in the valence band due to Coulomb interaction. In high quality crystal, the exciton transition can exhibit from ground state to excited state. Extrinsic effects are associated with dopants or defects in which, the optical transition takes place discrete in electronic states.

2.1.2 Properties of ZnO

- ZnO is obtained from mineral as a white powder.
- ZnO has band gap energy of 3.37 eV with an n-type carrier concentration.
- It has an exciton binding energy of 60 meV with P6mc space group.
- ZnO crystal that has thermo-chromic, changes color from white to yellow as it gets heated and returns to white color as it cools to room temperature.
- It can easily react with acid solution to form its product like ZnS with alkali solution to form like zincate.
- It has heat conductivity, melting point, heat capacity and low thermal expansion.
- The electron mobility of ZnO varies with respect to temperature, and has an approximate value of 2000 cm² (V.s) at 80 K.
- ZnO strongly absorbs UV light below 365 nm but it is transparent for visible light.
- ZnO exhibits semiconducting, piezoelectric and pyroelectric properties.
- ZnO is covalent and is ionic bond in nature with sp³ hybridization.

2.1.3 Applications of ZnO

- Photodiode (Lee et al., 2002)
- Solar cell (Gratzel et al., 2005)
ZnO is a multifunctional material, which can form diverse morphologies (one dimensional, two dimensional and three dimensional) namely nanorods (Vayssieres et al., 2003), nanotubes (Lu et al., 2009), nanowire (Xing et al., 2003), nanocombs (Zhang et al., 2006), nanobelt (Wang et al., 2006), nanoribbons (Fang et al., 2009), nano propeller (Gao and Wang, 2004), nanocages (Snure and Tiwari, 2007), nanorings (Xu et al., 2002), nanoplates, nanowalls (Pradhan and Leung, 2008a), nanosheets (Qui, et al., 2011), and microspheres (Guo et al., 2014). These diverse morphologies are easily formed on glass, FTO and ITO substrate. Among the aforementioned applications, ZnO nanostructures are potentially used for solar cell applications due to large surface area, high electron mobility and its bio safety.

2.2 Review of literature

Xu et al., synthesized novel polycrystalline rhombus like ZnO nanorod arrays (NRAs) on ITO substrate by applying a two steps method (Xu et al., 2010a). At very first, ZnO and ZnFOH were electrodeposited at 30 °C in a solution containing the absence and presence of NaF, respectively. Secondly, the vertical growth of ZnO NRAs was obtained by pyrolyzing the ZnFOH at 450 °C. The polycrystalline rhombus ZnO NRs consisted of nanoparticles and nanoporous. The authors constructed DSSCs and obtained the efficiencies of 0.69 and 0.47 %
for polycrystalline rhombus ZnO NRAs and single crystalline hexagonal ZnO NRAs, respectively. The increase in efficiency is due to increase in internal surface area.

Xu et al., fabricated hierarchical ZnO nanowire-nanosheet (NW-NS) architectures on ITO glass substrate by applying a two steps method (Xu et al., 2010b). In the first step, the ZnO NSs were synthesized by pyrolyzing the electrodeposited Zn$_5$(OH)$_8$Cl$_2$ NSs at 350 °C. In the second step, hierarchical ZnO NR-NS architectures were synthesized by immersing ZnO NSs in a solution containing Zn(NO$_3$)$_2$ and HMTA. They obtained an efficiency of 4.8 % for DSSC based on hierarchical ZnO NW-NS architectures, which was two times higher than the DSSC based on primary ZnO NS. The increase in efficiency was due to increase in the internal surface and multiple light scattering.

A porous hierarchical disk like ZnO nanostructure was hydrothermally synthesized on silica (Si) substrate at 95 °C by Wang et al., (Wang et al., 2010). The hierarchical ZnO nanostructure contained the porous ZnO nanowire grown with six symmetric directions that were like a disk. The DSSCs were fabricated by Wang et al., and the DSSC based on porous hierarchical ZnO nanostructures showed a higher efficiency of 2.49 % than DSSC based on ZnO NWAs. The increase in efficiency was due to increase in the surface area and in retaining the direct pathway to electron collection. The annealed hierarchical ZnO nanostructure exhibited a significant improvement in fill factor (FF) due to reduction in surface defects.

ZnO branched nanorod arrays (NRAs) were hydrothermally grown on FTO substrate by controlling Zn(NO$_3$)$_2$ and HMTA concentrations with Fang and his co-workers (Fang et al., 2011). At first, the team primarily grew ZnO NRAs on FTO substrate in a solution containing an equimolar ratio of Zn(NO$_3$)$_2$ and HMTA at 90 °C for 6 h. Afterwards, the
lateral growth of ZnO nanorods was grown on the facet of NRAs in a solution containing diaminopropane (DAP) at 60 °C for 6 h. The grown ZnO NRAs were in a well-defined hexagonal shape aligned perpendicular to the surface of the FTO substrate. The light absorption of the secondary branched ZnO NRAs was much higher than the primary ZnO NRAs due to light scattering effect. They obtained the efficiencies of 0.67 and 1.66 % for DSSCs based on primary and branched ZnO NRAs respectively.

Ameen et al., hydrothermally fabricated non-aligned and highly aligned ZnO nanotubes (NTs) on FTO and ZnO seeded FTO substrates respectively at 85 °C for 3 h (Ameen et al., 2011). The NTs were a hexagonal shape grown perpendicular to the surface of the ZnO seed. The presence of high intensity E2(high) mode and UV near band edge emission confirmed the NTs grown on ZnO seeded FTO substrate having higher crystallinity with lesser atomic defects. The absorption of aligned ZnO NTs significantly increased compared to the non-aligned ZnO NTs. They assembled DSSCs by using optimized non-aligned and aligned ZnO NTs and compared their efficiency with adequate parameters. The DSSC is fabricated by using the aligned ZnO NTs showed a higher $V_{oc}$ of 0.65 V, a $J_{sc}$ of 5.5 mA, a $FF$ of 0.61 and an efficiency of 2.2 % than the DSSC fabricated by using non-aligned ZnO NTs. These increased performances were attributed to higher charge transfer and collection efficiency of dye loaded aligned ZnO NTs.

Karst and his co-workers deposited ZnO nanowires/nanoparticles (NWs/NPs) on ZnO NPs seeded FTO substrate (Karst et al., 2011). Firstly, they hydrothermally grew ZnO NWs on ZnO NPs seeded FTO substrate in a solution containing an equimolar concentration of Zn(NO$_2$)$_3$ and HMTA at 90 °C for 3 h. Secondarily, ZnO NPs were deposited over the ZnO NWs by annealing the dip coated layered hydroxide zinc acetate (LHZA) NPs at 450 °C. The
hexagonal shaped NWs were grown along the c-axis to the surface of the ZnO seeded FTO substrate. The NWs/NPs composite film had a high dye loading \( (2.9 \times 10^{-8}\ \text{mol.cm}^{-2}) \) compared to the dye loading of NWs film \( (0.96 \times 10^{-8}\ \text{mol.cm}^{-2}) \). They evaluated an efficiency of 1.75 % which is three times higher \( J_{sc} \) for DSSC based on ZnO NWs/NPs composites than the DSSC based on ZnO NWs.

The high transparent and high quality ZnO NRAs were fabricated on ZnO seeded ITO substrate by controlling the deposition parameters such as reaction temperatures and solution concentrations in a solution containing Zn(NO\(_3\))\(_2\) and HMTA by applying a two steps chemical bath deposition method of Lee et al., (Lee et al., 2011). The resulting well-defined hexagonal ZnO NRAs were deposited at the optimized conditions of 30 mM Zn(NO\(_3\))\(_2\) concentration and 95 °C growth temperature. The deposited hexagonal wurtzite structured ZnO NRAs were oriented with respect to concentration of Zn(NO\(_3\))\(_2\). They also fabricated solid state dye sensitized solar cell (SS-DSSC) for optimized NRAs and obtained a conversion efficiency of 0.059 %.

Zhang et al., studied a novel bilayer structured ZnO film prepared on ZnO seeded FTO substrate (Zhang et al., 2011). The bilayer structure consisted ZnO NWAs as an under layer and polydisperse ZnO nanocrystalline arrays (NCAs) as an upper layer. The prepared bilayer ZnO was a hexagonal wurtzite structure grown along the (002) plane direction. They were found to diffuse light reflectance of ZnO NWAs/NCAs film notably higher than the ZnO NWAs film due to light scattering effect. The authors obtained the efficiencies of 1.04 and 3.02 % for ZnO NWAs and NWAs/NCAs respectively. The increase in efficiency was on account of its fast electron transport, improved light scattering and enhanced surface area.
Hierarchically assembled ZnO nanocrystallites (NCs) were deposited on ZnO buffer layer coated FTO substrates by employing a spray pyrolysis method at a substrate temperature of 250 °C by Memarian et al., (Memarian et al., 2011). They deposited the mixed layer on buffer layer by using a solution containing ZnO NPs and zinc acetate. The film consisting of NCs with sub-micrometer sized aggregates offered a large internal surface area and efficient light scattering. The compact buffer layer acted as an efficient blocking layer to avoid back reaction between collected electron at FTO substrate and electrolyte. The dye loading of film was found to be 1.5×10⁻⁷ mol.cm⁻². The efficiency of DSSCs fabricated with and without buffer layer was 7.5 and 2.6 %, respectively.

A ZnO nanowire/nanoparticle (NW/NP) composite was prepared on FTO substrate by Puyoo and his co-workers (Puyoo et al., 2012). The vertically aligned ZnO NW was hydrothermally synthesized on ZnO seeded FTO substrate in a solution containing polyethylenimine (PEI) at 90 °C for 5 h. Subsequently, the layered hydroxide zinc acetate (LHZA) NP was deposited on ZnO NW grown FTO substrate due to chemical bath deposition. The prepared LHZA NP on ZnO NW/NP composite film was converted into LHZA, zinc oxoacetate and ZnO at different annealing temperatures such as, untreated, 120 and 450 °C, respectively. The DSSC based on 120 °C treated film exhibited a better conversion efficiency of 4.7 % with improved $J_{sc}$ than the other DSSCs based on untreated and 450 °C film due to high surface area. The authors observed the highest $R_{rec}$ for DSSC based on 120 °C treated film owing to efficient blocking barrier to electron recombination at dye loaded zinc oxoacetate/electrolyte interface.

Kung et al., systematically optimized the growth of ZnO nanosheets/nanoparticles (NSs/NPs) on FTO substrate by adjusting sodium acetate concentration in a deposition
solution (*Kung et al., 2012*). ZnO nanosheets as an upper layer and nanoparticles as an under layer could be obtained by annealing the primarily electrodeposited \(\text{Zn}_5(\text{OH})_8(\text{OAc})_2\) at 300 °C. The optimized parameters such as sodium acetate concentration, deposition time and dye loading time for a well-defined double layer film of ZnO NSs/NPs were about 0.05 M, 10 min, 135 min, respectively. The optimized ZnO NSs/NPs film displayed a low transmittance compared to NPs film due to light scattering on the variation of refractive index at NSs/NPs interface. The authors estimated an efficiency of 4.65 % for optimized ZnO NSs/NPs based DSSC at a film thickness of 12.34 µm.

*Hu et al.*, developed a novel ultralong nanoporous ZnO nanobelt arrays (NBAs) on FTO substrate by pyrolyzing the hydrothermally grown intermediated Zn(OH)F NBAs at 500 °C for 2 h (*Hu et al., 2012*). First, The FTO substrate was dipped in a solution containing Zn(NO\(_3\))\(_2\) for 3 h. Subsequently, the Zn(OH)F NBAs was prepared by dipping the treated FTO substrate in a solution containing Zn(NO\(_3\))\(_2\), NH\(_4\)F and NH\(_3\) at 120 °C for 3 h. The developed ultralong ZnO NBAs were in a hexagonal wurtzite structure and were oriented to their preferential growth direction. The NBAs made a number of nanocrystals and porous that offered a large surface area. The DSSC based on 27 µm thickness of ultralong porous ZnO NBAs exhibited a high conversion efficiency (3.28 %) compared to DSSC based on ZnO NR owing to high internal surface area, electron collection efficiency and strong light scattering.

Different ZnO micro-nano morphologies were synthesized on functionalized FTO substrate by adjusting the solution pH using NH\(_3\) solution in a solution containing Zn(NO\(_3\))\(_2\) and HMTA at 90 °C for 9 h by Znou and his team (*Znou et al., 2012*). Different ZnO morphologies such as NWs, flower made of petals, and urchin made of NRs were
synthesized by changing the solution pH from 7 to 10. The synthesized different ZnO morphologies were a hexagonal wurtzite structure grown along the lateral growth direction. The reflectance of the flower like morphology was higher due to its bigger size of petals. Znou et al., assembled DSSCs for optimized morphology and obtained the efficiencies of 1.92 and 0.98 % for DSSCs based on dense urchin like ZnO and ZnO NWs, respectively. The increase in efficiency of the dense urchin like ZnO might be due to its higher surface area for dye loading.

Zhu et al., fabricated ZnO nanorod-nanosheet (NR-NS) hierarchical architectures on FTO substrate (Zhu et al., 2013). At first, they hydrothermally synthesized ZnO NR on spin coated ZnO seeded FTO substrate in a solution containing Zn(NO$_3$)$_2$, HMTA and PEI at 92 °C for 32 h. In the same method, the NS consisting of NPs was grown perpendicular to the facet of NR in a solution containing disodium citrate. The NR-NS was oriented along the (002) growth direction with a hexagonal wurtzite structure. The dye absorption and the diffused light reflectance of ZnO NR-NS structure were significantly higher than the NR structure owing to increase in the surface area and light scattering. The DSSC based on NR-NS showed a higher efficiency (1.13 %) with a lesser charge recombination at the dye/ZnO NR-NS/electrolyte interface compared to DSSC based on NR (0.66 %).

Shi and his scientific group synthesized asymmetric ZnO panel like hierarchical architectures (PHAs) that consisted of tiny nanosheets (Shi et al., 2013a). They fabricated DSSCs with different ZnO PHAs weight compositions such as 0, 30 and 60 % with ZnO NPs to increase the mechanical stability, surface area and electron mobility. The highly crystallized ZnO nanosheets (30 %) which interlaced with NPs significantly minimized the grain boundaries which offered a direct pathway for rapid transport and collection of free
electrons. The DSSC fabricated with 30% of PHAs exhibited a higher efficiency of 5.59% at a film thickness of 28.7 µm compared to other two compositions due to the increase in internal surface area and decrease in electron path length.

Different ZnO morphologies were fabricated on ITO substrate by using an aqueous solution growth method by Ganesh et al., (Ganesh et al., 2013). The diverse morphologies including ZnO NP, nanoplate (NPl), NR and microrod (MR) were a hexagonal wurtzite structure grown by changing the crystallographic orientation from (101) to (002) plane for changing the morphology from NP to MR. The film consisting of NP had higher dye absorption than other structures. The authors constructed DSSCs for different ZnO morphologies and estimated the efficiencies of 0.28, 0.50, 0.81 and 1.33% for NP, NPl, NR and MR, respectively. They ascertained and confirmed improvement in efficiency which was attributed to large surface area and less charge recombination at dye loaded NP/electrolyte interface.

Lin et al., electrochemically synthesized novel ZnO columns and sheet like structures on ITO substrate in the absence and the presence of sodium dodecyl sulfate (SDS) in an aqueous solution containing Zn(NO$_3$)$_2$ at 70 °C (Lin et al., 2013). The ZnO columns and sheets were a hexagonal wurtzite structure oriented along the (101) and (002) plane direction, respectively. The sheet like structure consisted of nanoporous. The authors obtained the efficiencies of 0.56 and 1.96% for DSSCs based on ZnO columns and sheets respectively. The enhancement in efficiency was ascribed to higher dye absorption.

Magne et al., electrochemically deposited ZnO NPs/porous light scattering layer on FTO substrate in a deposition solution consisting of ZnCl$_2$ at –1 V at 70 °C (Magne et al., 2013a). The porous ZnO layer which was made of sub-micrometer sized particles on a thin
layered ZnO deposited FTO substrate. The deposited porous ZnO layer was a hexagonal wurtzite structure grown along the (101) plane direction. The film consisting of porous ZnO layers had a higher diffuse light reflectance than the ZnO NPs due to light scattering effect. To increase the surface area, ZnO NPs were filled between voids of porous. Magne et al., constructed DSSCs and obtained the efficiencies of 1.13 and 2.54 % for DSSCs based on ZnO NP and ZnO NPs/porous sub-microparticles respectively.

The hierarchical ZnO rod-cluster architecture was hydrothermally synthesized on FTO substrate by varying the growth temperature, solution pH and growth time by Meng and his team (Meng et al., 2013). The synthesized hierarchical ZnO rod-cluster was a hexagonal wurtzite structure grown along the (002) plane direction. The hierarchical ZnO rod-cluster architecture synthesized at 120 °C at a pH of 10 for 18 h showed highest photo to current conversion efficiency of 2.42 % due to its structural superiority for light and dye absorption.

Magne and his co-workers electrochemically deposited ZnO porous films on ZnO blacking layer coated FTO substrate in the solutions containing ZnCl$_2$ and different eosin Y concentrations of 200 and 50 µM at deposition potentials of –0.8 and –1 V respectively for 20 min (Mange et al., 2013b). The film deposited at the lower and the higher deposition potentials showed porous and aggregated grains with nanoporous, respectively. The high intensity UV emission with a weak visible emission confirmed a higher crystal quality of the film deposited at lower potential than the other one. Dye absorption of the films deposited at lower and higher deposition potentials was 59 and 69 nmol.cm$^{-2}$ respectively. They observed that DSSC assembled with film deposited at the higher potential showed a higher efficiency of 4.4 % compared to DSSC assembled with the film deposited at lower potential (3.8 %).
Nayeri et al., deposited ZnO NRs on different seed layers like ZnO and Al doped ZnO (AZO) coated ITO substrate through a chemical bath deposition (CBD) method by varying solution concentrations, growth temperatures and times (Nayeri et al., 2013). The ZnO NRs grown on AZO seed layer were in a hexagonal shape oriented along the (002) growth direction, were with a high growth density and uniform distribution. The intensity of UV near band edge emission of the ZnO NRs grown on AZO seed layer got significantly increased with an increase in growth time from 3 to 9 h due to higher crystal quality. The efficiency of DSSC based on ZnO NRs grown on ZnO and AZO seed at the optimized conditions of 20 mM Zn(NO$_3$)$_2$ concentration, 95 °C growth temperature and 9 h growth time was found to be 0.13 and 0.34 %, respectively.

Different morphologies like ZnO needles, flower and needle-clusters were hydrothermally synthesized by changing the Zn$^{2+}$ precursor concentrations and stirring times at 100 °C by Qu and his group (Qu et al., 2014). The synthesized ZnO morphologies were preferentially oriented along the (101) plane direction with a hexagonal wurtzite structure. ZnO needle-clusters showed high light absorption and reflectance compared to other two morphologies. They fabricated DSSCs and estimated the efficiencies of 0.24, 0.85 and 2.22 % for ZnO needle, flower and needle-cluster, respectively. The DSSC based on ZnO needle-clusters exhibited higher $J_{sc}$ and $FF$ with an identical open circuit voltage ($V_{oc}$) due to increase in internal surface area and light scattering.

Raja and his co-workers prepared the vertically aligned and bundle like ZnO NRs on the dip coated ZnO seeded ITO substrate in an aqueous solution by containing Zn(NO$_3$)$_2$ and HMTA at 70 °C for 4 and 6 h, respectively (Raja et al., 2014a). The vertically aligned and bundle like ZnO NRs were hexagonal wurtzite structure oriented along the (002) and (101)
plane direction, respectively. The light absorption of the bundle like ZnO NRs was significantly extended compared to the vertically aligned one due to increase in the multiple scattering of incident light. The dye loading of the bundle like ZnO NRs was higher ($8.9 \times 10^{-8}$ mol/cm$^2$) than the vertically aligned ZnO NRs ($86.2 \times 10^{-8}$ mol/cm$^2$). They estimated the efficiencies of 0.74 and 0.83 % for DSSCs fabricated with vertically aligned and bundle like ZnO NRs respectively.

Zhu et al., fabricated ZnO nanorods and nanorods-nanosheets (NRs-NSs) on zinc foil by using a two step hydrothermal process (Zhu et al., 2014a). First, ZnO NRs were hydrothermally synthesized by immersing the Zn foil in a solution containing 1 % of NH$_3$ at 100 °C for 24 h. Subsequently, ZnO NSs were grown horizontally to the surface of the ZnO NRs in a solution containing Zn(NO$_3$)$_2$, HMTA and tri-sodium citrate at 70 °C for 6 h. The hexagonal wurtzite structured ZnO NRs was oriented perpendicular to the surface of Zn foil substrate. The ZnO NRs-NSs film had higher dye absorption and light reflectance than the ZnO NR film. The $J_{sc}$ got notably increased from 1.321 mA to 3.041 mA for ZnO NR-NS based DSSC owing to increase in the surface area as well as light scattering of the lateral growth of NS. Thereby the efficiency was increased by 0.67 %.

Self light scattering wrinkle structured ZnO film was fabricated on FTO substrate by using simple sol-gel method in a solution containing zinc acetate and monoethanolamine by Justin Raj et al., (Justin Raj et al., 2014). The wrinkle structured ZnO was in a hexagonal wurtzite structure oriented along the (101) plane direction. It consisted of a number of tree roots in the range of 400-800 nm in diameter, which are embedded with a large number of ZnO NCs. Although, the dye absorption of the wrinkle structure was significantly less compared NP film, the efficiency of the DSSC based on wrinkle structure showed a higher
(1.97 %) than the NP structure (1.17 %) due to multi scattering of incident light within the film.

Kuo et al., synthesized tree-like and NRAs on Al doped ZnO (AZO) seeded FTO substrate in a solution containing Zn(NO$_3$)$_2$ and HMTA at 90 °C for 9 h (Kuo et al., 2014). The tree and NRAs were a hexagonal wurtzite structure grown along the (002) growth orientation and composed of a number of NRs. Dye loaded tree like electrode had explored higher absorption than the NRAs electrode so that the DSSC constructed with tree like electrode exhibited a higher efficiency of 0.23 % compared to DSSC constructed with NRAs due to large internal surface area and multiple scattering of incident light. The DSSC constructed with tree-like electrode showed a longer electron lifetime (3.91 ms) than the NRAs (3.28 ms).

A mesoporous ZnO thin film was deposited on FTO substrate by pyrolyzing the chemical bath deposited hydrozincite at 300 °C for 30 min by Abdullah et al., (Abdullah et al., 2015). The hydrozincite was deposited in a solution containing Zn(NO$_3$)$_2$ and urea at temperatures of 60 and 80 °C respectively for 24 h. The ZnO film was a hexagonal wurtzite structure grown along the (100) plane direction. The ZnO thin film displayed flower like morphology. DSSCs based on mesoporous ZnO films deposited at 60 and 80 °C showed efficiencies of 1.81 and 2.25 % respectively. The improvement in efficiency was attributed to the increase in short circuit current density ($J_{sc}$) due to increase in thickness of 24 µm. The DSSC based on mesoporous film deposited at 80 °C had lesser charge recombination at dye loaded ZnO/electrolyte interface.

Kang and his team fabricated a novel tri-layer ZnO hierarchical microsphere on FTO substrate (Kang et al., 2015). The 1D ZnO NWAs were hydrothermally grown along the
(002) growth direction with a hexagonal wurtzite structure on electrodeposited ZnO seeded FTO substrate. Subsequently, the small and large ZnO hierarchical microspheres were placed over the ZnO NWAs. The tri-layered ZnO nanostructures had a higher light diffuse reflectance, light and dye absorption than the mono layered and double layered ZnO nanostructure due to large surface area and light scattering ability of ZnO microsphere. They fabricated DSSCs and obtained efficiencies of 0.43, 1.67 and 3.21 % for DSSCs based on mono, double and tri-layered ZnO nanostructures respectively. The DSSC based on tri-layered ZnO nanostructure had a low sheet resistance and high $R_{rec}$ compared to other two DSSCs.

ZnO NS was obtained on FTO and Indium tin oxide coated polyethylene naphthalate (ITO-PEN) substrates by pyrolyzing the chemical bath deposited layered hydroxide zinc nitrate (LHZN) at different temperatures by Yuki et al., (Yuki et al., 2015). The LHZN films were deposited at deposition temperatures of 60, 70 and 80 °C respectively for 24 h in a methanolic solution. The ZnO NS was a hexagonal wurtzite structure grown along the (101) plane orientation. The LHZN deposited on ITO-PEN substrate annealed at 120 °C for 72 h had a larger surface area of 18.9 m$^2$/g compared to LHZN deposited on FTO substrate annealed at 450 °C for 30 min. The dye loading was found to be 7.32 x 10$^{-8}$ and 7.16 x 10$^{-8}$ mol/cm$^2$ for films annealed at 120 and 450 °C respectively. They fabricated DSSCs and calculated the efficiencies of 2.08 and 2.01 % for DSSCs based on films annealed at 120 and 450 °C respectively.

Nayeri and his co-workers hydrothermally synthesized ZnO NTs on ITO substrate through a two steps approach. The ZnO NRAs were synthesized on sputtered Al doped ZnO seeded ITO substrate in an aqueous solution by containing Zn(NO$_3$)$_2$, HMTA and PEI at
90 °C (Nayeri et al., 2015). The optimized parameters for converting ZnO NRAs into NTs growth were at a growth temperature of 90 °C, an etching time of 5 h and a KCl concentration of 2 M. The hexagonal shaped ZnO NRAs and NTs were oriented along the (002) plane direction. The NTs etched in KCl for 5 h exhibited the better dye absorption and crystal quality with less atomic defects compared to the other etching times. The efficiency of DSSCs based on ZnO NRAs and NTs was 1.06 and 2.87 %, respectively. The DSSC based on NTs had a higher $R_{\text{rec}}$ than the DSSC based on NRAs.

Dhamodharan et al., deposited ZnO nanocrystalline (NC) thin film on ITO substrates by a spray pyrolysis deposition at different substrate temperatures in the range of 250-400 °C in an aqueous solution containing zinc acetylacetonate (Dhamodharan et al., 2015). The ZnO film deposited at a substrate temperature of 350 °C had well crystallized hexagonal structure grown along the (002) plane orientation and it also showed petal shaped grains with porous nature. The high intensity UV near band edge emission confirmed a better crystal quality of the film deposited at a substrate temperature of 350 °C than the other films. The film deposited at 350 °C had low resistivity, high carrier concentration, high hall mobility and conductivity compared to other films. They assembled DSSC for optimized ZnO NC thin film and evaluated an efficiency of 0.42 %.

Hierarchical ZnO NRAs were synthesized and analysed by Lu and his team on flexible stainless steel mesh by employing a two steps electrodeposition method in a solution containing ZnCl$_2$ at 80 °C for 30 min (Lu et al., 2015). In the first step, ZnO NRAs were electrochemically synthesized at –1 V. Prior to the second step, the synthesized ZnO NRAs were dipped in sol-gel solution containing zinc acetate to produce ZnO nanosheets. Hierarchical ZnO NRAs were synthesized by repeating the first step. The hierarchical ZnO
consisted of flower like structures that were formed by a large number of hexagonal shaped
NRs grown along the c-axis to the surface of the substrate. The hierarchical ZnO NRAs had a
higher dye loading than the primary ZnO NRAs due to the large surface area. As a result, the
DSSC fabricated with hierarchical ZnO NRAs showed a higher efficiency (0.24%) than the
DSSC fabricated primary ZnO NRAs (0.16%).

Iwantono et al., hydrothermally fabricated ZnO NRs on spin coated ZnO seeded FTO
substrate in a solution containing Zn(NO$_3$)$_2$ and HMTA at different growth temperatures (60,
70, 80 and 90 °C) and times (2, 4, 6 and 8 h) (Iwantono et al., 2015). The ZnO NRs grown at
the optimized conditions of growth temperature 90 °C and growth time 8 h had highly c-axis
growth with a hexagonal wurtzite structure. The grain sizes were increased by increasing the
growth temperatures. The NRs grown at 90 °C for 8 h had much higher absorption than other
conditions. They fabricated DSSC for optimized NRs and obtained an efficiency of 0.27%.

Sisman and his team electrochemically deposited NRAs, micro platelets (MPIs), NSs
and 3D nanofibrous (NFs) on ITO substrates in solutions containing different compositions
of Zn(NO$_3$)$_2$, NaCH$_3$COO, KCl and Na$_3$C$_6$H$_5$O$_7$ at 75 °C at –0.95 V (Sisman et al., 2015).
The different ZnO morphologies were hexagonal wurtzite structure grown along the c-axis to
the surface of the ITO substrate. The dye absorption and the light scattering ability of the
NFs were notably higher than the other morphologies. They estimated the efficiencies of
2.18, 2.55, 1.36 and 3.78 % for DSSCs based on NRAs, MPIs, NSs and NFs respectively.

Double layered ZnO NRAs/ellipsoids or spheres films were synthesized on ZnO
seeded FTO substrate by Wang et al., (Wang et al., 2015). The ZnO NRAs were
hydrothermally synthesized in an aqueous solution containing Zn(NO$_3$)$_2$, HMTA, PEI and
NH$_3$ at 88 °C for 7 h. It is followed by ZnO ellipsoid or spheres which were synthesized by
sonochemical method and coated over NRAs grown FTO substrate. ZnO NRAs/ellipsoids or spheres that were well interconnected by NPs, were a hexagonal wurtzite structure oriented along the (101) plane direction. The surface area of the ZnO ellipsoids and the spheres were found to be 46.91 and 58.36 m$^2$/g respectively. The light diffuse reflectance of ZnO NRAs/spheres was considerably higher than the other two structures. The authors found the efficiencies of 0.93, 2.26 and 3.19 % for DSSCs based on ZnO NRs, NRAs/ellipsoids and NRAs respectively.

Gaikwad et al., studied the effect of Zn source concentrations on ZnO thin films deposited on FTO substrate by successive ionic layer absorption reaction (SILAR) method in a solution containing Zn(NO$_3$)$_2$ and ammonia as a cationic source and hydrogen peroxide by (H$_2$O$_2$) keeping at 80 °C as anionic source (Gaikwad et al., 2016). The ZnO thin films deposited at 100 mM Zn source were in a hexagonal wurtzite structure with better crystallinity grown along c-axis to the surface of the substrate. The significant morphology change was observed from NRs to NFs as the concentration of the Zn was varied from 50 to 150 mM. The NRs deposited at 100 mM of Zn source had a higher light absorbance than the film deposited in other concentrations (50, 75 and 150 mM). The DSSC based on optimized NRs exhibited a higher $J_{sc}$ of 5.43 mA/cm$^2$ and $V_{oc}$ of 0.42 V with an efficiency of 0.70 %.

Nagaya and his co-workers electrochemically deposited eosin Y absorbed ZnO thin films on ZnO buffer layer coated FTO substrates in an aqueous solution containing Zn(NO$_3$)$_2$, dimethylamine-borate (DMAB) and different concentrations (0-200 µmol dm$^{-3}$) of eosin Y at 60 °C (Nagaya et al., 2016). Morphology of the films get changed from NRs to flake shaped aggregate with respect to eosin Y concentrations. Dye absorption of the thin films was increased with an increase in dye concentrations. The growth orientation of the
hexagonal wurtzite structured ZnO thin films showed the notable changes from (002) (c-axis) to (101) (a-axis) with an increase in the eosin Y concentrations owing to absorption of eosin Y on (002) growth direction. The efficiency of the DSSC based on photoanode deposited in a solution containing 100 µM of eosin Y was about 0.67 % at 1 µm film thickness.

Olive-shaped ZnO nanocrystallite (NC) aggregates were synthesized via an aqueous solution method in a solution containing Zn(NO$_3$)$_2$ and NaOH at 80 °C for 4 h by Chen and his group ([Chen et al., 2016](#)). The synthesized NC aggregates were in a hexagonal wurtzite structure grown along the preferred (101) plane direction. The surface area of the ZnO NC aggregates, NP and solid scatters was 20.60, 16.52 and 11.67 m$^2$/g respectively. The dye absorption and diffuse light reflectance of ZnO NC aggregates were higher than the NP and the solid scatters. The efficiency of DSSCs based on ZnO NP/NC aggregate and NP/solid scatters was 4.43 and 3.57 %, respectively.

Sutthana et al., deposited ZnO NP film on FTO substrate by applying an acid vapor texturing process in a solution containing HNO$_3$ at different texturing times ([Sutthana et al., 2016](#)). The NPs film texturing for 4 min, which showed a fine porous, had a high dye absorption compared to the other texturing times such as 2, 6 and 8 min. The DSSC based on film texturing for 4 min exhibited a higher efficiency of 2.08 % than the DSSCs based on other films. The DSSC based on film texturing for 4 min had a higher $R_{\text{rec}}$ of 240 Ω, indicating that less charge recombination has taken place at dye loaded ZnO/electrolyte interface.

Banik and his co-workers studied the role of Si nanospheres (NS) for its light scattering and energy barrier property on photovoltaic performance of ZnO based solar cells ([Banik et al., 2016](#)). Different ratios of ZnO/SiO$_2$ composites only showed diffraction and
vibrational peaks for a hexagonal wurtzite structure of ZnO, indicating a high degree of crystallite ZnO NP and an amorphous nature of SiO$_2$ NS. The increase in reflectance was observed with an increase in the concentration of SiO$_2$ NS due to multiple light reflectance. The surface area and the dye loading of the composites got continuously decreased with an increase in the SiO$_2$ concentration from 1 to 10 wt % due to incorporation of SiO$_2$ in ZnO/SiO$_2$ composites. The DSSC fabricated with 1 wt% SiO$_2$ loaded ZnO photoanode exhibited higher efficiency of 3.08 % with less charge recombination at ZnO/SiO$_2$/dye/electrolyte interface.

ZnO NFs were hydrothermally synthesized on ZnO seeded FTO substrate through a two step wet chemical method by Saleem and his team (Saleem et al., 2017). First, the ZnO seed layers were spin coated on FTO substrates in solutions containing both absence and presence of PEI. In the second step, the ZnO NFs were grown on ZnO seeded FTO substrate in an aqueous solution containing Zn(NO$_3$)$_2$ and HMTA at 95 °C for 8 h. The hexagonal wurtzite structured rod and blade like flowers were observed on ZnO seed deposited on the sol-gel solutions containing both absence and presence of PEI respectively. The blade like flower had a low transmittance and high dye loading compared to the rod like structured thin film. They also calculated the efficiencies of 1.08 and 2.23 % for DSSCs based on rod and blade like flower photoanodes, respectively.

Chen et al., hydrothermally developed ZnO NFs at 80 °C for 30 min (Chen et al., 2017). The ZnO NFs were in a hexagonal wurtzite structure grown along the (101) plane direction. The NFs consisted of NWs. The surface area of NFs and NPs is 74 and 27 m$^2$/g respectively. The dye absorption and the diffuse light reflectance got significantly increased compared to NPs. They constructed DSSCs and found the efficiencies of 4.39 and 5.95 %,
for DSSCs based on NFs and NPs respectively. The increased efficiency was due to increase in internal surface area and light scattering. The DSSC based on nanoflower had a higher electron lifetime.

2.3 Scope of the present work

From the literature survey, it could be understood that the efficiency of DSSCs very much depend on the morphology, crystallinity, surface area and crystal quality of the ZnO nanostructures. To attain higher efficiency, the photoanode containing nanostructures should posses a high dye loading, electron mobility, charge injection and collection efficiency. The diverse nanostructures have some positive and negative features.

The photoanode containing NPs offers a large surface area for high dye loading, but it is transparent to visible light. As a result, dye molecules anchored on ZnO could not capture most of the incident light. The NPs photoanode exhibits less electron collection efficiency due to trapping and detrapping of injected electrons at the interface of the NPs boundaries, which lead to the recombination between injected electrons or back transfer electron and either the oxidized dye molecules or oxidized iodide/tri-iodide species (Chen et al., 2012a).

The high crystallinity, less surface defects and low number of grain boundaries of one dimensional (1D) ZnO nanostructures provide high electron mobility due to shortening of the electron path length from excited dye molecule/ZnO interface to ZnO/FTO interface. Finally, it shows a high electron collection efficiency that reduces the recombination (Wang et al., 2010). Micro sized 1D nanostructure acted as a light scattering centre to improve the light absorption of dye molecules. But, the efficiency of 1D nanostructures photoanode is low due to low surface area as well as recombination that takes place owing to direct contact of oxidized electrolyte species and electron on FTO substrate (Xu et al., 2011).
The sub-microsphere consists of a large number of primary NPs and offers a large surface area for dye molecule loading as well as light scattering through the presence of secondary sphere rather than microsphere, Hence, the short circuit current density and photo conversion efficiency get significantly increased (Chou et al., 2007). But the recombination takes place between oxidized species of electrolyte and collection electrons due to contact of FTO substrate with electrolyte (Xu et al., 2011).

Aim of the study is;

The first and the foremost aim of the present work is to synthesize diverse ZnO morphologies on FTO substrate by applying chemical deposition methods such as electrochemical, sol-gel spin coating and hydrothermal. In order to inhibit the aforementioned problems and attain better performance of DSSCs, the combination of nanostructures as a single, double and multi layered ZnO nanostructures are fabricated on FTO, ZnO and ZnO-TiO$_2$ seeded FTO substrates respectively as a building block. The synthesized nanostructures are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared (FTIR), Raman and photoluminescence (PL) spectroscopy to analyze structural, morphological, functional, vibrational and optical properties respectively. The thickness of the film is measured by profilometer. UV-Vis spectroscopy is employed to study dye loading and light scattering ability of nanostructures. The optimized ZnO nanostructures are utilized to fabricate DSSCs that are analyzed by short circuit current density-voltage curves and electrochemical impedance spectra.

2.4 Materials for DSSC fabrication

Fluorine doped tin oxide (F:SnO$_2$) conductive substrate was procured from Latch scientific supply Pte. Ltd., Singapore. Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O) and
titanium oxide powder (TiO₂) were obtained from Merck, India. Hexamethylenetetramine (HMTA) was purchased from sd fine-chem limited, Mumbai, India. Ruthenizer 535-bis TBA (N719 dye), Surlyn spacer with a thickness of 65 µm, and electrolyte were acquired from Solaronix SA, Switzerland. Ethanol was purchased from Alfa Aesar, India. Potassium chloride (KCl) and tri-sodium citrate were obtained from Sisco Research Laboratories Pvt. Ltd., India. Deionized water was purchased from Nice chemicals Pvt. Ltd., India. All the chemicals were used without further purification.

2.5 Experimental flowcharts

2.5.1 ZnO thin film preparation in electrodeposition

![Flowchart for ZnO electrodeposition.](Figure 2.2)
In this dissertation work, ZnO thin films were electrodeposited by using three electrode potentiostatic set-up. The FTO substrate, Ag/AgCl and Platinum served as working, counter and reference electrodes respectively. The deposition solution consisted of zinc nitrate hexahydrate and potassium chloride in deionized water. The molecular oxygen was slowly aerated into deposition solution during whole deposition process at a constant stirring of an appropriate rotation per minute (RPM). The electrodeposition of ZnO thin films was carried out at an appropriate deposition potential at an appropriate bath temperature. The deposited thin films were rinsed with deionized water before they were subjected to further characterizations.

2.5.2 ZnO seed layer preparation in sol-gel spin coating technique

![Flowchart for ZnO seed layer deposition.](image)

**Figure 2.3.** Flowchart for ZnO seed layer deposition.
ZnO seed layer was coated on FTO glass substrates by employing a spin coating technique. A coating solution was prepared by dissolving equimolar ratio (1:1) of zinc acetate and monoethanolamine in isopropanol. The prepared solution was continuously stirred for an appropriate time until it became a transparent gel solution. ZnO seed layer was coated on FTO substrate at an appropriate RPM for appropriate time. After spin coating process, the coated films were annealed at 450 °C in air for 1 h to remove organic solvent and improve crystalline nature of the seed layer.

2.5.3 ZnO thin films preparation in hydrothermal technique

![Flowchart for hydrothermal growth of ZnO.](image)

**Figure 2.4.** Flowchart for hydrothermal growth of ZnO.
The ZnO nanostructured thin films were grown on seed layer coated FTO substrate by applying hydrothermal technique. The growth precursor contained an equimolar ratio (1:1) of zinc nitrate hexahydrate and hexamethylenetetramine in an appropriate ml of deionized water. The face of the seed layer was put down at 45° angle into the growth solution to avoid any precipitation taking place while growing ZnO from the top of the solution. The ZnO thin films were grown at an appropriate growth temperature for different growth times. Finally, the grown ZnO thin films were rinsed with deionized water, before they were subjected to further characterizations.

2.5.4 Photoanode preparation

![Flowchart for photoanode preparation](image)

**Figure 2.5.** Flowchart for photoanode preparation.
A dye solution consisted of a suitable molar concentration of N719 dye in ethanol. The solution was stirred until to get a clear solution. The optimized ZnO nano and microstructured thin films were sensitized in N719 ethanolic dye solution at room temperature for an appropriate sensitized time. 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 photoanodes.

2.5.5 Platinum counter electrode preparation in sol-gel spin coating technique

![Flowchart for counter electrode preparation](image)

**Figure 2.6.** Flowchart for counter electrode preparation.
A solution contained an appropriate molar concentration of chloroplatinic acid in isopropanol. The solution was stirred until to get a clear homogeneous solution. The platinum was spun on the holed FTO substrates at an appropriate RPM for an appropriate time. After that, the coated films were pre-heated at an appropriate temperature for an appropriate time. Once again the coating procedure was repeated to attain necessary thickness. The coated films were subsequently annealed at an appropriate temperature for an appropriate time. Finally Pt coated FTO substrates were used as counter electrodes.

2.5.6 Dye sensitized solar cell construction

![Flowchart for dye sensitized solar cell construction.](image)

DSSC was assembled by sandwiching photoanode and counter electrode between Surlyn spacer. The sandwiched photoanode and counter electrode was bound at 80 °C for 10 min. An electrolyte consisting of 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 cm$^2$ through holes on counter electrode in DSSC. Later on, the holes were closed by Surlyn spacer.

2.6 Materials Characterizations

The synthesized nano and microstructured thin films are characterized by following instruments:

Cyclic Voltammetry (CV) was carried out to investigate electrochemical reactions in formation of ZnO thin films by using an electrochemical workstation CHI600D. X-ray diffraction (XRD) analysis was performed to analyze crystal structure and crystallinity of ZnO films with the help of a X’Pert PRO PAN analytical instrument operated at 40 kV and 30 mA with CuK$_\alpha$=1.5406 Å. Scanning electron microscope (SEM) was carried out to observe the surface morphology of films using JEOL JSM-840A instrument operated at 30 kV. The functional group was studied by Fourier transform infra red (FT-IR) spectroscopy by using Thermo Nicolet 380 instrument in the range of 4000-400 cm$^{-1}$. Micro Raman spectra were recorded to study the vibration modes of films by means of Princeton instrument Acton sp 2500 under an excitation wavelength of 514.5 nm by using Argon laser. Photoluminescence (PL) spectra were performed using Varian Eclipse instrument to study the crystal quality and the defects presented in deposited films under an excitation wavelength of 325 nm. The light absorption, reflectance and dye absorption spectra were recorded with the help of Perkin Elmer’s LAMBDA 35 instrument. The thickness of film was measured by using Stylus profilometer (Mitutoyo SJ-301). Current density-voltage curves were recorded by using Keithley 4200 Semiconductor Characterization System under 100 mW light irradiation. Electrochemical impedance spectroscopy (EIS) spectra were...
carried out at an AC voltage of 10 mV in the frequency range of 100 kHz-0.1 Hz using micro auto lab µ3AUT70856 instrument.

2.7 Contents of the thesis

The present work contains nine chapters and the contents of thesis are given below:


CHAPTER – II : Materials introduction, review of literature and scope of the present work, thin film deposition, DSSC fabrication and thin film characterizations.

CHAPTER – III : Electrochemical deposition of one and two-dimensional nanostructured ZnO thin films for DSSC applications

CHAPTER – IV: Influence of hexamethylenetetramine on electrochemically synthesized one-dimensional ZnO nanostructured thin films for DSSC applications

CHAPTER – V : Electrochemical deposition of one-dimensional ZnO nanostructures on ZnO seed layer for DSSC applications

CHAPTER-VI : Hydrothermal synthesis of ZnO nanowire arrays on ZnO-TiO₂ seed layer for DSSCs applications

CHAPTER-VII : Hydrothermal growth of ZnO nanowire and nanoneedle arrays with flower structure on ZnO-TiO₂ seed layer for DSSC applications

CHAPTER-VIII: Chemical fabrication of ZnO hierarchical structure on ZnO-TiO₂ seeded FTO substrate for DSSC applications.

CHAPTER-IX : Summary and conclusions.