CHAPTER 1

INTRODUCTION, BACKGROUND THEORY AND LITERATURE REVIEW

1.1 INTRODUCTION

There is a tremendous research interest in the field of nanotechnology to develop reliable processes for the synthesis of nanomaterials over a range of sizes and chemical compositions. The synthesis and organisation of nanoparticles provide complementary tools for nanotechnology. Moreover, processing of nanoparticles or nanopowders into bulk shapes retaining nanosize is another challenging aspect as far as engineering applications are concerned.

Synthesis and assembly strategies of nanoparticles mostly depend on precursors from liquid, solid or gas phases; employ chemical or physical deposition approaches and similarly rely on either chemical reactivity or physical compaction to integrate the nanostructure building blocks within the final material structure. The variety of techniques used to prepare nanoparticles can be classified as top-down or bottom-up approaches. The bottom-up approach of nanomaterials synthesis first forms as a nanostructured building blocks (nanoparticles) and then assembles into the final material (Saravanan et al. 2008).

Nanoparticles have attracted much attention in recent years because of their characteristic size and geometry dependent physical and chemical properties (Caricato et al. 2006). The semiconducting oxide material at nanometre scale is also responsible for tuning their electrical, magnetic, optical and mechanical
properties. Hence, it is important to prepare nanocrystalline films with narrow size distribution (Kim et al. 2003).

Fundamental properties of nanostructured materials are widely studied because of their potential application in numerous fields such as electronic devices, opto-electronics, optics etc. Nanostructured materials have structures with dimensions in the nanometer length scale such as polycrystalline materials with nanometer sized crystallites, materials with surface protrusions spatially separated by few nanometers, granular or porous materials with grain sizes in the nanometer range (Oelhafen et al. 2005).

Nowadays, with the ever growing demand for energy and serious environmental pollution caused by extensive fossil fuels consumption, solar energy is becoming a promising energy resource to take the place of the conventional ones. The photo-voltaic cells prepared from nanostructured materials are the most effective approach to realize the use of solar energy (Yu et al. 2014). As the present work focuses on the effective use of solar cells, the challenges in developing more efficient solar cells are briefly discussed in the following sections.

1.2 OVERVIEW OF SOLAR CELLS

The commonly described photovoltaic (PV) effect was discovered by Becquerel, who demonstrated the flow of photocurrent when platinum electrodes covered with aqueous solution of silver bromide or silver chloride was illuminated with light (photo-electro-chemical effect). Smith and Adams made the first report on photoconductivity using Selenium in the year 1873 and 1876, respectively. The first organic compound, Anthracene to produce photoconductivity was observed by Pochettino in 1906 and Volmer in 1913. In the late 1950s and 1960s the probable use of organic material was predicted as photoreceptors in imaging systems. The scientific interest as well as the
commercial possibilities led to increase the research into photoconductivity and related issues (Spanggaard et al. 2004).

Photovoltaic cells are commonly classified as first, second and third generation devices based on the fundamental technology. In the first generation solar cells, single or multi-crystalline p-n junction silicon cells are the most commonly used PV converters and the silicon based photovoltaic devices have reached the power conversion efficiency of about 20%. But, high purity requirements for single crystals, high material cost, high fabrication temperature and negative environmental impact of the processing technologies are the major problems that should be resolved. The second generation PV devices are based on inorganic thin films; it is cheaper but less efficient than the first generation single junction crystalline PV cells. Thus, for further improvement, a new technology is required to produce third generation solar cells with higher efficiency and lower production cost. This is possible with advancement of technology in third generation solar cells such as dye sensitized solar cells (DSSCs) and semiconductor sensitized solar cells (SSSCs).

DSSCs are considered cheap and energy efficient solar cells because the manufacturing method requires low cost materials and simple fabrication processes. Since Gratzel and O’Regan fabricated DSSCs in 1991, extensive efforts have been made to increase the efficiency of the cells. However, highest recorded efficiency of DSSCs has not exceeded 12% over the last ten years. Therefore, new sensitizers or semiconducting materials are introduced to replace organic dyes of ruthenium polypyridine complexes, broaden the photo-response in solar spectrum and increase the efficiency of cell (Kouhnavard et al. 2014).

SSSCs based on nanocrystals of narrow band gap semiconductors have attracted great attention due to their potential low cost alternatives to existing cells. In such devices, semiconductor nanocrystals are absorbed instead of dyes as sensitizers to the surfaces of the wide band gap semiconductors. Compared to conventional organic dyes, sensitizers have very high extinction coefficient,
which could reduce the dark current and increase the open circuit voltage ($V_{oc}$). Therefore, a significant development in the field of SSSC has been made in the recent years. In spite of their great potential, the power conversion efficiency is generally affected by severe photo-corrosion when a sensitizer is in direct contact with an electrolyte (Yanzhong et al. 2012). Coating of zinc sulfide (ZnS) on semiconductor nanocrystals has been considered as one of the methods to overcome this limitation (Hsu et al. 2013).

SSSCs are emerging as third generation photovoltaic technologies based on the well-known prototype of the dye-sensitized solar cells. The multiple exciton generation (MEG) effect, low cost and facile synthesis make semiconductor nanocrystals particularly attractive over molecular dyes for solar cell applications by which the theoretical efficiency can be elevated up to 44% (Shengyuan et al. 2012).

1.3 SIGNIFICANCE OF PHOTOANODE FOR SSSCS

The photoanode (working electrode or photoelectrode) is the basic component for designing the semiconductor sensitized solar cells. The photoanode is generally fabricated by depositing a porous semiconductor material on a conducting substrate, followed by absorption of semiconductor sensitizers onto the porous semiconductor. In a sensitized solar cell, light is generally absorbed by the sensitizer, photogenerated electrons are then rapidly injected into the conduction band of the coupled semiconductor which leads to an electron-hole separation and this feature is essential for photoanode in sensitized solar cells (Balis et al. 2013).

Nanocrystalline titanium dioxide ($TiO_2$) network developed on a conductive substrate plays a crucial role in releasing electrons by light absorption. The released electrons can do their work if its recombination rate is slower than the charge transfer rate. Sensitization of porous TiO$_2$ with sensitizer helps in shifting the absorption region of TiO$_2$ to visible from ultra-violet, thus decreases
the band gap and consequently eases the electrons to the higher energy level by increasing the charge transfer rate. Shifting the optical absorption range of electrodes using semiconductor sensitized TiO\textsubscript{2} shows a possibility of enhanced efficiencies. The sensitizer absorbs most of the incident light resulting in accumulation of electrons in the working electrode and thus shifting the Fermi level of the TiO\textsubscript{2} particles. The potential drop between the back contact and the shifted Fermi level gives the photo-voltage in these cells. The sensitization of porous TiO\textsubscript{2} with sensitizer is to transport the electron to the conduction band of TiO\textsubscript{2} through the sensitizer upon illumination (Usha et al. 2014). The photovoltaic performance of the solar cell is closely related with the strategies of sensitization to the photoanode (Feng et al. 2012).

1.3.1 Importance of TiO\textsubscript{2}

Nanocrystalline TiO\textsubscript{2} has been studied broadly since the Honda-Fujishima effect discovered in 1972 due to its great potential in the field of dye-sensitized solar cells, photocatalysis, photo-induced hydrophilicity and so on. TiO\textsubscript{2} was found to be the most important material with highest activity because of its strong oxidizing ability, non-toxicity and long thermal photostability (Liu et al. 2007). TiO\textsubscript{2} thin films are widely used in optical device applications owing to their desirable optical properties and good stability in adverse environments. It has high refractive index, excellent transmittance in the visible and near-infrared (NIR) frequency and high chemical stability which makes it useful as anti-reflection coating material, sensors, solar cells, optical filters and photocatalysts. TiO\textsubscript{2} film is also a favorable material for the development of microelectronics as an alternative to silicon dioxide in the gate dielectric of metal oxide semiconductor field effect transistors (MOSFETs) due to its high dielectric constant (Lee et al. 2004).

Porous TiO\textsubscript{2} film is a vital material for the photoanode of solar cells which has a high surface area substrate for sensitizer and conductor of photo generated
electrons from sensitizer to anode (Hu et al. 2013). Among the three phases, anatase phase of TiO$_2$ is much preferred because its energy band gap is greater than the other phases. Again, the anatase phase provides better electron transport rate, higher diffusion coefficient and more sensitizer loading capacity than rutile and brookite TiO$_2$ phases (Pour et al. 2013) by obtaining energy either directly from sunlight or from light sensitizers, causing electrons to be excited to conduction band creating positive holes in valence band for effective charge separation in solar cell (He et al. 2013).

Nanoscaled TiO$_2$ in thin film or powder form is the most extensively studied semiconductor material. This metal oxide is a promising material frequently used as a photocatalyst in the advanced oxidation process (air or water purification) due to its non-toxicity, chemical stability, photocatalytic activity and low cost. Especially, thin films of nanostructured electrode materials have become essential in the fields of photovoltaics, energy storage, photoelectrocatalysis, sensing, etc. TiO$_2$ in crystallographic form of anatase has become an interesting candidate as a photoanode due to its excellent efficiency to generate the electron-hole pairs (Morozova et al. 2012).

The emerging field of nanoparticles is given a new window that has opened prospects of research in third generation photovoltaic solar cells working with a principle similar to the process of photosynthesis. TiO$_2$ is a wide band gap semiconductor with remarkable electrical and optical properties. The anatase phase of TiO$_2$ has a large band gap, low dielectric constant and high electron mobility and exhibits high efficiency when it is used in sensitized solar cell as electrode. Due to its wide band gap, anatase phase of TiO$_2$ absorbs radiation in ultraviolet region. The principle of sensitized solar cells lies in efficiently developing a network of TiO$_2$ nanoparticles on a glass plate coated with transparent conducting oxide. Sensitization of nanocrystalline TiO$_2$ network with a sensitizer enhances the efficiency of the cell because the anatase phase nanoparticles of TiO$_2$ provide larger surface to volume ratio for sensitizer
absorption. Apart from solar cell application, these thin films having high transparency may be utilized as optical filters in spectrometers (Usha et al. 2014). In optoelectronic devices, TiO$_2$ porous structure serves as the route for electron transport to the anode. Therefore, the morphology of TiO$_2$ thin films plays a crucial role in determining the efficiency of the devices (Dang et al. 2010).

### 1.3.2 Importance of CdS as sensitizer

In recent years, inorganic nanomaterials have been developed as another light harvester for solar cells in order to increase the efficiency. Sensitizers such as CdS, CdSe, PbS, PbSe and InP are used as thin film semiconductor absorbers in solar cells (Tubtimtae et al. 2012). Among these materials, cadmium sulfide (CdS) is one of the most important II–VI group semiconductors with direct energy band gap of 2.42 eV which has been widely used as a photoanode sensitizer (Meng et al. 2014).

The synthesis and characterization of semiconductor materials are of great interest for both fundamental and applied research, due to their tunable electronic, optical and catalytic properties. CdS has attracted much attention because of their novel properties and promising application in both optoelectronic and biological fields. CdS nanoparticles are very useful for optoelectronic application as it is possible to tune the band gap over the wide spectral range. CdS is a technologically valuable material for so many devices including sensors that have come up in the recent years (Dhawale et al. 2011). It has been used in the high efficiency solar cells, usually coupling with other materials such as TiO$_2$ or organic materials (Ziabari et al. 2012).

Sensitizer has a higher extinction coefficient compared to the conventional dyes, which could reduce the dark current and increase the efficiency of the solar cell. CdS has been paid much attention in sensitized solar cell because of its high potential in improving light harvesting efficiency in the visible region. It is the most widely studied nanocrystalline semiconductor because of its suitable band
gap, long life time, important optical properties, excellent stability and easy fabrication (Ranjitha et al. 2013).

1.3.3 Importance of ZnS

Stability is one of the main challenges as poor photostability has initially limited many applications based on CdS semiconductor material. Nowadays, ZnS has been investigated as the most compatible passivating material for CdS (Ahmed et al. 2012). ZnS coated over on the CdS-assembled TiO$_2$ film has also demonstrated to increase the overall energy conversion efficiency of the cell because the conduction band of ZnS is higher than the CdS which leads to effective energy barrier and passivation effects (Jung et al. 2012).

The superior performance of CdS-sensitized solar cell is obtained due to the following combined effects: energetically favoured electron injection from sensitizer to TiO$_2$ conduction band due to the upward shifted energy levels of sensitizer, favourable electron injection to TiO$_2$ and suitable surface modifications like ZnS coatings to inhibit electron recombination (Yang et al. 2014). The low power conversion efficiency of SSSCs can be mainly ascribed to numerous reasons, including less efficient transport of photoexcited electrons, bad charges separation efficiency and the difficulty of using suitable sensitizers to enhance the harvest of solar light (Li et al. 2015).

1.4 BACKGROUND THEORY OF THE MATERIALS

1.4.1 Overview of TiO$_2$

Titanium element was first discovered by Reverend William Gregor, an English pastor in 1791, which he called as menachanite but it was named as titanium after four years by Klaproth. The fundamental chemical reactions on which the present titanium industry operate were known before 1800, while it was not available in the markets until 1916. TiO$_2$ was discovered in 1821 but it was
not until 1916 that modern technology had evolved for immense production. Fujishima and Honda invented photo-electrochemical splitting of water over TiO$_2$ to form H$_2$ and O$_2$, opened a better possibility of solar energy conversion by semiconductors (Shon et al. 2008). Ever the discovery of TiO$_2$ element, it has drawn increasing interest in the field of research as shown in table 1.1.

**Table 1.1** Discovery and development of TiO$_2$ for potential applications

<table>
<thead>
<tr>
<th>year</th>
<th>development</th>
</tr>
</thead>
<tbody>
<tr>
<td>1791</td>
<td>discovery of the titanium element by William Gregor</td>
</tr>
<tr>
<td>1800’s</td>
<td>fundamental chemical reactions of titanium</td>
</tr>
<tr>
<td>1821</td>
<td>discovery of TiO$_2$</td>
</tr>
<tr>
<td>1916</td>
<td>commercial preparation of white pigment of TiO$_2$ by the sulfate method in Norway</td>
</tr>
<tr>
<td>1972</td>
<td>chemically split of water over TiO$_2$ to form H$_2$ and O$_2$ using Honda-Fujishima effect (photocatalytic reaction)</td>
</tr>
<tr>
<td>1980</td>
<td>photocatalysis on TiO$_2$ and Pt/TiO$_2$ powder (short circuit photoelectron chemical cell)</td>
</tr>
<tr>
<td>1985</td>
<td>photocatalysis on highly dispersed TiO$_2$ anchored on various supports and Photocatalysis in the zeolite (cavities and frameworks)</td>
</tr>
<tr>
<td>1987</td>
<td>Ti/Si and Ti/Al binary oxide photocatalysts, size quantization effect on the photocatalysis of TiO$_2$ and nanoscale TiO$_2$ particles</td>
</tr>
<tr>
<td>1990</td>
<td>TiO$_2$ coating on ceramic surface</td>
</tr>
<tr>
<td>1991</td>
<td>idea of sensitized photocatalysis (Gratzel solar cell), purification and detoxification of polluted water</td>
</tr>
<tr>
<td>1993</td>
<td>applications of TiO$_2$ photocatalysis in the purification of polluted water and air</td>
</tr>
<tr>
<td>1996</td>
<td>inactivation of pathogenic micro-organism in air and water</td>
</tr>
<tr>
<td>Year</td>
<td>Event</td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>1997</td>
<td>new function of TiO$_2$ thin film photocatalyst (super-hydrophilic phenomena)</td>
</tr>
<tr>
<td>1998</td>
<td>second generation TiO$_2$ in powder and thin film forms (ion-implantation and RF magnetron sputtering method)</td>
</tr>
<tr>
<td>2000</td>
<td>applications of TiO$_2$ photocatalysts on a global scale</td>
</tr>
<tr>
<td>2001</td>
<td>photocatalytic water splitting under visible light irradiation</td>
</tr>
<tr>
<td>2006</td>
<td>preparation of TiO$_2$ from waste water sludge for massive, environmental-friendly and functional TiO$_2$ production</td>
</tr>
</tbody>
</table>

1.4.1.1 Structure and properties of TiO$_2$

Titanium is a strong, light weight metal. It is as strong as steel and twice strong as aluminium, but, 45% lighter than steel and 60% heavier than aluminium. Titanium is broadly distributed over the surface of the earth and the ninth most abundant element in the earth’s crust, estimated as 0.62% (Shon et al. 2008). The naturally occurring ores are ilmenite, mineral rutile and brookite. The TiO$_2$ concentration in the ore varies from 45 to 60% depending upon the source.

Titania is a well-known and well-researched material due to the stability of its chemical structure, physical, chemical and optical properties. The standard properties of TiO$_2$ are shown in table 1.2. It exhibits three crystalline phases (figure 1.1) such as anatase (chains of TiO$_6$ octahedra sharing four edges), rutile (chains of TiO$_6$ octahedra sharing two edges) and brookite (chains of TiO$_6$ distorted octahedra sharing three edges) but its orientation in thin film form depends upon the conditions and parameters of the fabrication method. Among these phases, brookite phase is stable only at very low temperatures; so it is not so useful for practical applications (Dang et al. 2010).

Anatase phase has a wider optical band gap, smaller electron effective mass, higher fermi level and greater mobility of charge carriers than the
thermodynamically stable rutile phase (Mogyorosi et al. 2003). For these reasons it has been used in various applications as optical components including photocatalysts, optical filters, gas sensors, integrated optical amplifiers, solar cells and electrochromic displays (Pakma et al. 2009). In general, anatase phase of TiO$_2$ is more preferred because it supplies higher potential energy for the photogenerated electrons by offering a higher specific area; non-toxic, photochemically stable and relatively in-expensive (Macwan et al. 2011). The physical properties of TiO$_2$ are reported in table 1.3.

![Figure 1.1 Structure of TiO$_2$](image)

(a) $a = 3.784$ Å, $c = 9.515$ Å  
(b) $a = 4.593$ Å, $c = 2.959$ Å

Table 1.2 Standard properties of TiO$_2$
The elementary cells of TiO₂ crystal structures are shown in figure 1.2. Rutile and anatase phases are tetragonal which are more ordered than the orthorhombic structure. The anatase is the least dense structure having empty channels along the $a$ and $b$ axes.

**Table 1.3 Physical properties of TiO₂**
<table>
<thead>
<tr>
<th>polymorph</th>
<th>rutile</th>
<th>anatase</th>
<th>brookite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>structure</strong></td>
<td>tetragonal P42/mnm</td>
<td>tetragonal I41/amd</td>
<td>orthorhombic Pcab</td>
</tr>
<tr>
<td><strong>density</strong></td>
<td>4.25</td>
<td>3.89</td>
<td>4.12</td>
</tr>
<tr>
<td><strong>refraction index</strong></td>
<td>(\lambda = 600\ \text{nm})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\perp) to c axis</td>
<td>2.60</td>
<td>2.55</td>
<td>// to a or b axis</td>
</tr>
<tr>
<td>// to c axis</td>
<td>2.89</td>
<td>2.48</td>
<td>// to c axis</td>
</tr>
<tr>
<td>// to c axis</td>
<td>2.57</td>
<td>2.69</td>
<td></td>
</tr>
<tr>
<td><strong>dielectric constant</strong></td>
<td>(\perp) to c axis</td>
<td>(\perp) to c axis</td>
<td>78</td>
</tr>
<tr>
<td>89</td>
<td>31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>// to c axis</td>
<td>173</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>// to c axis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>band gap</strong></td>
<td>(\perp) to c axis direct</td>
<td>(\perp) to c axis direct</td>
<td>3.14</td>
</tr>
<tr>
<td>3.04</td>
<td>3.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>// to c axis</td>
<td>indirect 3.05</td>
<td>// to c axis</td>
<td></td>
</tr>
<tr>
<td>indirect 3.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>electron mobility</strong></td>
<td>crystal: 0.1–10 ([10^{-4}\ \text{m}^2/\text{Vs}])</td>
<td>crystal: 15–550</td>
<td>thin film: 0.1–4</td>
</tr>
<tr>
<td>thin film: 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Oxygen](image1.png)

![Titanium](image2.png)

![Rutile](image3.png)

![Anatase](image4.png)

![Brookite](image5.png)

![Srilankite](image6.png)
1.4.1.2 Applications of TiO$_2$

- TiO$_2$ is used in the manufacture of cosmetics, paints, electronic paper and other environmental uses (Shon et al. 2010).
- It is used in the pigment application such as printing inks, rubber, fibers etc.
- It is used as a material in the memristor, an electronic circuit element.
- It is also used as a solar energy conversion base on dye, polymer or sensitized nanocrystalline solar cells using conjugated polymers as solid electrolytes.

1.4.2 Discovery of CdS

Cadmium was first discovered by Friedrich Strohmeyer, a German chemist, in 1817 while analysing the samples of calamine (ZnCO$_3$). On heating the samples, he noticed that some samples of calamine glowed with a yellow colour while some others did not glow. After further investigation, he determined that the calamine that changed colour when heated contained trace amounts of a new element. There is only one mineral that contains significant amount of cadmium (greenockite), but it is not enough to mine profitably. Fortunately, small amount of cadmium were found in zinc ores. The production of the cadmium pigment was delayed until about 1820 because of the scarcity of the metal.

1.4.2.1 Structure and properties of CdS

Cadmium sulfide belongs to the cadmium chalcogenide family and it is highly favourable for solar cell application because of its suitable band gap energy. CdS can occur in four different crystalline structures, namely, hexagonal (wurtzite), cubic (zinc blende), cubic salt and distorted rock salt. Among these
four crystalline structures, hexagonal is the thermodynamically most stable and common one. Cubic CdS is a metastable structure; however, it can be still found in nature. The rock salt structure can exist only under pressure i.e., hexagonal CdS is subjected to pressures ranging from 2.6 to 4.2 GPa. The rock salt structure transforms into the distorted rock salt structure at a higher pressures ranging from 60 to 68 GPa. The chemically deposited CdS thin films show cubic, hexagonal or mixed (cubic+hexagonal) crystal structures depending upon preparative conditions. Hexagonal (wurtzite) and zinc blende (cubic) crystalline structures of CdS are shown in figure 1.3, where the green coloured (big) spheres represent the cadmium atoms while the yellow coloured (small) spheres represent the sulfur atoms (Ziabari et al. 2012).

Cadmium sulfide is a crystalline, inorganic compound that forms toxic fumes of cadmium oxides when heated and it is a semiconductor of electricity. Some general properties of CdS are shown in table 1.4.

![Figure 1.3](image) Structure of CdS (a) hexagonal and (b) zinc blende

<table>
<thead>
<tr>
<th>Table 1.4 General properties of CdS</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemical formula</td>
</tr>
<tr>
<td>molar mass</td>
</tr>
<tr>
<td>Property</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>Appearance</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Melting point</td>
</tr>
<tr>
<td>Boiling point</td>
</tr>
<tr>
<td>Refractive index (n_D)</td>
</tr>
<tr>
<td>Flash point</td>
</tr>
</tbody>
</table>

1.4.2.2 Application of CdS

- CdS is used as pigment in plastics, paints, textiles, ceramics and glass.
- It is also used in solar cells, smoke and radiation detectors, light emitting diodes and photomultipliers.

1.4.3 Discovery of ZnS

Zinc sulfide is a glowing element which was first discovered in 1866 by Theodore Sidot, a French chemist who noticed the glow and it was often used in nuclear physics for its phosphorescence glow. His research was presented by A. E. Becquerel, who was famous for the research in luminescence. In the early years of its discovery, zinc sulfide was used in x-ray screen and cathode ray tubes. Ernest Rutherford was one among the early users of zinc sulfide because it emits light upon excitation.

1.4.3.1 Structure and properties of ZnS

Zinc sulfide belongs to the II–VI family of semiconductor material receiving ever-growing attention due to its wide variety of applications. Owing to
direct wide band gap value (3.7 eV), it can be used in optoelectronic devices such as blue light-emitting diodes, electroluminescent devices, electro optic modulator, optical coating, n-window layers for thin film heterojunction solar cells, photoconductor and especially photovoltaic devices (Roy et al. 2006).

ZnS possess three polymorphs, namely, cubic zinc blende (ZB), hexagonal wurtzite (W), or it can change to cubic rock salt (RS) structure. Each phase has unique physical properties, different lattice vibration and nonlinear optical coefficients. In particular, cubic zinc blende is the thermodynamically most stable, while the hexagonal wurtzite polymorph is stable above 1293 K. However, the cubic rock salt structure can be obtained at relatively high pressures. Cubic (ZB) and hexagonal (W) phases have been used in industrial applications due to their size and shape dependent properties. Again, both phases are capable of being obtained in different ways to tune their properties to specific needs.

A conventional unit cell of the three polymorphs belongs to $F\bar{4}3m$ (ZB), $P63mc$ (W) and $Fm\bar{3}m$ (RS) of ZnS structure is shown in figure 1.4. In cubic zinc blende and hexagonal wurtzite structures, each Zn atom is surrounded by four S atoms forming tetrahedral clusters $[\text{ZnS}_4]$ which share one or two corners, respectively. Hexagonal wurtzite phase is more compact than a cubic zinc blind phase, and the hexagonal wurtzite phase shows a lack of a centre of symmetry which generates a residual polarization in this $[\text{ZnS}_4]$ cluster. The optimized hexagonal wurtzite structure belongs to the hexagonal group with the lattice parameters $a = 3.79$ and $c = 6.14$ Å. For cubic rock salt phase in the ZnS crystal, each Zn atom is surrounded by six S atoms at the corners of the $[\text{ZnS}_6]$ octahedral clusters (Porta et al. 2014).
Figure 1.4 Schematic representation of unit cells for ZnS phases (a) zinc blende (b) wurtzite and (c) rock salt

Zinc sulfide is an inorganic compound with a chemical formula of ZnS. The main form of zinc is found in nature. Although this mineral is usually black because of numerous impurities, the pure material is white in colour and it is widely used as a pigment. In synthetic form, zinc sulfide can be transparent and it is used as a window for visible and infrared optics. Some general properties of ZnS are shown in table. 1.5.

Table 1.5 General properties of ZnS

<table>
<thead>
<tr>
<th>chemical formula</th>
<th>ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>molar mass</td>
<td>97.474 g/mol</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>-----------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>density</td>
<td>4.090 g/cm³</td>
</tr>
<tr>
<td>melting point</td>
<td>1185 °C (1458 K) (sublime)</td>
</tr>
<tr>
<td>solubility in water</td>
<td>negligible</td>
</tr>
<tr>
<td>flash point</td>
<td>non-flammable</td>
</tr>
</tbody>
</table>

1.4.3.2 Applications of ZnS

- Zinc sulfide is used in electroluminescent lamps, infrared windows, domes and optical elements.

- It is used in printing inks, powder coatings, adhesives, thermoplastic pigmentation, insulating and sealing compounds.

- It is also used in elastomers, textile fibers, paper, mastics, lubricants etc.

1.5 LITERATURE REVIEW

This section deals with the review of prevailing literatures which supports the experimental work such as preparation and characterization techniques undertaken in this thesis.

1.5.1 Review on the preparation methods of bare TiO₂, undoped and doped CdS sensitized TiO₂ film

Many researchers have carried out the preparation of TiO₂ thin film by different coating techniques. Some of the earlier works have been summarized in this section. Kaewwiset et al. (2008) have reported the preparation of TiO₂ thin films on the glass substrate at room temperature using titanium tetraisopropoxide in isopropanol by dip-coating method. The surface morphology of the film showed that the grains were clearly observed when the coating layers were increased to 15.
Usha et al. (2014) have reported the synthesis of nanocrystalline multilayered thin films of TiO$_2$ through wet chemical route of dip coating process. The film showed high transparency in the wavelength range of 400–800 nm with good adhesion to the ITO substrate. The optical characterization of the film reveals higher band gap values of 3.45, 3.32 eV for 2-layered and 3-layered films respectively while further deposition of thin layers shows the value of band gap approaching towards the bulk TiO$_2$ with considerable decrease in band gap. The increase in thickness due to successive coatings of thin film layers was observed because of growth in crystal size as well as improving the grain contact on successive annealing treatment. The photo-conversion efficiency of the assembled solar cell was in the order of 7%.

Prabitha et al. (2014) have reported the preparation of TiO$_2$ thin films deposited on quartz substrates using ceramic TiO$_2$ target at an elevated substrate temperature of 573K by RF magnetron sputtering. The structural, optical and photoluminescence analysis of the films showed that the phase transformation depends on annealing temperature. The structural investigations using X-ray diffraction revealed that the as-deposited film was amorphous in nature. The existence of intense blue emission peak from photoluminescence of the film proved that the film was suitable for opto electronic display devices.

Wang et al (2007) have reported the preparation of nanocrystalline TiO$_2$ from a commercial product of TiO$_2$-sol suspension (average particle size of TiO$_2$= 3 nm) which was sonicated with additives, acetic acid and Triton X-100. TiO$_2$ powder (P25, Degussa) having large TiO$_2$ particles of sizes either 400 nm (anatase) or 25 nm were mixed with the above TiO$_2$ colloid to form the source solution for the preparation of the TiO$_2$ film by spray pyrolysis deposition (SPD) technique. It was observed that the dye sensitized solar cell device based on a TiO$_2$ film composed of 3 nm particles (colloid) with 25 nm particles showed a significant enhancement of the incident photon to current efficiency (IPCE) over a film without added large particles and over a film with 400 nm particles. The
film with 25 nm particles showed a maximum IPCE close to 1, when the light loss from the reflectance of glass substrate was taken into consideration. The increase of IPCE for the film with 25 nm particles was attributed to the enhancement of the light harvesting efficiency and efficient electron transfer yield from the nanoclusters formed in this film.

Among the different preparation techniques, spin coating is one of the important methods to prepare nanocrystalline TiO$_2$ film. This coating method allows developing the TiO$_2$ nanoparticles with both high surface area and high proportion of stable anatase phase (Carrera et al. 2008); the aforementioned TiO$_2$ characteristics are crucial for the preparation of photoanode which is the primary aim of the research work reported in this thesis. Moreover, the films prepared by this method are transparent, homogeneous, have uniform particle distribution and also show excellent adhesion to the substrate. Again, this method is very simple and easy for operation, films are easily anchored in the substrate (glass) and it can be used for the deposition of substrates which have complex surface or large surface area (Sonawane et al. 2002). So, few reported works based on the additives in spin coating technique have been summarized in the following section.

Guo et al. (2005) have reported the preparation of transparent porous TiO$_2$ thin film spin coated on glass substrates from a sol gel solution. Polyethylene glycol (PEG) was added to the coating solution as a structure-directing agent and the film thus prepared was transparent, nanoporous and crack free. The decomposition of PEG at high temperature was considered to be responsible for the generation of porous structure in the films. XRD pattern shows that all TiO$_2$ films display the characteristic diffraction peaks of a TiO$_2$ anatase structure.

Oftadeh et al. (2012) reported that spin coated anatase phase TiO$_2$ thin film on ITO glass substrate was used as a working electrode in dye-sensitized solar cells. The influence of different parameters including number of coated layers,
sensitization time, etc., was studied for TiO$_2$ film to investigate the performance of DSSC. It shows that the prolongation of dye sensitization time of TiO$_2$ increases the efficiency of the cell. The increase in thickness of TiO$_2$ film by increasing the number of coated layers can improve the absorption of dye through TiO$_2$ layers to enhance the open circuit voltage ($V_{oc}$) and the short circuit current density ($J_{sc}$) of DSSC.

The most common methods used to deposit a sensitizer on a porous metal oxide semiconductor are direct growth by chemical bath deposition (CBD) or successive ionic layer absorption and reaction (SILAR) method and deposition of pre-synthesized sensitizer using bi-functional organic linkers (Ruhle et al. 2010). The disadvantage of using the latter method is the inefficient charge separation due to organic linkers and poor surface coverage of sensitizer on the mesoporous metal oxide surface, which can lead to low conversion efficiency (Shen et al. 2008). So, the following section deals with the deposition of CdS as a sensitizer on prepared TiO$_2$ films (CdS/TiO$_2$) using chemical techniques.

Shengyuan et al. (2012) have reported the preparation of CdS/TiO$_2$ photoelectrode by electrospinning and successive ionic layer absorption and reaction method, respectively. The characteristic peaks of anatase phase of TiO$_2$ and hexagonal CdS were identified from the XRD pattern. The lattice spacing measured from transmission electron microscopy (TEM) was well consistent with (101) plane of anatase TiO$_2$ and (111) plane of CdS.

Jang et al. (2012) reported the method of CdS coating on a mesoporous TiO$_2$ films by high-pressure coating with liquid carbon dioxide (l-CO$_2$) as a coating solvent. The size and coverage of CdS over TiO$_2$ surface were controlled by the number of l-CO$_2$ coating cycles applied at a fixed precursor concentration. The formation of CdS on the mesoporous TiO$_2$ film was confirmed by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) analysis.
Some earlier research works report that the CdS nanoparticles would be easily corroded in solar cell system due to solar light illumination or interaction with electrolyte. So a protective layer coating is more essential for corrosion protection for CdS. For this purpose, a wide band gap semiconducting material is generally used as a protective layer on the surface of CdS/TiO₂. Thus, a high band gap semiconductor, ZnS (band gap, 3.8 eV) was coated on CdS/TiO₂ as a protection layer through SILAR method (Hsu et al. 2013).

The following literatures deal with the preparation of ZnS as a protective layer on CdS coated TiO₂ (CdS/TiO₂) film using chemical method. Jung et al. (2012) reported that the ZnS overlayers were deposited on the CdS assembled TiO₂ films by repeated alternative immersion of CdS/TiO₂ film into zinc acetate and sodium sulfide solution. In this, ZnS overlayers acted as an intermediate layer between the exposed TiO₂ surface and the electrolyte, leading to the suppressed recombination rate for the TiO₂/electrolyte and it can significantly enhance the charge-collection efficiency. Thus the ZnS overlayers on the CdS assembled TiO₂ (ZnS/CdS/TiO₂) film is used as photoanode in semiconductor sensitized solar cells which can significantly improve the overall conversion efficiency of the cell.

Hsu et al. (2013) reported the preparation of photoanodes consisting of ZnS passivation layer on CdS sensitized titania nanorods using hydrothermal and SILAR methods. ZnS layer onto the CdS/TiNR surface prevents the corrosion of the CdS nanoparticles and facilitates the photocarriers transportation to TiO₂. The open-circuit potential, short-circuit photocurrent, IPCE and solar conversion efficiency were further improved due to the deposition of ZnS passivation layer. The photoanode of 8ZnS/5CdS/2TiNR film achieved the highest efficiency of about 1%.

Doping is necessary in order to improve the optical and electrical properties of CdS sensitized TiO₂ film. Doping optically active transition metal ions like (Mn²⁺ or Co²⁺) can change the electronic and photophysical properties of
nanocrystal (Santra et al. 2012). Moreover, doping the transition metal ion with CdS can induce charge separation and recombination dynamics in sensitized solar cells by creating electronic states in the mid-gap region of the sensitizer (Yu et al. 2014). Hence, the dopant can act as shallow trap states thereby extending the life time of charge carriers. Thus, the long-lived charge carriers ascribed to the dopant can scavenge holes that help to boost the efficiency of photoelectrode (Smith et al. 2014).

The following literatures deal with the preparation of film using doped CdS nanocrystals on TiO$_2$ film. Yu et al. (2014) reported the preparation of double-layered TiO$_2$ film which has three dimensional (3D) flowers grown on one dimensional TiO$_2$ nanorods synthesized directly on transparent FTO conducting glass substrate by a facile hydrothermal method. It was further sensitized by CdS and used as photoanode in Mn-doped CdS sensitized solar cells. The 3D TiO$_2$ flowers with the increased surface areas can absorb more doped CdS nanocrystals which increased the absorption of light and accelerated the electron transfer rate. The power conversion efficiency (PCE) of Mn-doped CdS/TiO$_2$ flower-rod solar cell under one Sun illumination was found to be 1.09%, which was 105.7% higher than that of the CdS/TiO$_2$ nanorod solar cell (0.53%).

1.5.2 Review on the structural studies of bare TiO$_2$, undoped and doped CdS sensitized TiO$_2$ thin films

An x-ray diffraction study was used to determine the crystalline nature of the material. It also gives information on grain size and phase composition. A brief note about the X-ray diffraction studies carried out by researchers on TiO$_2$ thin films has been reviewed in this section.

Liu et al. (2011) have reported that the prepared TiO$_2$ films on ITO glass by doctor-blade method have nanoscale particles with anatase phase structure. Therefore, the different precursors titanium(IV) isopropoxide (TTIP) and titanium(IV) ethoxide (TTIE) used for preparing TiO$_2$ films did not affect its
crystalline structure. The XRD results show that TTIP-TiO$_2$ and TTIE-TiO$_2$ films were composed of both anatase and rutile phases. Rutile phase was formed on the film during high calcination temperature, 500°C. The predominant peaks of TTIP-TiO$_2$ and TTIE-TiO$_2$ became sharper as the calcination temperature increased, indicating an increase in its crystallinity. Nevertheless, the XRD patterns show that these TiO$_2$ films had a structure with short-range mesophase order, which is a typical characteristic of TiO$_2$.

Li et al. (2012) investigated the crystal phase and crystalline size of the as-prepared TiO$_2$ nanoparticles from XRD pattern that exhibited good crystallinity with all characteristic peaks attributing to the anatase phase of TiO$_2$. Figure 1.5 shows the XRD pattern of T-120, T-140, T-160 and T-180 corresponding to samples prepared by microwave-assisted hydrothermal method at different temperatures 120, 140, 160 and 180°C, respectively. D-140 corresponds to the sample prepared by drying the sample T-120 at 140°C. The crystalline size of nanoparticles in the microwave treated samples (T-120 to T-180) increased from 6.2 to 10 nm with the increasing heating temperature from 120 to 180°C. For sample T-120 and the sample after drying process (D-140) show that the crystalline size of TiO$_2$ was increased from 6.2 to 7.9 nm.
Figure 1.5 XRD patterns of as-prepared TiO$_2$ nanocrystals (a) T-120, (b) T-140 (c) T-160 (d) T-180 and (e) D-140

Some of the literatures based on the structural studies of undoped CdS/TiO$_2$ have been given in this section. Zhang et al. (2009) reported the XRD patterns of the bare TiO$_2$ film prepared with TiO$_2$ powder (P25, Degussa, average particle size 25 nm) and compared the unannealed sample with annealed CdS-sensitized TiO$_2$ film. The CdS nanocrystals assembled on the TiO$_2$ film exhibit six prominent CdS peaks in the diffraction pattern which are located at $2\theta = 26.7^\circ$, $36.6^\circ$, $43.8^\circ$, $51.8^\circ$, $60.9^\circ$ and $66.8^\circ$ which are attributed to (002), (102), (220), (112), (104) and (203) planes respectively. XRD pattern of the TiO$_2$/CdS bilayer film reveals that the CdS nanocrystals deposited by CBD process are polycrystalline in nature. The XRD peaks of TiO$_2$ are weakened during the deposition of CdS and after the annealing process, the CdS peak corresponding to (002) plane becomes sharper than the unannealed one indicating that the annealing process can improve the crystallization quality of the CdS nanocrystals.

Ahmed et al (2012) reported the Raman spectra of TiO$_2$ films coated with various number of CdS SILAR cycles. It was found that the film based on (CdSx3)/TiO$_2$ and (CdSx5)/TiO$_2$ are nearly identical to that of the bare TiO$_2$ film without CdS coating. A new strong peak appeared at 299 cm$^{-1}$ and a weak peak detected at 598 cm$^{-1}$ in the Raman spectrum of (CdSx7)/TiO$_2$ film. The intensity of both the peaks seemed to be increased significantly in the (CdSx11)/TiO$_2$ film. The peak at 299 cm$^{-1}$ is attributed to the longitudinal optical (1LO) phonon mode of CdS and the peak at 598 cm$^{-1}$ is due to its overtone (2LO). The evolution of Raman spectra of TiO$_2$ mesoporous film deposited with CdS by different number of SILAR cycles (CdSxn, where n is the number of SILAR cycles) are shown in figure 1.6.
Yu et al. (2014) have exhibited the XRD patterns of TiO\(_2\) nanorod, TiO\(_2\) flower-rod and CdS/TiO\(_2\) flower-rod photoelectrodes. It is worth noting that the XRD patterns of TiO\(_2\) flower-rod and TiO\(_2\) nanorod show the same sharp and intense diffraction peaks suggesting that both the films were well crystallized and indexed to rutile TiO\(_2\). In the XRD pattern of CdS/TiO\(_2\) flower-rod, an additional diffraction peak indexed to cubic CdS can be discerned apart from the diffraction peaks of rutile TiO\(_2\). Furthermore, no other peaks could be observed indicating the high purity of the films.

The following literature deals with the structural properties of doped CdS nanocrystals on TiO\(_2\). Smith et al. (2014) investigated the structural properties (XRD, Raman) of undoped and doped (Mn and Co) CdS on titania nanotube arrays (T-NTA) synthesized by electrochemical anodization. With the addition of Mn and Co, it was observed from XRD spectra that the peak positions of CdS
shifted to a higher angle relative to undoped CdS and the lattice parameters were also found to decrease suggesting the compression of lattice due to the substitution of Mn or Co that have smaller ionic radii compared to Cd. The Raman spectra of undoped and doped CdS show the characteristic peaks of tetragonal structure of anatase phase of titania with the additional peak of CdS at 304 cm\(^{-1}\) due to the first longitudinal optical (1LO) phonon scatter mode of CdS. There is a slight red shift in the 1LO peak for doped CdS compared to undoped one implying a small relaxation of compressive strain on the CdS nanocrystal surface which is consistent with the reduction in lattice parameters determined from XRD analysis.

1.5.3 Review on the optical properties of bare TiO\(_2\), undoped and doped CdS sensitized TiO\(_2\) thin films

Some literatures based on optical property of the TiO\(_2\) films prepared from various techniques have been reviewed in this section. Liu et al. (2005) investigated the photoluminescence (PL) spectra of TiO\(_2\) films excited at 320 nm corresponding to a photon of energy 3.88 eV which is larger than the band gap of TiO\(_2\). The PL peak observed at 368 nm corresponds to 3.37 eV is ascribed as direct electron-hole recombination which would be equal to or slightly bigger than the TiO\(_2\) band gap. The emission band appeared at 400 to 500 nm corresponding to 3.1 to 2.63 eV arises from indirect band gap and surface recombination processes.

Suciu et al. (2009) reported the UV spectra of TiO\(_2\) spray coated films and compared the behaviour before and after calcination. It shows that the bandgap electronic transition of anatase TiO\(_2\) film is indirect. After heat treatment the intensities of absorption peaks of TiO\(_2\) film increased and the peak position shifted slightly to a higher wavenumber. The energy band gap of indirect transition was calculated to be about 3.45 eV, which is larger than of 3.2 eV reported for the bulk TiO\(_2\) anatase, indicating the presence of quantum size effect.
Lee et al. (2010) reported the UV-Vis spectra of the nano-sized and nanoporous TiO$_2$ powders to determine the relationship between the solar energy conversion efficiency and spectroscopic properties. The optical band gap of nanoporous TiO$_2$ was red-shifted and showed higher absorption than that of nano-sized TiO$_2$. The band gap in a semiconductor material is closely related to the wavelength range absorbed, where the absorption wavelength decreases with increasing band gap. The nanoporous TiO$_2$ had a shorter band gap than nano-sized TiO$_2$; so it is easier to move excited electrons from the valence band to the conduction band on the surface.

Some of the literatures based on the optical studies of undoped CdS/TiO$_2$ have been discussed in this section. Chang et al. (2007) have evaluated the amount of CdS nanocrystals incorporated in a TiO$_2$ film from the UV-vis absorbance spectrum of the film. It shows that the absorbance of the film increases with an increase of chemical bath deposition cycles, indicating an increased absorption amount of CdS nanocrystals. Furthermore, the redshifts of the absorption shoulder and the onset position observed by increasing the CBD cycles implies the growth of the CdS nanocrystals. The large increment in absorbance of the film indicates a higher surface area offered for absorption, attributable to the better penetration in the mesoporous TiO$_2$ matrix.

Prabakar et al. (2009) reported that the optical property of CdS/TiO$_2$ electrode showed the variation of absorbance spectra with the CBD dipping time of the film sintered at 450°C. The observed absorbance increased due to the increase of CBD dipping time, indicating an increased adsorption amount of CdS. Furthermore, it was seen that the absorption edge shifted towards longer wavelength with increased dipping time implying the growth of the CdS nanoparticles.

Kontos et al. (2011) reported that the PL spectrum of CdS/glass exhibits a strong peak at about 530 nm which is close to the band gap emission of bulk CdS
arising from radiative excitonic recombination while a rather broad emission band occurs at 625 nm due to the recombination of trapped carriers by defect states. The frequency of the former emission band indicates the growth of nanocrystals with size appreciably larger than the Bohr exciton radius of CdS (~2.8 nm). Moreover, the width of the CdS excitonic peak in the CdS/glass film exceeds largely than that of bulk CdS, indicating a broad size distribution of the CdS nanocrystals. However, upon CdS deposition on TiO₂, the PL intensity of the excitonic emission was drastically suppressed, verifying the effective quenching of the radiative recombination of photoexcited carriers by electron transfer from CdS to TiO₂.

Tubtimtae et al. (2012) have reported the absorption spectra for 3-layered and 4-layered CdS/TiO₂ films over a spectral range of 350 to 750 nm. The prepared CdS films show a broad absorption in the range of 350–500 nm. An absorption edge at 520 nm can be clearly identified suggesting that the larger absorption has a larger amount of CdS material.

Feng et al. (2012) investigated the effect of prolonged deposition time of CdS with TiO₂ nanotube which shows the significant shifting of the absorption edge of the spectra towards the visible region. This red-shift displays the increase in particle size of CdS with the deposition time which induced the absorption edge at about 510, 525, 550, 570 nm. Furthermore, the growth of CdS in the TiO₂ nanotube extended the absorption spectrum into the visible region of TiO₂ film with a band edge at 510 nm as shown in figure 1.7.
Figure 1.7 Absorption spectra of TiO$_2$ nanorods covered with CdS deposited for 0, 2, 3, 4 and 5h

The following literature deals with the optical properties of doped CdS nanocrystals on TiO$_2$. Santra et al. (2012) investigated the CdS deposited TiO$_2$ film showing an absorption onset around 520 nm, which corresponds to a bandgap of 2.4 eV. Furthermore, Mn-doped CdS/TiO$_2$ films showed a red shift in the absorption region with an onset around 570 nm. The overall photocurrent response matched the absorption features with the photocurrent onset around 600 nm for CdS electrodes. Both undoped and doped CdS electrodes exhibited a broad response with maximum IPCE, ~ 60%. But, Mn-CdS/TiO$_2$ films displayed a significant increase (20%) in the photocurrent as compared to the films without dopant which indicates the importance of Mn-doping of the metal chalcogenide film.

1.5.4 Review on the surface morphology of bare TiO$_2$, undoped and doped CdS sensitized TiO$_2$ thin films
Some of the reported literatures based on the surface morphology of the TiO₂ films have been reviewed in this section. Kuznetsova et al. (2007) reported the SEM images of spin coated TiO₂ films displaying spherical nanometric grains and pores. The images also showed that the higher PEG concentration provides higher porosity to the films and cracks were observed due to larger thickness of the film. The differences in crystallite size from XRD and grain size from SEM were ascribed to the agglomeration of smaller grain particles.

Park et al. (2008) reported the compared SEM images of a commercial (P25) TiO₂ films deposited on FTO glass and synthesized TiO₂ films. The surface morphology of the prepared films showed that the TiO₂ spherical nanoparticles were well distributed and it had a porous structure in which the nanoparticles were all bonded together through a sintering process. Such a porous structure permits not only the absorption of larger amount of dye molecules but also the formation of the networking among the TiO₂ molecules. It was noted that the synthesized TiO₂ film was smoother than the P25 film and also appeared to have smaller crystallites.

Some of the literatures based on the surface morphology of undoped CdS/TiO₂ film have been summarized. Jung et al. (2012) showed the comparison between the surface morphology of bare TiO₂ film and CdS coated TiO₂ film. It is observed from the SEM image that the surface area of TiO₂ in 3-layered CdS(3)/TiO₂ film is not fully covered by CdS nanocrystals but the 8-layered CdS(8)/TiO₂ film is almost fully covered by CdS nanocrystals. Jang et al. (2012) have taken the low magnification and HR-TEM images as shown in figure 1.8 for the sample prepared by 6-layered CdS with TiO₂ for knowing the morphology of the film. The low magnification TEM image shows that the particles are isolated and spherical-shaped CdS are found on the TiO₂ surface. It is further confirmed by HR-TEM that the atomic rows with a spacing
of 0.206 nm are clearly observed, which corresponded to the (220) plane of cubic-phase CdS crystallites, in addition to the (101) plane of anatase TiO$_2$ phase with a lattice spacing of 0.352 nm. The energy dispersive X-ray spectroscopy (EDX) linked to HR-TEM also showed a Cd:S atomic ratio of 1:1 that confirmed the formation of stoichiometric CdS.

Figure 1.8 HR-TEM images of the CdS(6)/TiO$_2$ film

Hsu et al. (2013) reported the field emission scanning electron microscopy (FE-SEM) image of 5CdS/2TiNR film wherein the CdS nanoparticles were deposited on the surface of titania nanorods indicating the diffused Cd$^{2+}$ and S$^{2-}$ ions to the bottom of the nanorods to form the desired CdS nanocrystallites. The images of 8ZnS/5CdS/2TiNR film showed that the nanostructured ZnS forms as a thin layer on the surface of the film. The HRTEM image of CdS/TiNR also reveals that the crystalline TiO$_2$ nanorods grow along the [001] direction with the lattice spacing of CdS, $d = 3.2 \pm 0.1$ Å corresponding to (101) plane in hexagonal CdS.

Yang et al. (2014) reported the surface morphology of the film based on electrospinning of TiO$_2$ nanostructures and subsequent CdS deposition via. SILAR followed by dipole treatment (DT). The low magnification SEM images of the film showed dense porous structures and significant coverage of CdS on
larger TiO$_2$ “rice grain” structures were observed in high magnification SEM images. The cross sectional SEM images revealed that the thickness of the electrode was ~10 μm.

The following literature deals with the surface morphology of doped CdS on TiO$_2$. Yu et al. (2014) have reported the formation of Mn-doped CdS/TiO$_2$ flower-rod structure from FE-SEM and TEM analysis. It was observed from the SEM that the surface of the Mn-doped CdS/TiO$_2$ flower-rod became rougher than the bare TiO$_2$ flower-rod. So, it can be noticed that the Mn-doped CdS can be uniformly absorbed on TiO$_2$ flower-rod through SILAR method. TEM image of the Mn-doped CdS sensitized TiO$_2$ flower-rod showed that the film was composed of small nanoparticles distributed on its surface.

1.5.5 Review on the electrical properties of bare TiO$_2$, undoped and doped CdS sensitized TiO$_2$ thin films

The following literature deals with the electrical properties of TiO$_2$ thin film. Hosseini et al. (2013) reported the electrical conductivity of the prepared TiO$_2$ films using the current-voltage measurements. The resistivity values of the films prepared at 2000, 5000 and 8000 rpm were reported as 2.6 x 10$^3$, 4.8 x 10$^3$ and 0.21 Ω cm, respectively. The lowest resistance value was observed for the film coated at a spin rate of 8000 rpm with a calculated resistivity value which was almost 10$^4$ times lower than those obtained for the films coated at a spin rate of 2000 and 5000 rpm.

The following section reviews the electrical property of undoped CdS on TiO$_2$ film. Feng et al. (2012) reported that as the CdS deposition time was increased to 4 or 5 h, the current density observed was significantly lower than the 3 h loaded photoelectrode. The reason is that the thinner film had higher CdS loading on TiO$_2$ nanorods which allow for more efficient transfer at the CdS/TiO$_2$ interface and more efficient transfer at the CdS/electrolyte, minimizing electron-hole recombination in CdS. However, the longer deposition time results in an
excess deposition of CdS on the TiO$_2$ nanorods. The thick CdS coating would reduce the collection probability because it could result in a longer transport path length for the photogenerated electron-hole pairs in the CdS sensitizer before being separated and collected; thus acts as a potential barrier for charge transfer and weaken the photocurrent generated from visible light by excitation of electron-hole pairs in the CdS.

Hsu et al. (2013) reported the sequential deposition of nanocrystalline CdS onto the surface of the titania nanorods (TiNR) to enhance absorption in the visible light region. ZnS layer was coated onto the CdS/TiNR surface to prevent the corrosion of CdS nanoparticles and to facilitate the photocarriers transportation to TiNR. $V_{oc}$, $J_{sc}$, solar conversion efficiency ($\eta$) and IPCE are further improved in the cell by the deposition of ZnS passivation layer. The obtained IPCE of CdS sensitized solar cell was 1.84% under AM 1.5 G illumination with $J_{sc} = 4.19$ mA cm$^{-2}$, $V_{oc} = 0.82$ V and fill factor (FF) = 54%.

The following section deals with the electrical properties of doped CdS on TiO$_2$. Santra et al. (2012) reported that the Mn-doped CdS films show broad absorption in the visible region and the highest conversion efficiency highlights the importance of Mn-doping of the metal chalcogenide films. An increase in the photovoltage was observed in the Mn-doped CdS ($V_{oc} = 583$ mV) and also exhibited a significant increase (20%) in the photocurrent as compared to the corresponding semiconductor films without dopants. The short circuit current and open circuit voltage was increased in Mn-doped CdS film and Mn-doping was reflected in the high overall power conversion efficiency of the cell.

Thambidurai et al. (2012) have reported that the conductivity of CdS and Co-doped CdS nanoparticles was found to increase with the increase in temperature as more charge carriers could overcome the activation energy barrier to participate in electrical conduction. So the conduction mechanism in CdS and Co-doped CdS may be due to the thermally activated process. The conductivity
was found to increase with Co-doping concentration up to 5.02%, while beyond this concentration the conductivity was found to decrease with further increase in Co-doping concentration. It has been reported that the increase in conductivity with increasing cobalt concentration can be related to the increase in the number of mobile charge carriers in the nanoparticles and the decrease in conductivity at higher cobalt concentration may be due to the aggregation of ions which lead to the formation of ion clusters.

1.6 OBJECTIVE OF THE WORK

The present work focuses on the use of undoped and doped sensitizers on the photoanode to improve the light harvesting ability and the electron transfer rate by reducing the charge recombination rate at the interfaces. The following objectives are set for carrying out the research work:

- To synthesize undoped (ZnS/CdS/TiO₂) and doped (ZnS/Mn-CdS/TiO₂ and ZnS/Co-CdS/TiO₂) photoanode films by chemical route using spin coating and SILAR methods

- To analyze the structural, morphological, optical and electrical properties of undoped and doped (ZnS/Mn-CdS/TiO₂ and ZnS/Co-CdS/TiO₂) photoanode films.