CdSe AND TiO_2 PHOTOANODE BY ELECTROPHORETIC DEPOSITION FOR QUANTUM DOT SENSITIZED SOLAR CELL

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by

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LIST OF SYMBOLS

%	Percentage
°	Degree
°C	Degree Celsius
ml	Milliliter
wt%	Weight percentage
V	Voltage
g	Gram
h	Hour
s	Second
hv	Photon energy
2θ	Diffraction angle
nm	Nanometer (10^{-9} m)
μm	Micrometer (10^{-6} m)
β	Full-width at half-maximum (radius)
C	Capacitance
η	Photoconversion efficiency
h^+	Holes
λ	Wavelength
α	Absorption coefficient
D	Crystallite size
Z'	Real impedance
Z''	Imaginary impedance
R_s	Series resistance
R_{ct}	Charge transfer resistance
f	Frequency

ε	Dielectric constant
I	Current
J_{max}	Current density at maximum power point
V_{max}	Voltage at maximum power point
J_{sc}	Photocurrent density at short circuit
V_{oc}	Open circuit voltage
P_{in}	Intensity of the incident light
E_g	Band gap energy
h	Plank's constant

LIST OF ABBREVIATIONS

CB	Conduction Band
VB	Valence Band
DA	Direct Absorption
CE	Counter Electrode
FTO	Fluorine Doped Tin Oxide
EIS	Electrochemical Impendence Spectroscopy
J-V	Current Density-Voltage
UV-vis	UV-Visible Spectroscopy
QDSSC	Quantum Dots Sensitized Solar Cell
DSSC	Dye Sensitized Solar Cell
HRTEM	High Resolution Transmission Electron Microscopy
EPD	Electrophoretic Deposition
QD	Quantum Dot
SILAR	Successive Ionic Layer Adsorption and Reaction
CBD	Chemical Bath Deposition
DA	Direct Adsorption
CQD	Colloidal Quantum Dot Solar Cell
EDL	Electrical Double Layer
FF	Fill Factor
XRD	X-Ray Diffraction
RCA	Radio Corporation of America

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FOTOANOD CDSE AND TIO_2 MENGGUNAKAN PEMENDAPAN ELECTROFORESIS BAGI SEL SOLAR DOT KUANTUM TERPEKA

ABSTRAK

Nanopartikel CdSe telah digunakan sebagai pemeka foton di dalam sel solar terpeka berkuantum dot (QDSSC). Dalam kajian ini, nanopartikel CdSe telah disintesis menggunakan kaedah pancutan hangat dengan jumlah ligan TOPO yang berbeza. Nanopartikel CdSe diserakan di dalam kloroform berikutan proses penulenan. 8 g TOPO CdSe telah digunakan dalam proses pemendapan. CdSe dimendapkan kepada substrat tin oksida terdop fluorin (FTO) menggunakan kaedah pemendapan elektroforesis (EPD) dengan parameter yang berbeza. CdSe dimendapkan kepada saput TiO_2 manakala campuran CdSe-TiO_2 dimendapkan kepada substrat FTO. Nanopartikel TiO_2 telah berjaya disediakan melalui pengubahsuaian menggunakan asid propionik dan n-heksilamina dengan melarutkan nanopartikel TiO_2 di dalam kloroform. TiO_2 dimendapkan kepada dimendapkan kepada substrat tin oksida terdop fluorin (FTO) menggunakan kaedah pemendapan elektroforesis (EPD) dengan parameter yang berbeza. Bagi saput CdSe/TiO_2, TiO_2 pertama sekali dimendapkan kepada FTO sebelum dipanaskan pada suhu 450 °C selama 3 jam. Seterusnya, CdSe dimendapkan kepada saput TiO_2 panas. Bagi saput campuran CdSe-TiO_2, CdSe dan TiO_2 telah dicampur dan dimendapkan kepada substrat FTO. Saput CdSe/TiO_2 dan saput campuran CdSe-TiO_2 telah disediakan menggunakan kaedah EPD sebagai fotoanod. Bagi QDSSC, saput CdSe/TiO_2 dan saput campuran CdSe-TiO_2 telah digunakan sebagai fotoanod dan kuprum (II) sulfida (Cu_2S) yang bertindak sebagai elektrod penyangkal telah digunakan di dalam elektrolit polisulfida. Kesemua fotoanod, elektrod penyangkal dan elektrolit telah dipasang bagi penilaian I-V dan

EIS. Kecekapan tertinggi bagi saput CdSe/TiO_2 adalah sebanyak 2.1% manakala bagi campuran CdSe-TiO_2 sebanyak 0.04%. Daripada hasil penilaian EIS, nilai R_{ct} bagi saput berlapis CdSe/TiO_2 dan saput campuran CdSe-TiO_2 adalah masing-masing 51 Ω dan 75 Ω. Oleh itu, saput berlapis CdSe/TiO_2 menghasilkan kecekapan yang lebih tinggi berbanding saput campuran CdSe-TiO_2 di dalam penggunaan QDSSC.

CDSE AND TIO_2 PHOTOANODE BY ELECTROPHORETIC DEPOSITION FOR QUANTUM DOT SENSITIZED SOLAR CELL

ABSTRACT

CdSe nanoparticles was used as a photon sensitizer in quantum dot sensitized solar cell (QDSSC). Mesoporous structure is desired for TiO_2 wide band gap semiconductors to provide large surface area for absorption of more QDs in harvesting visible light efficiency. Common method to make QDSSC is to complete the CdSe with TiO_2 for charge transfer. But, the problem with this system is that photoexcited electron need to travel a long pathway (the thickness of TiO_2) before its reach to the conductive substrate, where the photoexcited electron is susceptible to recombination with the sub-band gap state of TiO_2. Mixed CdSe-TiO_2 photoanodes will create efficient electron injection from CdSe conduction band to the TiO_2 electrode effectively in order to reduce the recombination and improve the efficiency. In this research, CdSe nanoparticles were synthesized by hot injection method and using different amount of TOPO ligand. CdSe nanoparticles were dispersed in chloroform after purification process. 8 g TOPO amount of CdSe were used for deposition process. CdSe was deposited on fluorine doped tin oxide (FTO) substrate by using electrophoretic deposition method (EPD) with various EPD parameter. CdSe was deposited on TiO_2 film and mixing CdSe-TiO_2 were deposited on FTO substrate. TiO_2 nanoparticles were successfully prepared by modification using both propionic acid and n-hexylamine and TiO_2 nanoparticles dissolved in chloroform. TiO_2 was deposited on fluorine doped tin oxide (FTO) substrate by using electrophoretic deposition method (EPD) with various EPD parameter. For CdSe/TiO_2 film, TiO_2 was deposited on FTO first then this film was heated 450 °C for 3 hours. Then, CdSe was deposited

on heated TiO_2 film. For mixed CdSe-TiO_2 films, CdSe and TiO_2 was mixed together and deposited on FTO substrate. CdSe/TiO_2 film and mixed CdSe-TiO_2 film were prepared by EPD method as photoanode. For QDSSC, CdSe/TiO_2 film and mixed CdSe-TiO_2 film was used as photoanode, copper (II) sulfide (Cu_2S) as counter electrode and was used polysulfide electrolyte. These photoanode, counter electrode and electrolyte were assembled for I-V and EIS measurements. The highest efficiency of CdSe/TiO_2 film was 2.1% and 0.04% for the mixed CdSe-TiO_2 films. From the result of EIS measurement, the R_{ct} value of CdSe/TiO_2 films and mixed CdSe-TiO_2 films were 51 Ω and 75 Ω. Thus, the CdSe/TiO_2 films produced higher efficiency than mixed CdSe-TiO_2 films in QDSSC application.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Rapid depletion of non-renewable energy resources, and over exploitation of conventional fossil fuels has aggravated the problems of global warming and climate change. Renewable energy has been a global issue and the demand for it has increased because of issues associated with the conversion of fossil fuel to electricity. When fossil fuels are converted to electricity, the process often result in harmful side effects such as pollution that threatens human health, and the release of greenhouse gases associated with climate change. Therefore, global research attention has been driven towards alternative, renewable, and clean energy sources such as wind, solar, tide, biomass, and biofuel (Abolhosseini et al. 2014). Although there are several potentially renewable sources of energy, solar energy is considered as a more desirable source of energy. In fact, it has attracted much attention and interest as an environment friendly energy alternative of the future which could help to prevent global warming, weather change and greenhouse effect.

The earth gets about 4.3×10^{20} of energy from sun in just one hour. This value is enough for the solar cells to harvest the sunlight and transfer the light directly into electricity without the evolution of carbon dioxide, since the planet needs only about 4.1×10^{20} J of energy per year (Lewis et al. 2005). Besides, the electric energy obtained from solar cells is clean. Based on this, a wide range of solar cell technologies are currently being developed. Some of the notably types of solar cells are dye-sensitized solar cells (Grätzel 2003), bulk heterojunction solar cells (Blom et al. 2007), depleted heterojunction solar cells (Pattantyus-Abraham et al. 2010), and hybrid organic-inorganic solar cells (Chandrasekaran et al. 2011).

In the development of solar cells, the technology has progressed in a way that they can be categorized into three generations - first, second and third generation (Werner 2004). The first-generation solar cells or photovoltaic cells are based on a single crystalline silicon wafer, while the second-generation solar cells or photovoltaic solar cells utilizes the inorganic thin film structure in the cell assembly. The second-generation solar cells are cheaper to produce compared to the single junction crystalline photovoltaic cell of the first generation. However, the efficiency of the amorphous thin film solar cells i.e., 14% is lower than the efficiency inherent in the single junction crystalline photovoltaic cell of the first generation which can go as high as 27%. Theoretically, single junction cells should be able to exhibit a maximum efficiency of ~33%, a limit set by Shockley-Queisser thermodynamics.

However, profitable commercialization of the solar cell technology is aimed at achieving efficiencies greater than 33% at lower production costs. The onset of this breakthrough is the third-generation photovoltaic cells. In the third-generation photovoltaic cells, higher efficiency devices were possible at lower production cost. Dye-sensitized solar cells (DSSCs), quantum dot-sensitized solar cells (QDSSCs), colloidal quantum dot solar cells (CQD) and organic solar cells are notable types that were developed under the third-generation solar cells or photovoltaic cells. Over the last ten years, the improvements in DSSCs has maintained the highest record ever reported, which is 12% (Jun et al. 2013; Choi et al. 2013).

At the beginning, dye-sensitized solar cells (DSSCs) with inorganic ruthenium-based dyes were made available at a low-cost and established as high-efficiency solar cells in the early 90s (Oregan & Gratzel 1991). Subsequently, numerous researches have focused on the development and characterization of different dyes for application

in DSSCs (Noor et al. 2011). In one of the developments, the QDSSC solar cells in which the dye is replaced with inorganic quantum dot (QD) nanoparticles were developed (Nozik 2002). The quantum dot was based on the DSSC's structure and used as an effective substitute to the dye due to its excellent opto-electronic properties (Grätzel 2003). Hence, quantum dot sensitized solar cells (QDSSCs) have been drawing much attention as third generation solar cells. Being semiconductor nanoparticles, the physical and chemical properties of the QDs are size-dependent. The QDs are especially appealing owing to their high extinction coefficients compared to the conventional dyes. Therefore, the attractive properties of the quantum dots solar cells revolve around the salient characteristics, such as tunability band gap of the sensitizers which offers the possibility of efficiently converting visible light to electric energy (Kamat 2008). In addition, it exhibits narrow emission spectrum, good photostability (Salant et al. 2010), broad excitation spectra, high extinction coefficient and multiple exciton generation (Quantum et al. 2010). Particularly, the ability of QDs to produce multiple exciton generation where a single absorbed photon can generate more than one electron hole-pair is fascinating. Figure 1.1 shows the efficiency chart by NREL, to compare all the three-generation solar cells.

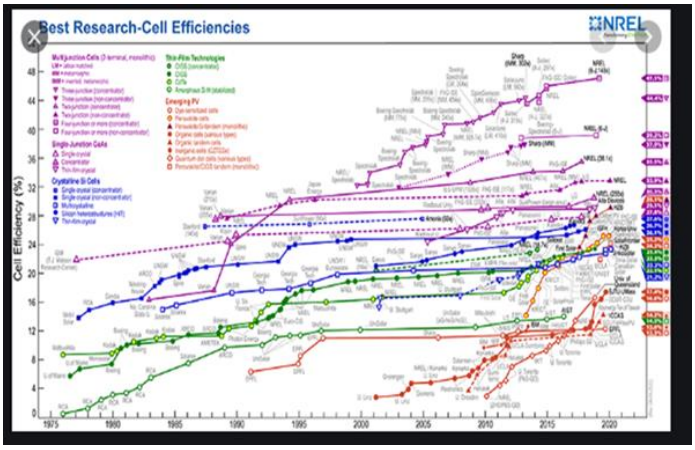

Figure 1.1 Shows the efficiency chart by NREL, to compare all the three-generation solar cell.

In recent times, cadmium chalcogenide (CdX, X= S, Se, Te, etc.) QDs have attracted more attention in QDSSC research. The widespread research activities taking place currently on CdX QDs are due to their distinct properties, such as ease of fabrication, tunability of band gap energy through size control and possible multiple exciton generation as stated earlier. It has been observed that CdX absorbs photon efficiently because it has a bulk material band gap above 1.3 eV (band gap for CdS, CdSe and CdTe are 2.25 eV, 1.73 eV and 1.49 eV respectively) (Peter 2011). Among these materials, CdSe is the most widely studied, mainly due to its easy synthesis, stability, and good performance in sensitized devices. In addition, CdSe has a wider absorption range (< ca. 720 nm) which is in the range of greatest solar irradiances, 300-800 nm. This makes CdSe more advantageous as light harvesting nanoparticles. CdSe is one of the most important materials from group II-VI semiconductors, CdSe being the n-type semiconductor with the wurtzite crystal structure for both bulk material and nanoparticles. When the particle size of the CdSe is smaller than or comparable to its exciton Bohr radius of 5.8, the band gap increases with decreasing particle size due to the quantum confinement effect. Hence, CdSe QDs can be used as coating layers, light absorbers and as a stabilizer for the solar cell when it is coupled with wide band gap semiconductor. The CdSe QDs is stable with polysulfide electrolyte and as a result, several attempts have been made to study the combined deposition of CdSe QDs onto TiO_2 mesoporous photoanode with polysulfide as the electrolyte, to fabricate quantum dots sensitized solar cells.

In the QDSSC, the excited electrons in CdSe QDs, which absorb light in the visible range, can be transferred from the CdSe conduction band (CB) to the TiO_2 conduction band (CB). By tuning the particles size of the CdSe through quantization effect, the charge separation and the energies at the band edges can be optimized (Jun

et al. 2013). Kongkanand and co-workers reported that by varying the size of CdSe QDs assembled on TiO_2 films, improvement in photoelectrochemical response and photoconversion efficiency can be achieved. Figure 1.2. shows that with the decrease of CdSe particle size, photocurrent increases due to the shift of the CB to a more negative potential. This in turn increases the driving force for charge injection and the electron charge transfer rate increases from CdSe quantum dots to TiO_2 nanoparticles.

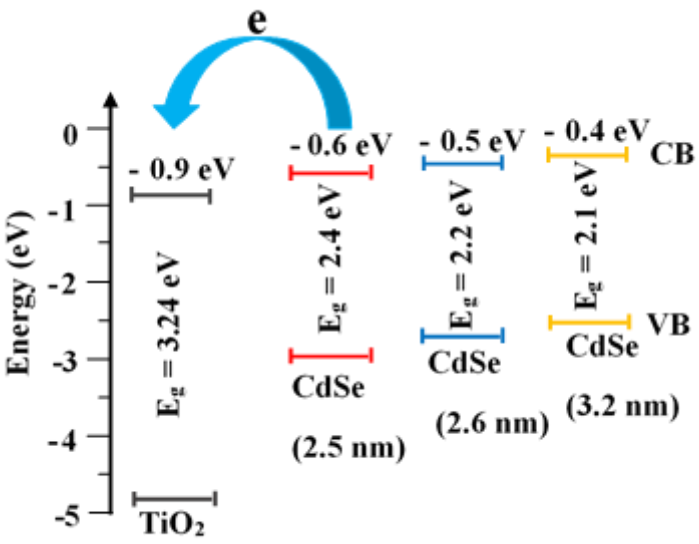

Figure 1.2 Schematic diagram illustrating the energy levels of different-sized CdSe QDs and TiO_2.

The creation of thin films of TiO_2 nanoparticles is of particular interest to scientists and industry due to its properties and its variety of potential applications. For instance, TiO_2 is the preferred material for semiconductors due to its photocatalytic activity, chemical stability, nontoxicity, and low cost compared to other materials. Additionally, TiO_2 is known to exhibit other important properties including large band gap, high electric resistivity, a high dielectric constant, and high oxidative power. These properties make it suitable to be used as capacitors in microelectronic devices, gas sensors, quantum dot synthesize solar cells, dye-based solar cells, optical filters,

antireflection coatings, and sterilization materials (Viana et al. 2010). To create these thin films with TiO_2 nanoparticles, two major processes must be employed. The first process involves the creation of nanoparticles that have the desired shape and properties needed for their intended use. The second process is to create the films of these particles through deposition. For both major processes, there are numerous methods to achieve the desired result.

There are various methods to synthesize nanostructured TiO_2. The notable methods include hydrothermal method (Andersson & Lars 2002), solvothermal method (Wahi et al. 2006), sol-gel method (Bazargan et al. 2012), direct oxidation method (Ryu et al. 2008), chemical vapor deposition (CVD) (Shinde & Bhosale 2008), sonochemical method (Arami et al. 2007), and microwave method (Ferrari et al. 2005). However, among these methods, sol-gel method is seen as a relatively simple approach which can produce highly crystalline anatase TiO_2 nanoparticles with different sizes and shapes. In another vein, there are several reports on the deposition of TiO_2 for QDSSC photoanode, such as through spin coating method (Chou et al. 2011), liquid-phase deposition techniques (Deng et al. 2016), screen printing (Abdul et al. 2017), doctor bladed (Deng et al. 2015), spray pyrolysis (Esparza et al. 2015), electrodeposition (Tan et al. 2009), and sputtering (Li et al. 2012). Notwithstanding, the scope of this study is limited to the particle synthesis through the sol-gel process, and the creation of films using electrophoretic deposition.

Notably, the unique crystal structure, photocatalytic activity, and photoluminescence properties of titanium dioxide nanoparticles are largely responsible for its various applications. Specifically, titanium dioxide is found to have three prominent crystal phases: anatase, rutile, and brookite. In nature, the most found crystal phase is rutile due to its stability. However, due to temperatures most

commonly used in the heating process during nanoparticle synthesis, the anatase phase becomes the most stable (Chen & Mao 2007). Considering that the anatase and rutile phases are the most used phases in the preparation of suspensions for electrophoretic deposition, only the properties and synthesis of these two phases will be analysed in this research.

Salant et al. reported the TiO_2 nanoparticles deposited on FTO (Salant et al. 2010b) and Chiang et al. reported the TiO_2 nanoparticles deposited on TCO through EPD method for QDSSC (Chiang et al. 2015). Likewise, Chen et al. fabricated TiO_2 photoanode on FTO through EPD method for DSSC (Chen et al. 2011). The TiO_2 nanoparticle films composed of large particles which led to higher conversion efficiencies in QDSSCs. This is because a more open structure of the TiO_2 layer facilitates the transport of QDs prior to adsorption, leading to higher QD loadings. In turn, the blockage of nanochannels (mesopores), which could make some parts of the electrode inactive, is prevented. Hence, mesoporous TiO_2 nanoparticle films (for example, commercial P25 nanoparticle) have been extensively studied as the photoanodes for QDSSCs and DSSCs, due to the appreciable internal surface area and good electron transport (Wang 2014).

Mesoporous structure is desired for TiO_2 wide band gap semiconductors to provide large surface area for absorption of more QDs in harvesting visible light efficiency. Therefore, TiO_2 is an attractive material for the solar cells' application because of its surface photochemistry, physical and chemical stability as semiconductor material. In addition, TiO_2 is an n-type semiconductor with wide band gap of 3.0 eV for rutile and 3.2 eV for anatase. The anatase is preferred for use in solar cells because of its higher mobility and catalytic properties. The conduction band, E_{cb}

of anatase TiO_2 is -4.21 with respect to absolute vacuum scale (AVS). So, it is otherwise called E_{cb} -4.21 eV versus vacuum. The wide band gap of bulk TiO_2 favours absorption of a portion of solar spectrum from ultraviolet down to ~ 400 nm. The mesoporous TiO_2 is coated with these QDs using colloidal QD or in situ fabrication and pre-synthesized QDs (also known as ex situ fabrication) (Liu & Kamat 1993, Emin et al. 2011).

The general structure of a QDSSC and its operation is depicted in Figure 1.3 (Jun et al., 2013). The working mechanism of the QDSSC is similar to that of the DSSC. When the QDs (CdSe) is subjected to band gap excitation, upon illumination, electron–hole pairs are formed in the QDs. The electrons will enter the conduction band (CB) of the QD and the hole remains in the valence band (VB). The excited QD injects the electron from its CB into the CB of the wide band gap semiconductor (TiO_2) and in doing so, it is itself oxidized with the hole remaining in the valence band. The injected electron from the QD percolates through the porous TiO_2 network and ultimately reaches the conducting glass. It then travels from there through the external load and completes the circuit by entering back through the counter electrode. The generated voltage is perceived as an evidence of the solar energy conversion to electric energy. This voltage corresponds to the difference between the quasi-Fermi level of the electron in the photoanode and the redox potential of the polysulfide electrolyte, which usually consists of a (S^{2-}/S_x^{2-}) redox couple. The oxidized QD is then restored (hole is filled with electron) when it is reduced by S^{2-} from the electrolyte and in turn it is oxidized into S_x^{2-} that diffuses to the counter electrode.

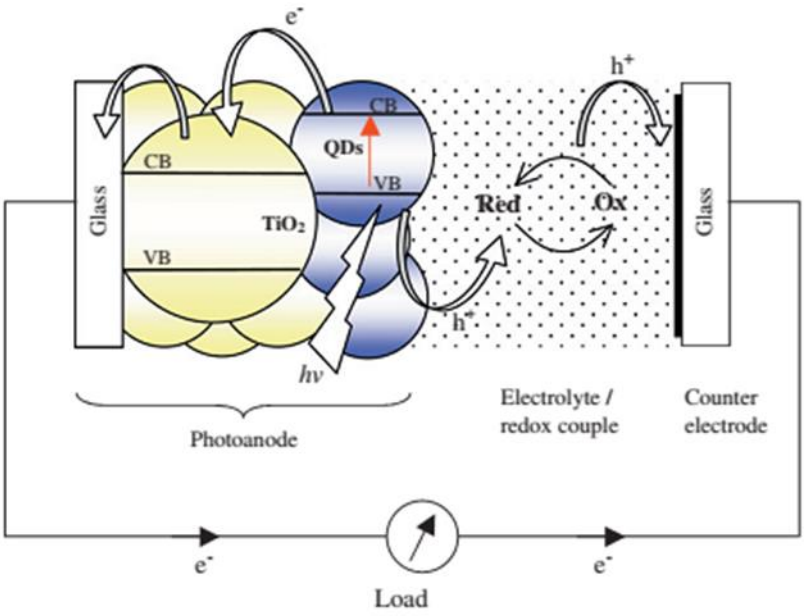

Figure 1.3 Structure and operating principle of a typical QDSSC (Jun et al., 2013).

1.2 Problem Statement

High coverage CdSe nanoparticles films can generate high power conversion efficiency in CdSe-sensitized QDSSCs. However, high coverage of CdSe nanoparticles films are difficult to obtained in the absence of linkers. Several methods are available to obtain high coverage of films, but it is distinctly related to the nature of the nanoparticles synthesized and deposited on the substrates. Commonly, chemical bath deposition (CBD) (Choi et al. 2014), successive ionic layer adsorption and reaction (SILAR) (Emin et al. 2011), bifunctional molecular linkers (Song et al. 2012), and direct adsorption (DA) methods (Wang et al. 2017) are used for preparing quantum dots and attaching them to the wide band gap semiconductor material and substrate surfaces. However, the major drawbacks of the CBD and SILAR methods is the wastage of solution after every deposition. Other disadvantages of these methods include slow growth of particles form a film at the substrate surface, long deposition time, poly-disperse nanoparticles in solution and non-uniform coverage to substrate.

The bifunctional molecular linkers approach is equally limited by low repeatability due to the instability between quantum dot (QD) to linker, and linker to substrate interaction. On the other hand, the DA method often leads a high degree of QD aggregation and a low surface coverage when QDs are attached on the wide band gap semiconductor film (Lana-villarreal & Bisquert 2009). In contrast, the electrophoretic deposition (EPD) method has several desirable advantages. Specifically, the deposition time is short, it requires only simple apparatus, it allows easy control of the thickness and morphology of a deposited film, and there is strong adherent QD deposition onto the wide band gap semiconductor material and substrate surfaces.

Lee and co-workers investigated photovoltaic cells by electrophoretically depositing the CdSe nanoparticles on ZnO which yielded 0.5% power conversion efficiency (Lee et al. 2014). Chiang and co-workers investigated the preparation of photo-electrodes, where an aliquot of a commercial TiO_2 suspension was deposited onto the TCO by the EPD for DSSC. Conversion efficiency 0.04% was reportedly rpoduced (Chiang et al. 2015). In another study by Salant et al. 2010a, electrophoretic deposition method was used to generate high power conversion efficiency in CdSe sensitized QDSSCs. Asides these, electrophoretic deposition (EPD) was previously employed to deposit semiconductor, metallic, and insulating nanoparticles on conductive substrates and polymers (Jia et al. 2008). Significantly, the deposited CdSe QDs adhered strongly both on negative and positive electrodes (Islam et al. 2004). Rosenthal and co-workers fabricated photovoltaic cells by EPD of CdSe nanocrystals on flat TiO_2, yielding low conversion efficiencies, while Islam and co-workers studied the smooth and robust films of CdSe nanocrystals by EPD method (Islam et al. 2004). For QDSSC application, Salant and co-workers fabricated CdSe nanoparticles deposited on TiO_2 by EPD method and their efficiency value is 1.7% (Salant *et al.*,

2010b). Likewise, Kumar and co-workers studied the functionalized electrophoretic deposition of CdSe quantum dots onto TiO_2 electrode for QDSSC, which yielded an efficiency of 0.16% (Kumar 2012). On the other hand, Zarazúa and co-workers stated EPD significantly decreased the Au NPs deposition times to TiO_2 layer (Zarazúa et al. 2016). Generally, several different types of QDs have been deposited using EPD, including CdSe (Smith et al. 2009), CdTe, PbS, and PbSeS (Benehkohal et al. 2012), CdSSe (Santra & Kamat 2012), CdSeTe (Esparza et al. 2017), $CuInS_2$ (Sensitized et al. 2013), $CuInS_2$/ZnS (Liu et al. 2019), and CdSe/CdS nanorods (Salant et al. 2012).

This work aims to shows that the EPD on the TiO_2 electrodes indeed provides a driving force leading to highly effective QD deposition on the mesoporous TiO_2 surface. It is known that the EPD method has the advantage of obtaining better CdSe QDs deposition onto TiO_2 layers with reduced deposition time and it can facilitate easier deposition. Hence, this study aims to use EPD method not only to fabricate the photoanode CdSe/TiO_2 but also to study the effect of the mixed CdSe-TiO_2 nanoparticles. The efficiency of optimize photoanode CdSe/TiO_2 is increased in this study. So far, the combination of CdSe and TiO_2 has not been experimented by researchers to make the QDSSC. Although, mixing the CdSe and TiO_2 can facilitate better contact between CdSe and TiO_2 which can in turn improve the performance of the solar cell. However, the problem with this system is that photoexcited electron need to travel a long pathway (the thickness of TiO_2) before it reaches the conductive substrate, where the photoexcited electron is susceptible to recombination with the sub-band gap state of TiO_2. Mixed CdSe-TiO_2 photoanodes will create efficient electron injection from CdSe conduction band to the TiO_2 electrode effectively, to reduce the recombination and improve the efficiency. A novel attempt to mix CdSe-TiO_2 nanoparticles deposit on FTO substrates may produce positive results.

1.3 Research Objectives

The principal objectives of this research are:

i. To synthesize and evaluate the CdSe nanoparticles with different amounts of TOPO and TiO_2 nanoparticles in chloroform for EPD method.

ii. To investigate the electrophoretic deposition (EPD) of CdSe nanoparticles, TiO_2 nanoparticles and mixed CdSe-TiO_2 nanoparticles on FTO glass substrate.

iii. To evaluate the performance of QDSSC with optimum photoanode.

1.4 Research Scope

This research study aims to explore the use of CdSe and TiO_2 for fabrication of photoanodes for QDSSC application. The role of amount of TOPO and the purification process in synthesizing high-efficient nanoparticles for enhanced deposition on the FTO substrate. The CdSe and TiO_2 nanoparticles were prepared in chloroform. In this research, the behaviour of synthesized nanoparticles such as TiO_2 and CdSe for different amounts of TOPO which acts as a capping ligand. TOPO capped CdSe nanoparticles are soluble in chloroform however, TOPO has incompatibility issues when applied for EPD method. The preparation of TiO_2 in polar and aqueous solvents is also explored. The most suitable method to synthesize TiO_2 in chloroform would be established. Furthermore, the possibility of performing layer by layer deposition and co-deposition of CdSe and TiO_2 has been investigated. A series of experiments were carried out using the EPD process of CdSe, TiO_2 and mixed CdSe and TiO_2. In an attempt to identify and determine the effect of different EPD parameters on the deposition thickness, parameters like applied voltage, deposition

time, electrode gap and volume of CdSe and concentration of TiO_2 were varied and studied. The fabricated CdSe/TiO_2 and CdSe-TiO_2 films were used as photoanodes, Cu_2S as a counter electrode and polysulfide electrolyte in QDSSC, and the performance of the fabricated QDSSC was studied using J-V and EIS measurements.

1.5 Organization of Thesis

The thesis was organized in five chapters. The brief summary on the chapters are described as follows:

a) Chapter One includes a brief introduction about the research study, problem statements, objectives, and the scope of this research work.

b) In Chapter Two, a comprehensive review of literature on the formation, synthesis methods and electrophoretic deposition methods, properties for CdSe and TiO_2 is presented. The fundamentals forming the basis for EPD applications are also discussed in detail. Also, the working principle of QDSSC for the photoanode, photocathode and the electrolyte are included.

c) Chapter Three details the information about raw materials used in this study, the experimental design and the methods and procedures followed to deposit CdSe and TiO_2 by EPD method. A brief explanation on the characterization techniques of CdSe/TiO_2 and mixed CdSe-TiO_2 films is also described.

d) Chapter Four presents the experimental results and a thorough discussion on the formation behaviour of different TOPO amounts in CdSe nanoparticles solution. The effect of the EPD parameters on the deposition characteristics for deposition of CdSe, TiO_2 and mixed CdSe and TiO_2 films have been elucidated. Different characterization methods were adopted to examine and evaluate the

behaviour of the deposited coatings, which is comprehensively analyzed in this section.

e) Chapter Five summarizes the findings and provides the directions and suggestions for further studies on this work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

QDs are categorized as smaller than nano semiconductor particles. In general, particles with sizes between 1-100 nm are regarded as nanoparticles. They act as a path between bulk materials and atomic or molecular structures. QDs composed of tiny semiconductor particles of a few nano meters size, having optical and electronic properties that differ from those of larger light-emitting diode (LED) particles. Their optoelectronic properties change as a function of both size and shape (Kagan *et al.*, 2000). Larger diameter QDs (5–6 nm) emit longer wavelengths, with different colour emission such as orange or red. Meanwhile, smaller diameter QDs (2–3 nm) emit shorter wavelengths, yielding colours of either blue or green, although the specific colour and size vary depending on synthesized temperature and reaction time to get the desired nanoparticle size. Figure 2.1 shows the colour change with different sizes of nanoparticles depending on synthesized temperature and reaction time under UV-irradiation (blue fluorescence colour is 2.1 nm at 110 ℃ for 40 min, dark-green fluorescence colour is 2.4 nm at 120 ℃ for 50 min, yellow-green fluorescence colour is 2.7 nm at 150 ℃ for 60 min, yellow fluorescence colour is 3.0 nm at 190 ℃ for 80 min, orange fluorescence colour is3.7 nm at 220 ℃ for 100 min, red fluorescence colour is 4.3 nm at 250 ℃ for 120 min) that the size values were calculated from the absorbance spectra, according the equation of (Yu et al. 2003).

Chalcogenide nanoparticles such as CdSe, CdS, CdTe and etc. are commonly used as quantum dots (QDs) sensitizers in electronic application. Cadmium selenide (CdSe) nanoparticles (QDs) have been received an increasing attention for quantum dots sensitized solar cell (QDSSC) application due to their exceptional optical

properties, ease of fabrication, tunability of band gap energy, narrow emission spectrum, good photo stability, broad excitation spectra, high extinction coefficient and multiple exciton generation. CdSe is an inorganic compound and it is classified as an II-VI semiconductor of the n-type. CdSe absorbs photon efficiently because its absorption wavelength is in the visible range and the band gap value of a CdSe is 1.73 eV (Peter 2011). The conventional applications of CdSe are for transparent to infra-red (IR) light and pose limitation in photo resistors and windows applications for instruments utilizing IR light.

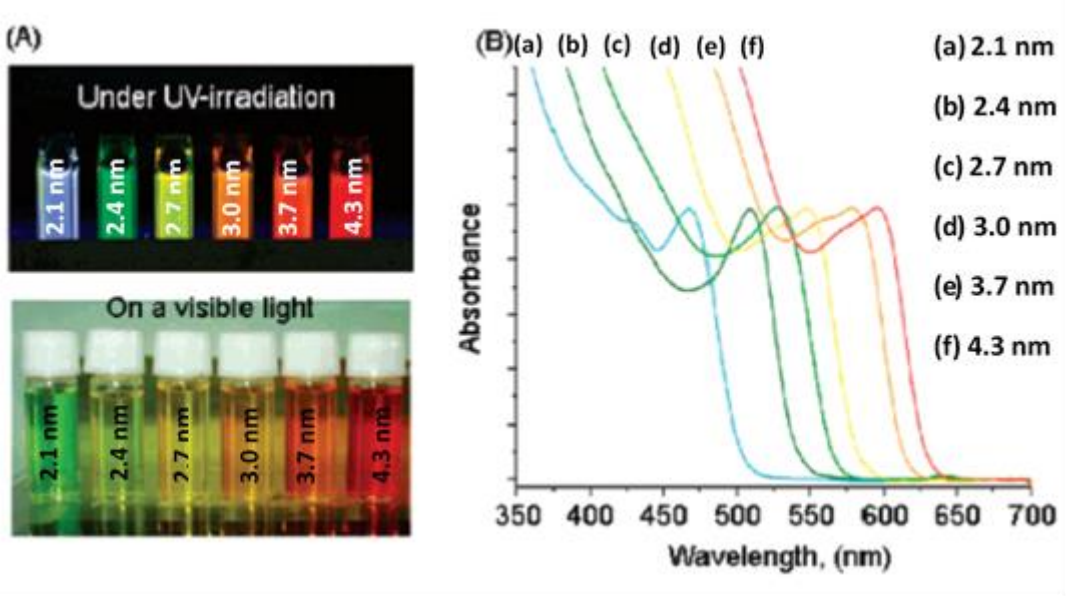

Figure 2.1 Different sizes CdSe quantum dots, synthesized at a slow-increasing temperature gradient with different color light emissions (A) images under UV irradiation and on visible light (B) normalized absorbance spectra (Zlateva et al., 2007).

2.2 CdSe Nanoparticles

2.2.1 Properties of CdSe Nanoparticles

CdSe is an inorganic compound and it is classified as an II-VI semiconductor of the n-type. CdSe nanoparticles possess wurtzite (hexagonal) and zinc blende (cubic)

structures. They promote excellent opto-electronic properties. The physical and chemical properties of CdSe nanoparticles are size-dependent. While synthesizing semiconductor nanoparticles, the deposition parameters can be varied in order to control the size of the nanoparticles (Mastai et al., 1999). By altering the particle size, the band gap can be changed further to match a desired band gap range. It is critical to understand the physical and chemical characteristics of the CdSe nanoparticles for a better research focus. The energy level diagram of CdSe nanoparticles is presented in Figure 2.2 (Vinitha & Divya 2018). When the absorbance wavelength of CdSe increases, its particle size will also increase while the band gap value decreases. CdSe absorbs photon in the visible range of ~ 700 nm efficiently since the band gap value of CdSe is 1.73 eV (Peter, 2011). CdSe has attracted a great amount of attention in the QDSSC research due to its advantages such as ease of fabrication, tunability of band gap energy, narrow emission spectrum, good photostability, broad excitation spectra, high extinction coefficient and multiple exciton generation (William & Yu et al., 2003).

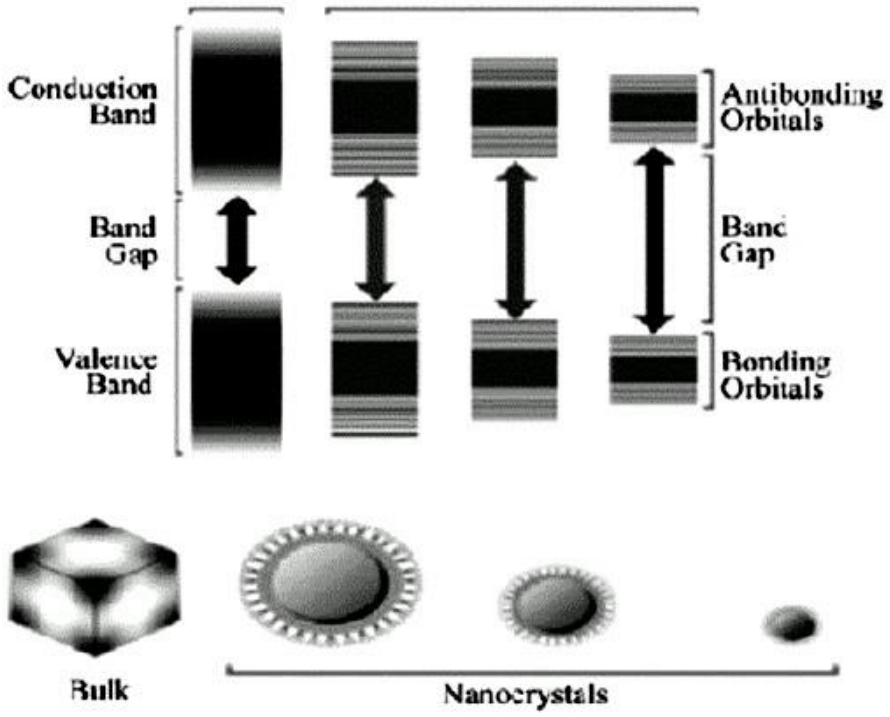

Figure 2.2 Energy level diagram of CdSe nanoparticles (Vinitha & Divya, 2018).

2.2.2 Synthesis of CdSe Nanoparticles

Murray, Morris and Bawendi had proposed a synthesis of CdSe nanoparticles in which the main concept is based on the pyrolysis of organometallic reagents by firstly injecting them into a hot coordinating solvent (Murray et al., 1993). Murray and co-workers used dimethylcadmium $(CH_3)_2Cd$ as the organometallic precursors while trioctylphosphine oxide (TOPO) as the hot coordinating solvent operating at 300°C. TOPO was chosen as the coordinating solvent since TOPO has a high boiling point and enables reaction to take place above the nucleation temperature. Besides, TOPO allows nanoparticles to be soluble in organic solvents and prevents agglomeration. Peng & Peng (2001) reported that impurity such as phosphonic acid presents in TOPO, which leads to a fluctuation in the synthesis of CdSe nanoparticles. Furthermore, dimethylcadmium $(CH_3)_2Cd$ is very toxic, unstable at room temperature and air-sensitive which required this method to be modified as suggested by Qu & Peng (2002). In order to solve this problem, they had suggested to synthesize CdSe QDs by replacing dimethylcadmium $(CH_3)_2Cd$ with cadmium acetate Cd $(CH_3CO_2)_2$ (Mekis et al., 2003), cadmium carbonate $(CdCO_3)$ (Qu et al., 2001) or cadmium oxide (CdO) (Peng & Peng, 2001). Co-solvent such as tetradecylphosphonic acid (TDPA) is added to supplement the unknown impurity and slow the nucleation process so that the size distribution is not distorted when the system cools to the growth temperature (Qu & Peng 2002). Besides, the use of TDPA can also help to produce large batches of nanoparticles with a narrow dispersity as larger volumes of reagents can be nucleated. The second co-solvent, hexadecylamine (HDA) can also be added to provide resistance towards Ostwald ripening. The use of TOPO/TDPA/HDA help in maintaining a narrow dispersity of nanoparticles up to seven hours at growth temperature whereas the use of

only TOPO and TDPA yields a major broadening of the band edge absorption and large polydispersity in less than an hour (Rosenthal et al., 2007).

2.2.3 Growth Mechanism of CdSe Nanoparticles during Synthesis

Precursors of Cd and Se coordinated in trioctylphosphine (TOP) are normally kept at a temperature below the reaction threshold before injection into the pre-heated TOPO matrix. The matrix serves to engulf the precursor droplets and promotes the subsequent chemical reaction into it between the Cd and Se ions forming seeds of nanoparticles. Figure 2.3 shows the growth of the CdSe nanoparticles with addition of coordinated Cd and Se ions on the surface with Cd bounds to TOPO and Se bounds to TOP. Hot injection leads to an instantaneous nucleation, quenched by fast cooling of the reaction mixture and because supersaturation is relieved by the nucleation burst. In 1950, La Mer and Dinegar had found that the production of monodispersed colloids requires a temporarily discrete nucleation event followed by a slower controlled growth of the existing nuclei (Donegu et al., 2005 and Geissbühler, 2005).

In the synthesis of quantum dots, the two common events that will occur are the nucleation process in which precursors at a higher temperature will decompose to form a supersaturated monomer followed by a burst of nucleation and growth of this nuclei from molecular precursor. The synthesis begins with the rapid injection of organometallic reagents into hot coordinating solvent to produce a discrete homogeneous nucleation. Then, further nucleation is prevented when depletion of reagents through nucleation and sudden temperature drop occur. Crystallites growth will continue when reheating is applied on the solution. At this stage, the crystallites growth appears to be consistent with Ostwald ripening is where small crystallites which less stable were dissolved into the large crystallites. Therefore, the size of crystallites is

dependent on the reaction time in which larger particles will be formed when the reaction time is longer, and relatively small nanoparticles will be produced when the reaction time is shorter. Figure 2.4 shows the growth and nucleation of quantum dots based on the La Mer model (Farkhani and Valizadeh, 2014).

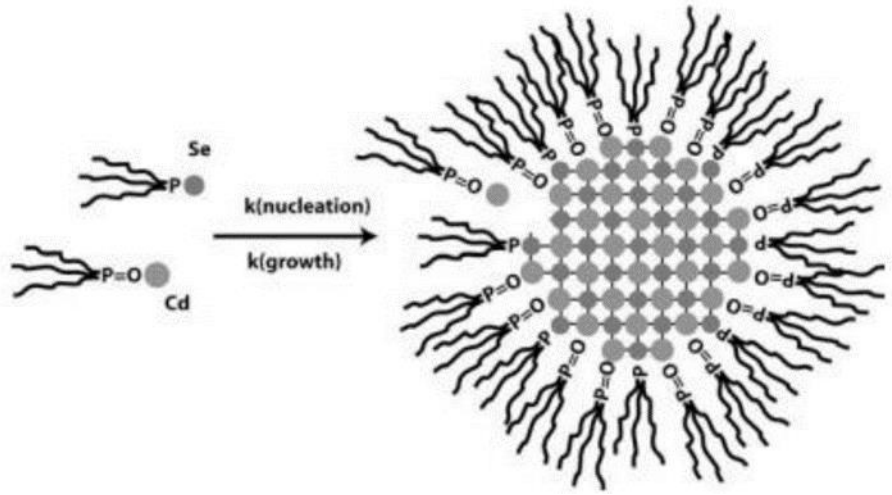

Figure 2.3 Growth of CdSe nanoparticles onto TOPO matrix (Geissbühler, 2005).

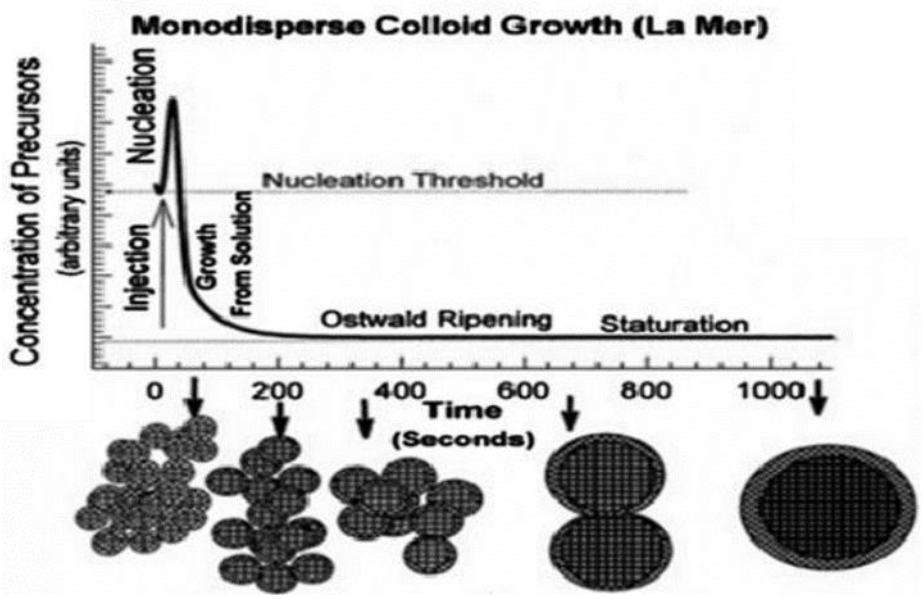

Figure 2.4 Stages of growth and nucleation of quantum dots based on La Mer model (Farkhani and Valizadeh, 2014).

2.2.4 TOPO Ligand

CdSe nanoparticles are prepared as colloidal suspension and quenched in solvent in order to control the growth of the CdSe nanoparticles. Organic ligands are frequently used as the capping ligand in the production of quantum dots such as those consisting of CdSe. These ligands can prevent oxidation and stabilize nanoparticles in solution as shown in Figure 2.5. Hydrophobic ligands such as tri-octyl phosphine (TOP) and tri-octyl phosphine oxide (TOPO) cannot absorb water (Aldana et al. 2001) while hydrophilic ligands such as mercaptopropionic acid (MPA) and mercaptoundecanoic acid (MUA) in contratry can absorb water (Schultz et al., 1997).

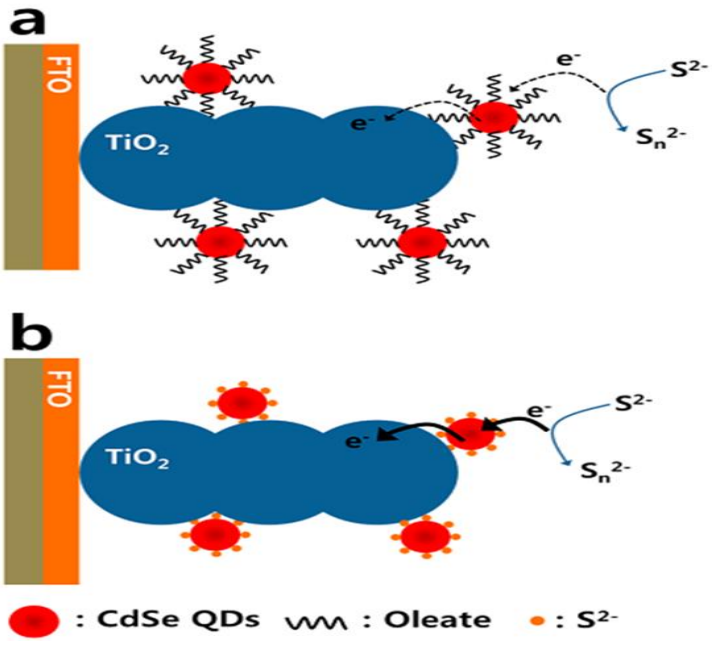

Figure 2.5 Schematic diagram of charge transferring at the interfacial region in QDSSC based on colloidal CdSe QDs capped by (a) long organic chain, oleate; and (b) atomic level inorganic ligand, S^{2-} (Yun et al., 2014).

Wu et al., (2005) described that the capping ligands; tri-octylphosphine oxide (TOPO), hexadecyl hexadecanoate (HH) and benzophenone (BP) were used for the synthesis of high-quality CdSe nanocrystals. TOPO appears to play an important role in the preparation of monodisperse CdSe nanoparticles. CdSe nanoparticles nucleate and grow rapidly in the presence of TOPO, reaching a limiting diameter of 5 nm within

approximately 1 min. Only a small amount of TOPO (3% or less of the reaction mixture) is required to achieve a narrow particle size distribution. Zhen et al., (2009) reported that TOPO is used as the capping ligand in the preparation of CdSe nanowires. The organic capping ligands; TOPO is also used in the colloidal synthesis of CdSe nanorods. The length of the organic capping ligand has a profound effect on the growth kinetics of colloidal CdSe nanorods and the stability of the nanorod solution. By results, the shorter the alkylphosphonic acid ligand, the more elongated and more branching are the nanorods. When mixtures of alkylphosphonic acids are used, higher molar fraction of the shorter ligand produces more elongated and branched nanorods (Wang et al., 2007).

In this thesis, different amount of TOPO was used in the synthesis of CdSe nanoparticles. In this case, TOPO served the synthesis by solubilizing the growing CdSe nanoparticles. CdSe is unlikely to escape from TOPO capping as well as being deposited in the EPD process due to the long ligand TOPO structure. However, in few cases, only TOPO can be deposited instead of CdSe nanoparticles. This condition can cause disturbance in the EPD process.

2.2.5 Optical Properties of CdSe Nanoparticles

The synthesis of different sizes of CdSe nanoparticles can be identified using the UV-vis spectroscopy. The size of CdSe quantum dots is controlled by the time of growth of CdSe nanoparticles before quenching in toluene. The size of CdSe QDs is determined the wavelength from UV-vis spectroscopy. Figure 2.6 (Yuan and Krüger, 2011) shows the UV-vis spectra and photoluminescence spectra of different sized CdSe QDs, in which a shorter wavelength corresponds to a small particle size and a longer wavelength corresponds to a big particle size. These quantum dots of different sizes can

emit light of different color due to the quantum confinement effect. Bigger quantum dots give lower energy fluorescence, which is possible to emit red light whereas smaller quantum dots emit blue light. This shows that the light coloration is directly related to the energy levels of the quantum dots while the size of the quantum dots is inversely proportional to the energy band gap. Therefore, larger quantum dots have more energy level but with lower band gap energy, which are more closely spaced. This can allow larger quantum dots to absorb photons by consuming less energy (Mahajan, 2013).

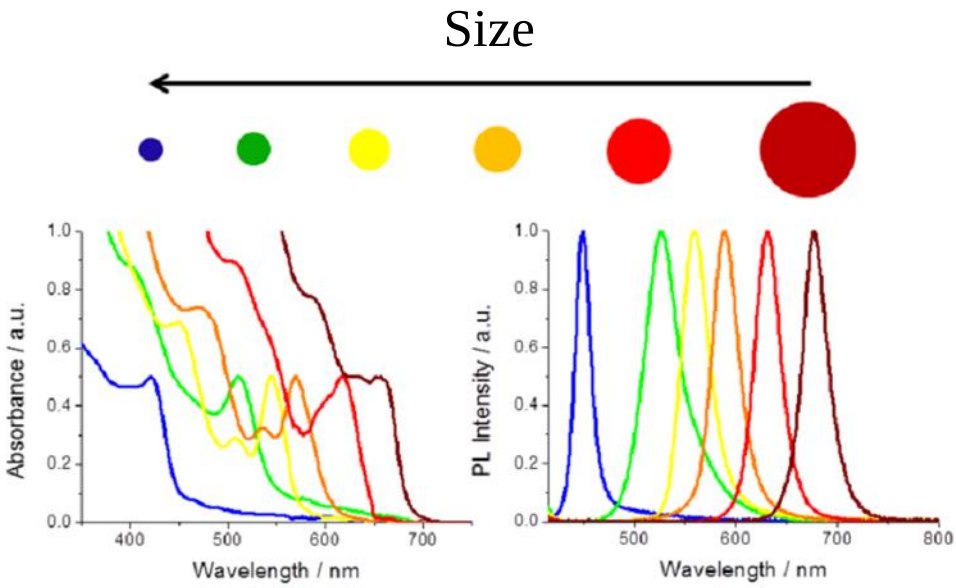

Figure 2.6 Absorption spectra and photoluminescence spectra of different sized CdSe quantum dots (Yuan and Krüger, 2011).

2.2.6 Purification of CdSe Nanoparticles Solution

Knowledge on the distribution of ligands in the QD organic system after purification process is critical in predicting and interpreting the structural, electronic, and optical properties of solutions and films of QDs. This distribution is dependent on the strength of the respective QD ligand interactions and the relative solubility of the ligands in the solvent system. Morris-Cohen et al., (2010) purified QDs by using 5 ml

of chloroform (ACS grade, VWR) with 10 ml of methanol (ACS grade, VWR) and isolated an orange pellet through centrifugation at 3500 rpm for 5 minutes.

CdSe QDs synthesized with TOPO contain nominal surfactants such as TOPO, TDPA, HDA and TOP including 10 different phosphorus-containing impurities such as n-octylphosphonic acid (OPA). Figure 2.7 shows the chemical structure of the ligands present in a QD organic system. Morris-Cohen et al., (2010) found that in L-type ligands, HDA, TOPO and TOPSe are present in both bound and unbound states whereas in X-type ligands, OPA, PPA and stearate are bounded to the surface of QDs. Hence, the purpose of a purification process is to remove the excess ligands such as TOPO, TDPA, HDA and TOP from the synthesis process of CdSe (Morris-Cohen et al., 2010). The methanol and CdSe solution the nanoparticles were precipitated and isolated by centrifugation. After centrifugation two layers of solution form with the colourless solution on top and the CdSe powder in the bottom. The colourless solution was poured out and the CdSe powder re-dispersed in chloroform or toluene which the purification is done completely using methanol for CdSe QDs that capped by TOPO. During purification process, methanol is used as the flocculating agent because it is miscible with toluene and can readily dissolve the bound ligands. Murray et al., (1993) proposed that quantum dots agglomeration is induced by Van der Waals forces, in which the capping agents will leave the quantum dots surface and dissolving within the methanol-toluene mixture and results in aggregation. Subsequently, Jia et al., (2008) investigated that the smoothest films can be deposited when the nanocrystals are washed two or three times before electrophoretic deposition. However, they claimed that if nanoparticles are washed more than three times, then rough and clumpy films will be produced (Jia et al., 2008). Figure 2.8 displays that as purification process continues, the L-type ligands are being removed from the system while the X-type ligands are unchanged throughout