

DESIGN AND FABRICATION OF COMPONENTS OF DYE SENSITISED SOLAR CELLS

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I dedicate this work to my adorable children: Owenkosi, Nkonzo and Okuhle.

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ABSTRACT

In recent decades there has been increasing global concern about the sustainability of our use of fossil fuels, which has led to increased interest in carbon-free sustainable renewable sources such as solar energy. Dye sensitized solar cells (DSSCs) are a cheap and clean technology that harnesses solar energy efficiently and convert it to electrical energy. A DSSC consists of a transparent working electrode coated with a dye-sensitized mesoporous film of nanocrystalline particles of semiconductor e.g. TiO₂, an electrolyte containing a suitable redox couple and a platinized counter electrode. All the components of the DSSCs play vital roles in controlling the performance of the cell. The synergy of these components of the cells also needs to be investigated to optimise their interaction and create efficient and stable DSSCs. The information gathered from this investigation can give insight on how to improve the efficiencies of DSSCs. In this research study the semiconductor, transparent conducting layer and sensitizer were designed, optimized one at a time and their effect on the overall efficiency of the DSSCs studied. In this way it was easy to observe the effect of the individual components on the efficiency of the DSSCs.

The conventional DSSCs usually use TiO₂ as a semiconductor. In this research TiO₂ was doped with cerium (Ce) to enhance its optical properties by reducing the band gap. A series of Ce-doped TiO₂ with Ce content ranging from 0.1 to 1 mol % were successfully synthesized by an acid catalyzed sol-gel method, and their performance as the photoanodes of dye-sensitized solar cells (DSSCs) was investigated. Ce doping resulted in a red shift in the absorption of the TiO₂ indicating narrowing of the band gap. The band gap first narrowed with increase in concentration of dopant up until 0.9 % dopant concentration. After this optimum doping concentration the band gap widened again. DFT calculations showed that Ce doping introduces Ce4f impurity states located just below the conduction band resulting in band gap narrowing. Ce content (0.9%) doped TiO₂ photoanodes improved the performance of DSSCs with a conversion efficiency of 2.11% compared to 0,21% for the one with a pure TiO₂ under 1 sun, AM1.5.

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Graphitised/TiO₂ nanocomposites were also used a semiconductor to slow down recombination of electrons and holes in the cells. Electrophoretic deposition (EPD) was used to deposit graphitised/TiO₂ nanocomposites onto an FTO electrode for application as photoelectrode in dye-sensitized solar cells (DSSCs). An enhanced power conversion efficiency (PCE) of 2.25% was observed for the 0.5 wt% graphene oxide/TiO₂ (GO/TiO₂) based DSSC which was higher than that of the conversion efficiency of pure TiO₂ nanoparticles (i.e. 0.52%). Graphene oxide led to high migration of photoinduced electrons to the conduction band of the collection electrode and inhibition of charge carriers recombination resulting in enhanced photoconversion efficiency. A GO content above 0.5 % resulted in a reduced transparency leading to a decrease in the PCE. 0.5 wt % GO/0.9 Ce–TiO₂ Ce based DSSC showed a slightly enhanced efficiency of 2.45%. 0.5 rGO/TiO₂ based DSSCs had a high efficiency than 0.5 rGO/TiO₂ due to improved conductivity of rGO nanosheets and suppressed recombination of charge carriers.

To cut down DSSC production costs a silver wire network transparent conducting polyethylene electrodes was fabricated and used as an indium tin oxide (ITO) alternative substrates in DSSCs. The transmittance of the AgNW network was 82 % which is comparable to ITO substrates. Titanium oxide (TiO₂) films on the AgWN/PET substrates were obtained using the electrophoresis method. These substrates were sensitised and used to fabricate a dye sensitised solar cell. From the measured current–voltage or I-V characteristic under AM1.5 illumination of the formed DSSC using AgWN substrates, an open circuit voltage (Voc) of 0.377 V, a short circuit current (Isc) of 0.0067 mA and a fill factor (FF) 25.7 % with an efficiency of 0.00862 % were obtained from a cell of 0.075 cm² working area. The stability of the cell improved when a room temperature ionic liquid electrolyte was used.

Gold nanofiber transparent electrodes were also prepared by the electrospinning techniques and used as an alternative to indium tin oxides substrates. Transparent conducting gold nanofiber (AuNF) transparent conducting electrodes were fabricated by using a low–cost electrospinning process and used as photoelectrodes for DSSCs. TiO₂ was deposited on these electrodes by using an electrospray method. DSSC using AuNF as transparent electrodes had a power efficiency of 0.52%, compared to devices made with FTO electrodes (1.48%). DSSCs.

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Versatile dyes with increased spectral response, stability and suppressed recombination of holes and electrons were synthesised and used as a sensitizers for DSSCs. The boron dipyrrin (BODIPY) chromophore was combined with a carboxy coumarin moiety to create donor–acceptor (dyad) system dyes. Regenerative dyad dyes were formed through covalently linking a porphyrin chromophore to a manganese(II) ion through bridging ligands. These chromophores and also porphyrin and BODIPY dyes were used as sensitisers for DSSCs. The regenerative dye based DSSCs showed a photoconversion efficiency of 4.09% which was higher than the efficiency of the parent porphyrin (2.57%). The enhanced efficiency was attributed to the manganese bypridine cluster in the ZnTPP–Mn bpy supramolecule which acted as an electron donor to the photo-oxidized porphyrin continuously regenerating the porphyrin and preventing its decay

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LIST OF ABBREVIATIONS

AgWN	Silver Wire Network
AuNF	Gold Nanofibre
CS	Charge Separation
DSC	Differential Scanning Calorimetry
DSSC	Dye Sensitised Solar Cell
EDS	Energy dispersive spectroscopy EPR
FTIR	Fourier Transform Infrared
GAC	Granular Activated Carbon
GO	Graphene Oxide
IR	Infrared
NMR	Nuclear Magnetic Resonance
PET	Photoinduced Electron Transfer
PS	Polystyrene
rGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
TCE	Transparent Conducting Electrode
TCF	Transparent Conducting Film
ТЕМ	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TOF-SIMS	Time of Flight Secondary ion Mass Spectroscopy
UV-Vis	Ultraviolet-Visible
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

CHAPTER 1 INTRODUCTION

1.1 Introduction

Access to affordable and clean energy sources, particularly electricity, is a key concern globally as shown by the 2012 launch of the UN Sustainable Energy for All Initiative. Solar energy is one of the clean and renewable energy sources that can be used as a complimentary resource to fossil fuels. Photovoltaic cells are used to convert solar energy into electrical energy. One of the photovoltaic cells that has attracted attention is the dye sensitised solar cell (DSSC). DSSCs are thin-film photovoltaic cells that convert visible light into electrical energy mimicking the ability of plants to turn sunlight into useful energy. A DSSC consists of a transparent working electrode coated with a dye-sensitized mesoporous film of nanocrystalline particles of semiconductor e.g. TiO₂, an electrolyte containing a suitable redox couple and a platinized counter electrode. DSSCs employ light harvesting and charge carrier transport processes to convert visible light. Photoconversion begins with the photoexcitation of the sensitizer resulting in the injection of an electron into the conduction band of the oxide, generating the oxidized form of the dye. After electron injection, the ground state of the dye is subsequently restored by electron donation from an electrolyte reductant, which in turn is regenerated by the reduction of the electrolyte oxidant at the counter electrode.

DSSCs are currently best applied to relatively low-density applications and portable gadgets like cell-phones, computers and laptops, communication, lighting, etc. Recent advances in DSSC technology include more efficient nanostructured semiconductors, high–efficiency sensitizers and non–volatile robust electrolytes. The use of these new components in fabrication of DSSCs has enhanced the performance and stability of DSSCs making them more efficient. Perhaps as the efficiencies increase DSSCs will become attractive and are more likely to enhance or replace existing technologies such as roof-top or other solar where there is "low density" collection.

DSSCs have the following advantages over other solar PV like p/n or photoelectrochemical PV cells. The nanocrystalline semiconductors used in the DSSC functions as a unipolar component, i.e., there will be virtually no holes in the semiconductor.¹ This is the case because in the DSSC the sensitizer is selectively photoexcited by a photon with the right photo energies not the wide gap semiconductor, in contrast to the case for the p/n or photoelectrochemical PV cells. The semiconductor does not absorb the photon energies that excite the dye. The photogenerated electron is injected into the semiconductor, leaving the hole in the oxidized sensitizer. Since the hole is not in the semiconductor, chances of recombination of the photogenerated electrons and holes are low. Another advantage is that the semiconductor has high surface area making it possible for more dye molecules to be adsorbed onto it, resulting in more sunlight per surface area being absorbed than in standard silicon-based solar panels. The thin film of the semiconductor means that it actually is slightly more efficient at higher temperatures. Even though the conversion efficiency of dye-sensitized PV cells is lower than that of some other thin-film cells, their price to performance ratio is high. They are generally robust and can be made thin and flexible and hence they are an attractive replacement for current technologies in low density applications such as rooftop solar collectors. DSSCs are useful even in "low-light" conditions like indoors or under cloud cover, while other PVs don't work when charge carrier mobility is low. In direct sun silicon PVs heat up and electrons get promoted into the conduction band thermally leading to loss of efficiency. In DSSCs this not a problem since they work by injecting electrons injected from the photoexcited sensitiser to the conduction band of the semiconductor. DSSCs are economical, easy to manufacture and constructed from abundant and stable resource materials.

1.2 Problem Statement

DSSCs are attractive candidates for photoconversion, but have lower photoconversion efficiencies of about 14% when compared to silicon solar cells (40%). Currently the cost production for DSSCs is high, 3-4 EUR/Wp. ² These factors have limited the implementation of DSSCs in large scale. In order to overcome such high costs, photoconversion systems must either be made from

cheaper materials, or become more efficient. There has been a significant research in improving the efficiencies of DSSCs by many research groups worldwide. All the components of the DSSCs play vital roles in controlling the performance of the cell. The synergy of these components of the cells also needs to be understood to optimise their interaction and create efficient DSSCs.

The transparent conductive oxide glass (indium tin oxide) substrate which acts as a current collector used in most DSSCs exhibits an ideal transparency and resistivity at room temperature. Indium tin oxide (ITO) glass electrodes have the following disadvantages: they are expensive, brittle and break down easily due to exposure to the sun. These electrodes make it difficult for DSSCs to be incorporated in flexible structures. The use of plastic electrodes can lead to design of cells with different shapes to suite their application. However, plastic substrates have lower efficiencies of 2.3% [under 1 sun (100 mW/cm²) illumination]. Finding an alternative for ITO in making transparent conducting electrodes (TCEs) is also another option to lower costs.

Currently, most DSSCs use organic solvent-based liquid electrolytes. These solvents are volatile and temperature dependant: at low temperatures they freeze and at high temperatures they expand and leak rendering the cell less efficient and unusable. Less volatile liquids are required to improve the thermal stability of DSSCs and hence enhance their efficiencies. Attempts have been made to substitute the liquid electrolyte by solid materials ³ and polymer electrolytes.⁴ However, DSSCs using these solid materials show lower efficiencies than those of DSSCs using organic liquid based electrolytes. This is attributed to insufficient penetration of the solid materials into the nanoporous electrode and fast charge recombination in DSSCs. ⁵ Room temperature ionic liquids (RTILs) electrolytes have been employed as iodide-based liquid electrolytes to replace organic solvent-based liquid electrolytes solar cells to design efficient and stable electrolytes for DSSCs. ⁶

Recombination of the injected electrons with the holes in the sensitizer or the redox couple at the TiO₂/dye interface significantly reduces the charge-collection efficiency at the counter electrode, and thereby decreasing the total efficiency of the cell. Long-

lasting charge separation is important for all light-induced electron transfer processes and in particular the photovoltaic processes used by DSSCs. Schmidt-Mende et al. (2005) used TiO₂ films containing hydrophobic sensitizers that contain long aliphatic chains (4–8) and observed that the recombination reaction was greatly suppressed. ⁷ The explanation was that the aliphatic network, acted like a shield, thereby preventing triiodide from reaching the TiO₂ surface. Long lasting charge separation can also be achieved by increasing the separation between the electrons delocalized on TiO₂ and the positive charge localized on the dye. ⁸

The spectral response of most dyes used in today's DSSCs is narrow and it should be increased to the red spectrum to broaden the photon harvesting potential of the sensitisers. Natural dyes (e.g. carotenoids, chlorophylls) were initially used as sensitisers in solar cells, but these cells have low efficiencies of 2.9%. ⁹ Panchromatic dyes have a broader photon harvesting potential up to 920 nm and cells which use these dyes show improved efficiencies. ¹⁰ Dyes or light harvesters which are environmentally friendly and low cost are considered suitable replacements of the currently used dyes in DSSCs. There is also a need for broad spectrum dyes to harvest as much solar energy as possible.

1.3 Justification

The sun is an obvious source of cheap and renewable energy, and its utility in DSSCs will lead to the production of clean energy without any emission of the greenhouse gases. In Africa solar energy promises to be a viable option as many places receive a high sun insolation and some of the raw materials for solar cells like titanium are available in countries like South Africa and Mozambique.

TiO₂ has shown to be a good semiconductor for photoconversion technologies as it is cheap, chemically stable and inert towards the electrolyte species. It also has a lattice structure suitable for dye bonding due to conduction band, which is located slightly below the lowest unoccupied molecular orbital (LUMO) level of the dye in order to facilitate efficient electron injection. ¹¹ The crystalline form, anatase, has improved electron transfer properties and helps slow down recombination reactions in DSSCs. TiO₂ has a wide band gap of 3.2 eV limiting its use in the visible region

of the spectrum. To increase its activity in the visible region of the solar spectrum cerium metal was used. These dopants narrow down the band gap by inserting bands above the valence band or beneath the conduction band.

BODIPY dyes are good sensitisers for DSSCs because they absorb strongly in the UV region and emit relatively sharp fluorescence peaks with high quantum yields leading to high efficiency cells. Porphyrins are also widely used as dyes for DSSCs. Recombination in porphyrins can suppressed by linking manganese clusters to the porphyrin to create self-regenerative dyes. The clusters prevent the dye from degrading as it is continuously replenished by the electrons donated by the clusters. ¹² This mimics the photosynthetic unit in green plants whereby a tetramanganese cluster serves as an electron donor to regenerate the photosensitizer P680 by transfer of electrons to the photo-oxidized form, P680⁺. ¹³

Price reduction can be achieved by replacing ITO with a conducting wire network on polyethylene naphthalate (PEN). Metal wire network is the next generation conducting material with the potential to replace ITO in transparent conducting electrodes (TCE). TCEs are 85% transparent in comparison to ITO and less expensive than ITO electrodes.¹⁴

Room temperature ionic liquids (RTILs) possess low volatilities and excellent ionic conductivities. They are also nonflammable, and have high thermal stability, making them suitable for long term outside DSSCs applications avoiding problems such as leakage and evaporation of the organic solvent containing electrolytes.

1.4 Objectives of the study

The aim of this research study is to optimise the components of the DSSCS to produce cells with improved synergistic working of the individual components.

This research project was undertaken with the following specific objectives:

 To dope TiO₂ with cerium (Ce) to enhance its optical properties by reducing the band gap.

- (ii) To use graphiticed/TiO₂ nanocomposites to slow down recombination of electrons and holes in the cells.
- (iii) To cut down DSSC production costs by using silver wire network transparent conducting flexible polyethylene naphthalate (PEN).
- (iv) To use room temperature ionic liquids (RTIL)] as alternative electrolyte solutions instead of iodine based electrolyte.
- To prepare gold nanofiber transparent electrodes as an alternative to indium tin oxides substrates
- (vi) To use of versatile dyes with increased spectral response, stability and suppressed recombination of holes and electrons.

1.5 Dissertation outline

The thesis is divided into eight chapters. The following thesis outline gives a brief description of the content of chapters to follow.

Chapter 1 outlines motivation and scope of the work

Chapter 2 gives an extensive current literature review that relates to the study undertaken.

Chapter 3 to *6* are presented as papers and chapter 3 has been submitted for publication.

Chapter 3 Reports on the synthesis, characterisation and theoretical calculation of Ce-doped TiO₂ for dye sensitised solar application. A series of Ce-doped TiO₂ with Ce content ranging from 0.1 to 1 mol % via an acid catalyzed sol-gel method were synthesized, and its performance as the photoanode of dye-sensitized solar cells (DSSCs).

Chapter 4 Describes the fabrication of graphiticed/TiO₂ nanocomposites based photoelectrodes to slow down recombination of electrons and holes in DSSCs.

In *Chapter 5* a cost-effective silver wire network transparent conducting flexible polyethylene naphthalate (PEN) electrode is prepared and its use as a TCE for the photoanode investigated.

Chapter 6 a low cost and facile method to fabricate gold nanofibers TCE is developed based on electrospinning technique of polystyrene polymer template.

Chapter 7 reports the design and synthesis of organic donor (D)- π bridge-acceptor (A) sensitizers to increase their spectral response, stability and reduce recombination of holes and electrons. Novel regenerative dyad dyes were also synthesised through covalently linking a chromophore to a manganese(II) ion through bridging ligands

Chapter 8 consists of conclusions on the whole research study and recommendations for future studies.

The *Appendix* presents selected chromatograms and spectra.

CHAPTER 2 LITERATURE REVIEW

This chapter aims to review the theoretical background necessary for understanding the experimental results on dye sensitised solar cells (DSSCs). A brief history of DSSCs is outlined. The underlying fundamental operating principle of photoconversion starting from light harvesting by the sensitizer, charge separation, electron transfer from the electronically excited chromophore into the conduction band of the semiconductor oxide, and migration of the injected electrons through the mesoporous film to the collector electrode are described. The back reactions that compete with the above processes are also discussed. Materials used in constructing DSSCs currently are analysed and the use of alternative materials to those used in traditional DSSCs and their feasibility and advantages are critically discussed.

2.1 Evolution of Dye Sensitised Solar Cells

A solar cell or photovoltaic cell is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect, which is a physical and chemical phenomenon. The photovoltaic effect was experimentally demonstrated first by French physicist Edmond Becquerel. In 1839, at age 19, he built the world's first photovoltaic cell in his father's laboratory. ¹⁵ The first practical photovoltaic cell was publicly demonstrated on 25 April 1954 at Bell Laboratories. ¹⁵ The inventors were Daryl Chapin, Calvin Souther Fuller and Gerald Pearson. These first crystalline silicon solar cells achieved a 4.5% efficiency, followed in 1954 with devices with 6% efficiency. These became the first generation (1G) of solar cells. The 1G solar technology comprises photovoltaic cells based on thick crystalline films of semiconductors (mainly silicon). Photoconversion efficiencies as high as 40 % have been reported for these cells, which is one of the reasons they dominate the market. ¹⁶ However, the high fabrication cost and the usage of toxic chemicals in producing highly purified silicon during the manufacturing process has motivated the search

for an environmentally friendly, low-cost solar cell. The second generation (2G) of solar cells was developed with the aim of reducing the high costs prevalent in 1G by employing thin film technology. The advantages of thin film solar cells include the ease of manufacture permitting a reduction of the production cost, a wider range of applications with attractive appearance, and possibilities of using flexible substrates. They also employ a less extensive fabrication process. While the 2G addresses the cost issues associated with thick films, the performance of such 2G solar cells is known to be poor compared to their 1G counterparts. ¹⁷

The work on DSSC which form the third generation (3G) solar cell began in 1870, when Vogel and his group in Berlin, produced the first panchromatic film by associating a dye and a halide semiconductor. ¹⁸ Soon after that the first photoelectrode was developed with similar photochemical theory. In 1887, James Moser reported on the fabrication of a dye sensitized photochemical cell. ¹⁹ In 1960s, intense research on the photochemical and working principles for photochemical cells was done. Electrochemical measurements verified that the cell operates by injecting photogenerated electrons into the conduction band of a wide bandgap planar semiconductor. However, these cells showed very low light harvesting efficiency and the photoconversion efficiency was below 1 %. ²⁰

The major breakthrough for DSSC was realized in 1991 when O'Regan and Grätzel reported on the production of dye sensitised solar cells (DSSCs). ²¹ In these cells the planar smooth semiconductor was replaced by a mesoporous nanocrystalline semiconductor film, possessing a high surface area for dye loading. The nanometer-sized TiO₂ particles, enhances the effective surface area by a thousand-fold, thus making light absorption efficient even with only a dye monolayer on each particle. This arrangement mimics what happens in nature, whereby absorption is enhanced by stacking the chlorophyll-containing thylakoid membranes of the chloroplast to form the grana structures. ²² This approach dramatically improved light absorption and improved photoconversion efficiencies of DSSCs in the last 20 years, from 5 % to a confirmed record of 14.1% which was achieved M Grätzel and his team at École Polytechnique Fédérale de Lausanne (EPFL). In **Figure 2.1** the efficiency trend of all the generations of solar cells is summarized. It can be seen that for first

generation devices the highest efficiency was reached almost twenty years ago. Work on DSSCs is relatively a new research presently in progress, and shows a steady increase in efficiency. Despite the reasonable success of 3G cells, significant improvements in device performances are required if this technology is to be competitive with the previous PV generations in terms of cost per watt.



Figure 2.1: Reported best research cell efficiencies ²³.

2.2 Dye Sensitised Solar Cells

Photosynthesis is a process by which solar energy is converted into chemical energy which is then used to drive the metabolic processes of autotrophic organisms. Nature has designed a suitable system to carry out this process. This system consists of light absorbing donor (D) molecules which form an antenna non-covalently linked to an acceptor (A), and they are called donor-acceptor (D–A) systems. The donor molecules, (chlorophyll in green plants) capture light and transduce it to nearby molecules until it reaches the photosynthetic reaction centre (PRC). Photo–induced electron transfer leads to charge separation (CS) which should be long enough to convert solar energy into chemical energy. Photosynthetic systems are complex in nature and attempts have been made to design artificial photosynthetic models which can mimic the primary processes of natural

photosynthesis e.g. DSSCs. DSSCs are photoelectrochemical cells based on principles similar to natural photosynthesis. In a DSSC, the organic dye monolayer (sensitizer) replaces light absorbing pigments (chlorophylls), the wide bandgap nanostructured semiconductor layer replaces oxidized dihydro-nicotinamide-adenine-dinucleotide phosphate (NADPH. ²⁴ Photovoltaic action begins when the sensitizer undergoes optical absorption followed by electron transfer (ET) to a wide band gap semiconductor of nanocrystalline morphology then charge separation. These processes eventually result in the conversion of solar energy to electrical energy.

A typical DSSC (**Figure 2.2**) consists of a photoanode and counter electrode (CE) with a redox electrolyte filled in between. The photoanode is usually a sintered porous film of sensitised TiO₂ nanoparticles deposited on a transparent conducting substrate. Chemisorbed to the surface of the nanocrystalline film is a monolayer of a dye (photosensitiser). The cathode of a DSSC is a glass plate with a thin platinum (Pt) film which serves as a catalyst. An iodide/triiodide solution is used as the electrolyte. Both electrodes are pressed together and sealed so that the cell does not leak. The components of the cell with their functions are discussed in the following sections.



Figure 2.2 Schematic of a dye sensitised cells ²⁵

2.3 Transparent Conducting Electrodes

A typical TCE is made of glass with a conducting film coated on one side, and is used in both the photoelectrode and counter electrode of DSSCs. The electrically conductive oxide (TCO) part of the TCE acts as a current collector by extracting separated charge carriers from the active layer while allowing light to pass through absorbing region. ²⁶ Typically, DSSCs are constructed with two TCE as current collectors for the deposition of the semiconductor and catalyst. Requirements for a good DSSC substrate are low sheet resistance and high transparency. Also it should have the ability to prevent impurities such as water and oxygen from entering into the cell. Glass substrates currently used in DSSCs fit well with all these requirements. However, the rigidity, weight, and frangibility limit the potential integration of DSSC devices in portable electronics and their conformability to flexible devices. Recently, flexible DSSCs have been developed by replacing the rigid conductive glass substrates for the working and counter electrodes.

Conductive plastics, like ITO-PET (indium–doped tin oxide coated Polyethylene terephthalated) ITO-PEN (indium–doped tin oxide coated polyethylenenaphtalate), metal foils have come up as suitable alternatives.

DSSCs based on the flexible substrates can be fabricated as devices with low cost production by applying roll-to-roll production technology. They also offer advantages of low cost, lightweight, and less shape limitations for the flexible devices. The handling, installation, and shipping cost in particular would be greatly reduced, and the application of DSSCs could be expanded because of the lightweight and resilient properties of plastic substrates. ²⁷ Flexible DSSCs have attracted considerable interests due to the potential of practical applications and the acceleration of the commercialization of DSSCs ²⁸ and have been introduced by many researchers. The use of flexible electrodes can also lead to design of cells with different shapes to suite their application.

2.3.1 Plastic Electrodes

Poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN) and poly(ether sulfone) PES) flexible substrates have been used as alternatives to glass in DSSCs to reduce the production of DSSCs and also to make the DSSCs easy to be incorporated in a variety of structures. These substrates have the following characteristics: low thermal shrinkage, great hydrolysis resistance good thermal conductivity, low moisture absorption, excellent solvent resistance. ²⁹ The sheet resistance of ITO/polymer substrates reaches 10–15 Ω / sq, close to the typical value of the FTO-coated glass (7–15 Ω / sq) maintaining high transparency in the visible spectrum. ²⁹

However, plastic films have these challenges: they are very sensitive to water and oxygen permeation and this limits the outdoor use of plastic based DSSCs. The permeation of oxygen and water molecules from the outside and their interaction with dye and charge mediators affects the stability of the DSSC. Secondly, plastic substrates have low efficiencies due to their thermal instability at higher sintering temperature (450–550 °C) of the TiO₂ layer leading to poor adhesion of the

nanoparticles with the substrates. Hence the usage of these polymer substrates limits the calcination of the working electrode to temperatures below 200 °C

To reduce the permeation rate and satisfy the stringent barrier requirement which is a water vapor transmission rate (WVTR) less than 10⁻⁶ g/m²·day ³⁰, organic and or inorganic multilayers e.g TiO₂ can be deposited on the polymers by processes such as self-assembled monolayer and atomic layer deposition.³¹ This will increase the durability of the DSSCs while reducing the external toxicity of the solar cells. To address the thermal stability challenge, alternative low temperature methods of deposition of TiO₂ onto plastic substrates have been used by different research groups. These include low-temperature hydrothermal growth ^{32, 33}, microwave heating ³⁴, laser annealing ³⁵, electron beam annealing ^{36, 37}, mechanical compression ³⁸, cold isostatic pressing (CIP) ³⁹, a lift off and transfer technique ⁴⁰, chemical sintering ⁴¹, direct current reactive magnetron sputtering , electrophoretic deposition ⁴², UV light-assisted chemical vapor deposition ⁴³, etc. All these fabrication methods result in DSSCs with lower efficiencies than the glass based DSSCs.

The restriction of high temperature heat treatments in plastic is the major factor responsible for the relatively low conversion efficiency of plastic based flexible DSSCs. Thus, some modifications are required in the preparation of TiO₂ pastes and alternative techniques have to be employed to improve necking in TiO₂ particles and adherence of the TiO₂ film with the substrate. Alternatively more thermally resistant polymers such as clays and polyimides can be used. ²⁹.

2.3.2 Metal Electrodes

In contrast to the flexible plastic substrates, metal based photoelectrodes offer an advantage for high temperature sintering processes which is a key requirement for high quality TiO2 nanoparticle film. Metal substrates are flexible and therefore allow roll to roll manufacturing of DSSCs with lower production costs. When selecting a metal substrate, the work function of the metal should be considered as it determines the contact types, i.e. Ohmic contact or Schottky contact. An Ohmic
contact is a metal to semiconductor contact of very low resistance that is independent of applied voltage (that is, current through that contact follows Ohm's Law). A Schottky contact is a potential energy barrier for electrons formed at a metal-semiconductor junction. Metals with work function equal to or slightly more than that of the semiconductor are desirable as an Ohmic contact. Metals that can form a semiconducting layer during the sintering process make good substrates. Examples include zinc (Zn), tungsten (W), and titanium (Ti). Considering the work function, promising metal substrates for DSSCs are Ti, stainless steel (StSt), W and Zn. W oxide layer is WO₃. However, W is expensive since it is a rare metal. Ti is most desirable metal substrate of the DSSCs because the thermally oxidized layer might have very similar work function with the TiO₂ semiconductor. ⁴⁴ Ito et al. fabricated a flexible DSSCs with a Ti-metal substrate and obtained .an efficiency of 7.2% ⁴⁵ The disadvantage of Ti-metal substrate is that it has finger-grained boundaries at the surface, which convert to the finger-grained TiO₂ blocking layer which promotes electron recombination.²³ The oxidation of StSt leads to the formation of a Fe₂O₃ interlayer, which has a large energy level mismatch with the TiO₂ working electrode. ⁴⁶ Also StSt is susceptible to corrosion in an iodine based liquid electrolyte. ²³ As such the photoconversion efficiency of StSt based DSSCs are lower than those made from Ti substrates. The other challenge with using StSt substrates is the electrical resistance at the TiO₂/StSt interface. ⁴⁷ The resistance reduces charge mobility and the overall efficiency of the cell. To improve the resistance, Yun et al. roughened electrochemically the StSt foil substrate by using sulfuric acid with some additives in order. ⁴⁷ This treatment resulted in enhanced electrical contact area between TiO₂ particles and StSt substrates of the DSSCs. Meng and co-workers used a compact titanium layer between a StSt substrate and a TiO₂ film working electrode to reduce charge transfer resistance between the Ti/TiO₂ interface.

2.4 Transparent Conducting Films (TCFs)

The conducting materials of TCEs can be classified as continuous thin films such as transparent conducting oxides (TCOs), metal thin films, large-area graphene and conducting polymers. ⁴⁸ The other type is based on networks of one dimensional

(1D) nanomaterials including CNTs, graphene nanoribbons, metal nanowires and nanowires of oxides and other compounds. ⁴⁸ Currently, most TCEs in DSSCs use transparent conducting oxides (TCOs), owing to their high electrical conductivity and optical transparency. One of the most widely used TCOs are indium tin oxide (ITO) and fluorine doped indium tin oxide (FTO) owing to their high transparency, low sheet resistance and ideal resistivity at room temperature. ⁴⁹ However ITO has the major drawback of being expensive. Indium, the ITO film's primary metal, is rare and its price fluctuates due to market demand making indium expensive. Even though indium can be recycled, the real consumption is high resulting in a high depletion rate of. It is also not ideal for highly flexible electronics, due to its brittleness. Under mechanical bending or stretching, crack generation in the ITO film leads to much deteriorated electrical properties. ⁵⁰ ITO requires expensive deposition processes at high temperatures, hindering the deposition on some substrates. ⁵¹ It also shows low transparency in the near infrared region (NIR) region. In addition to the above disadvantages, fluorine-doped tin oxide (FTO) based devices suffer from current leakage due to FTO structural defects. ⁵² To address these shortcomings and lower the costs of DSSCs much effort has been devoted to the investigation of novel ITOfree electrodes. These alternatives should exhibit comparable sheet resistance to ITO at high transmittance and be cheap. Other interesting characteristics could be high flexibility, and lightweight so that they are compatible with flexible substrates of DSSCs.

Carbon nanotube networks, graphene, conducting polymers, metal mesh and silver nanowires are emerging alternatives conducting materials for ITO. **Figure 2.3** shows a comparison of the various nanomaterials that can replace ITO. Metal mesh and silver nanowires can be ideal alternatives since they show a high conductivity and are cheaper than ITO. Graphene on the other hand has a comparable conductivity to these but expensive. What is interesting with these materials is their compatibility with flexible substrates. Nevertheless, most of the performance of the ITO alternatives in terms of sheet resistance and transparency are still inferior to ITO.



Figure 2.3: Comparison of the various nanomaterials competing in the ITO replacement space. Source: Touch Display Research

2.4.1 Carbon Nanotubes

Carbon nanotubes (CNTs) are tubular structures consisting of a hexagonal arrangement of sp2 hybridized carbon atoms formed by rolling single, double or multiple graphene sheets. Depending on the number of layers they are made up of, they are named single-walled (SWCNT), double-walled (DWCNT) or multi-walled carbon nanotubes (MWCNT).

CNTs have already attracted much interest for incorporation into DSSCs because of their excellent thermal, electrical, and optical properties, high catalytic activity, low cost, and abundance. ⁵³ The fabrication process of ultrathin, transparent, optically homogeneous, electrically conducting films on various substrates is simple and cheaper compared to depositing ITO. Feng et al. demonstrated an easy and cost effective roll-to-roll process to fabricate CNT-based TCFs (CNT-TCF) from flexible and stretchable multi-walled. ⁵⁴ Touch panels assembled by using these CNT conducting films showed superior flexibility and wearability and comparable in linearity to touch panels based on indium tin oxide (ITO) films. Another interesting advantage of CNTs films is that the films exhibit optical transmittance comparable

to that of commercial indium tin oxide in the visible spectrum and also in the infrared spectral region. ⁵⁵ Hu et al. successfully demonstrated the transparency of SWNTs in the near infra-red region. ⁵⁶ This makes CNTs effective for use in the infrared range, which allows applications for infrared solar cells. A small amount of CNTs is needed for TCF as a film with thickness in the range of 1–100 nm exhibit high electrical conductivity and high optical transparency. ⁵⁷ This is due to an inherent network architecture arising from the 1D nature with a high aspect ratio. ⁵⁸

Research on incorporation of CNTs into DSSCs started in the early 20th century and in 2003 they were successfully used in DSSC cathode to catalyse the reduction of the triiodide species in the electrolyte. ⁵⁸ In DSSCs, CNTs can be used in both the photoanode and counter electrode. CNTs can be incorporated into devices of different shapes because they are flexible. Studies have shown that a SWCNT film outperforms indium tin oxide (ITO) in flexure resistance. ⁵⁹ Electron mobility is high in CNTs and is enhanced by their tubular one dimensional (1D) structure and this also helps to slow down charge recombination. The thickness of CNTs can be optimised to make it transparent to allow the passage of light through. Furthermore, CNTs are good conductors of electricity, mechanically strong and chemically stable, making them an ideal material for transparent conducting materials. It is also worth noting that the bandgap of SWCNTs can vary from zero to 2.0 eV depending on their structure. Thus, one can obtain the desired bandgap energy with a work function of the semiconductor to enhances charge extraction and mobility.

A DSSC containing transparent CNTs film as the working electrode in a DSSC was fabricated by Kyaw et al. ⁶⁰ These cells showed low efficiencies due to the catalytic property of the CNTs which allows the collected electrons at the working electrode to recombine with I³⁻ at the electrolyte/working electrode interface limiting photoelectron transfer to the external circuit. ⁶⁰. To circumvent the problem of direct contact with between the CNTs and the electrolyte, a compact metal oxide can be electrodeposited onto the CNT film prior to the deposition of the porous metal oxide layer as seen in **Figure 2.4**. This inhibits the charge-transfer kinetics at CNT/redox solution interface and enhances the conductivity of the CNT film. Kyaw et. al. used a thin titanium oxide film which serves as a retardation medium to electron transfer kinetics in the cell without sacrificing the electrical and optical properties of CNT. ⁶⁰

The efficiency of DSSCs with TiO₂ thin film was 1.8 % showing improvement to those withoutPET-CNT substrates with a sheet resistance of 470 Ω /sq were used TCF in photoanodes of DSSCs by Du et al. and these devices achieved overall conversion efficiency of η = 2.5% (compared to η = 3.7% for PET-ITO substrates. ⁵³



Figure 2.4: Recombination of electrons with I³⁻ at the CNT/electrolyte interface in the case of bare CNT electrode, (b) inhibiting the charge-transfer kinetics at the interface by using a thin TiO2 layer. Adapted from ⁶⁰

Du et. al. reported on the use of a compact ZnO bottom layer electrodeposited onto the CNT film prior to the deposition of the porous ZnO layer to prevent direct contact between the CNTs and the electrolyte and the achieved overall conversion efficiency of 2.5%.⁵³

2.4.2 Graphene

Graphene is a 2 dimensional sheet of carbon arranged in a honeycomb lattice, with sp^2 – hybridization. It was discovered in 2004 at the University of Manchester by physicists Andre Geim and Konstantin Novoselov when they isolated a single-layer of graphene using a scotch tape method also known as the micromechanical cleavage technique. Long-range π –conjugation in graphene yields extraordinary ⁶¹ thermal, mechanical, and electrical properties make graphene to appeal to researchers from a myriad of different backgrounds

Graphene have been explored for different applications in the photoelectrode and cathode of DSSCs. In photoelectrodes graphene scaffolds can act as an electron

collector and transporter ⁶², as an interfacial layer to enhance charge-transfer performance and enhance photoinduced charge transport, ⁶³ to reduce the back-transport reactions ⁶⁴, improve the conductivity of the TiO₂ nanoparticle film ⁶⁵ and recently as transparent conductive films as an alternative to ITO (**Figure 2.5**) ⁵²



Figure 2.5: Developed CNT transparent conductive film production process

Graphene TCF make good alternatives to ITO in DSSCs because of their high transparency, conductivity and high electron mobility ⁶⁶. Graphene also shows a high optical absorption property; approximately 2.3% of light is captured per sheet ⁶⁶ meaning that the transmittance of single layer graphene can reach more than 97% in the visible region. These films also show good optical transparency in the near-infrared region, increasing the spectra where DSSCs can do photoconversion. In addition, graphene has a low sheet resistance and hence shows good conductivity. Moreover, the resilience of graphene-based TCF upon flexing as a function of resistance graphene films is making them ideal in particular, for flexible DSSCs. ⁶⁷ The compatibility of graphene based TCF with high temperature processes is also an added advantage of using graphene TCFs in DSSCs. Graphene TCF can sustain processes up to 1100°C without significant degradation in terms of sheet resistance and transmittance (contrary to ITO, which deteriorates above 900°C). Graphene has a tunable work function (WF), a desired work function for efficient carrier injection of ~4.42 eV, which is close to that of an FTO (4.4 eV) can be obtained to improve the efficiency of DSSC efficiency.

Wang et. al. pioneered the use of graphene as TCF in solid-state dye-sensitized solar cells (**Figure 2.6**). ⁵² These reduced graphene oxide (RGO) films were fabricated from exfoliated graphite oxide, followed by thermal reduction. The obtained films exhibited a superior transparency over ITO/FTO of more than 70% in both the visible and near-infrared regions. The overall power conversion efficiency of the DSSCs was 0.26% which was lower than that of the device with a standard FTO electrode (0.84%). The low efficiency of the graphene film-based cell was attributed to the series resistance of the device. Selopal et. al. investigated the use of graphene TCF film in DSSCs, (**Figure 2.6 c**). ⁶⁸ The film was composed of polycrystalline few-layers graphene, covering homogeneously an area of 1 cm². The cells had a photoconversion efficiency as high as 2% under one sun irradiation (AM 1.5 G, 100 mWcm⁻²). These results are attributed to the use of a large continuous homogeneous graphene film, which ensured fast continuous conduction of photo generated electrons while slowing down charge recombination as shown in **Figure 2.6 b**.



Figure 2.6: Schematics of different graphene films based on (a) overlapping micro-platelets and (b) continuous film. (c) Scheme of a dye sensitized solar cell based on graphene-coated front contact. ⁶⁸

2.4.3 Nanowires

Metal nanowires are fast becoming a competitive alternative to ITO due to the high conductivity, sheet resistance of 20 Ω /square at transmittance of 95%, which is even better than ITO. They allow a solution-based roll-to-roll technology, which significantly reduces the overall cost for mass production of TCFs and overall cost of TCFs. However chemical instability towards the trodide species of the iodide/triodide couple makes them not suitable for use in DSSCs. This redox couple

corrodes the NWs, disrupting electron conduction leading to DSSC failure. To prevent corrosion, the wires can be covered with a very thin layer of metal which is stable towards iodine electrolytes. This additional layer should not reduce the transparency of the TCF and also its work function should match that of the NWs. Zhu *et.al* coated copper nanowires (CuNW) TCEs with aluminum-doped zinc oxide (AZO) thin-film coatings, or platinum thin film coatings, or nickel thin-film coatings to prevent the corrosion of the NWs by iodine based electrolytes. ⁶⁹ Alternative electrolytes like iodine free electrolytes and room temperature ionic liquids should be used in NW transparent conducting film based DSSCs.

2.4.4 Hybrid Structures

CNTs, graphene and NWs show potential as materials for TCEs in DSSCs but then their individual performance is still inferior to ITO. New efforts in graphene research attempts to improve its properties by developing structures transforming 2D graphene into 3D nano-architectures. In these 3D structures graphene acts as a platform for support, scaffold, or a 2D planar substrate for anchoring 1D nanomaterials ⁷⁰ Hybridization of graphene with 1D nanostructures e.g. CNTs, metal nanowires, provides a promising means of integrating the attributes of both materials. Transformation of 2D graphene into functionalized graphene structures of different dimensions can also effectively prevent restacking of graphene nanosheets due to the strong π - π stacking and van der Waals interactions between the graphene sheets. Yen at. al. proved that the adsorption of MWCNTs on graphene reduced the $\pi-\pi$ interaction between graphene sheets preventing aggregation.⁷¹ The selection of component materials and optimum ratio of the component materials and synthesis techniques are critical parameters, which determine the electrical and optical properties of the hybrid films. ⁷² Several hybrids have been reported; graphene/CNT (G/CNT) ⁷³, graphene/ nanowire ⁷⁴, graphene/metal grid ⁷⁵ etc. The hybrid electrodes are suitable for fabrication of flexible DSSCs since their building components are flexible and can play diverse roles in photoanodes ⁷⁶ and counter electrodes in DSSCs. ^{76,77}

2.4.4.1 Carbon nanotube/Graphene Hybrid Structures

CNTs can be functionalized onto the surface of graphene to form a hybrid electrode with good synergistic properties allowing for an increased active surface area and faster electron transfer kinetics. The hybrid material also offers a greater degree of dye adsorption and lower levels of charge recombination. The hybrid structures can be grown by the following techniques: self-assembly ^{78, 79}, template–assisted synthesis ⁸⁰, sonication ⁷¹ etc. Dong et. al. used a CNT/graphene hybrid on metal foil ⁷⁵. The graphene base was grown via chemical vapor deposition and a catalyst was arranged in a pattern on top. When heated again, carbon atoms in an aerosol feedstock attach themselves to the graphene at the catalyst, which lifts off and allows the new nanotubes to grow. Flexible DSSCs with the new cathode showed a PCE of 3.9%, outperforming that of 3.4% for the DSSC with a Pt cathode. The good performance was attributed to the elimination of transfer of films as the graphene and nanotubes are grown directly onto the nickel substrate that served as an electrode. The hybrid also had less contact resistance with the electrolyte, allowing electrons to flow more freely.

2.4.4.2 Graphene/metal nanowire hybrids

To achieve high conductivity and high transparency graphene based TCs, highlyconductive metal nanowires can be anchored onto graphene sheets. However, the reliability and long-term stability of these TCs decreases because of corrosive nature of the iodine based electrolytes towards the nanowires. Metals such as Pt and Ni have shown stability towards the iodide/triiodide redox couple. Dong *et. al.* used Pt and Ni to make flexible graphene/metal grid hybrid TCEs for dye sensitized solar cells (**Figure 2.7**) ⁸¹ Since Pt is highly catalytic in the iodide/triiodide redox couple reaction, the grids were covered by a thin layer of compact TiO₂ as a protective layer to avoid contact between Pt and the electrolyte. The efficiency of the DSSC with graphene/Pt grids was 0.4%. The graphene/Ni grids hybrid electrodes do not need the TiO₂ coating to form a workable solar cell, although the sheet resistance of the Ni grids



Figure 2.7 Schematic illustrations of transparent electrode and a DSSC⁸¹

A number of challenges remain in the development of hybrid materials. These challenges include: precisely controllable amount of the individual materials for making the hybrid in order to achieve the requirements for the applications in different fields, retaining individual structural properties and conductivity and suitable method for large scale and low cost production. These are the possible reasons why their use as replacements for ITO in DSSCs is still rare.

2.5 Semiconductor

A semiconductor is a crystalline or amorphous solid substance that has conductivity between that of an insulator and that of most metals, either due to the addition of an impurity or because of temperature effects. It contains a lower band, the valence band (VB), which is partially filled with electrons and an upper band, conduction band (CB), which is essentially empty. The band gap, the energy (E_g) separates the valence and the conduction band, where no available states exist for the electrons. E_g can be defined as the energy difference between the maximum valence band energy (E_v) and the mimimum conduction band energy (E_c). In semiconductors there is a small enough gap between the valence and conduction bands such that thermal or other excitations have possibility of exciting electrons to reach and populate the conduction band. When an electron is injected from the valence band into the conduction band, the atom from which the electron emerges is left with a negative charge deficiency, i.e. a positive net charge, also called a hole.

In DSSCs the semiconductor serves as a scaffold for dye anchoring, electron transport, and electrolyte diffusion. It receives injected photogenerated electrons from photo excited dye molecules and provides the conductive pathway from the to the transparent conducting substrate. TiO₂ is the semiconductor widely used in DSSCs because

- i) It provides mesoporous structure with a high surface area for higher dye loading.
- ii) Suitable band gap adjusts for electron injection from most successful commercial dyes
- iii) High electronic mobility for photogenerated electrons and helps slow down recombination reactions in DSSCs.
- iv) More stable compare to other metal oxides, nontoxic and highly abundant.

TiO₂ largely exists in three polymorphs in nature: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). The structures of the polymorphs can be described in terms of chains of TiO₆ octahedra, where each Ti⁴⁺ ion is surrounded by an octahedron of six O²⁻ ions (**Figure 2.8**). The polymorphs differ on their crystal structure by the distortion of each TiO₂ octahedral and by the assemblage patterns of the octahedral chains. Rutile and brookite exhibit corner as well as edge-sharing TiO₆ units. ⁸² Anatase is m octahedrals connected by their vertices while in rutile, the octahedron shows a slight distorted orthorhombic and the edges are connected. In brookite, stronger distortions in TiO₂ brookite, all bond lengths and both vertices and edges are connected .



Figure 2.8 Crystal structures of anatase, rutile and brookite ⁸³

Anatase is the preferred polymorph used in DSSCs since it is the most active phase of TiO₂ because of its surface chemistry and potentially higher conduction-band edge energy. ⁸⁴ Furthermore, anatase has the lightest average effective mass of photogenerated electrons and holes as compared to rutile and brookite. The light effective mass results in enhanced charge mobility from the interior to surface of anatase TiO₂ particle, thus resulting in the lowest recombination rate of photogenerated charge carriers. TiO₂. ⁸⁵ The electron lifetime in anatase is higher than in rutile, suggesting a stable and efficienct charge separation and slow recombination of electrons and holes.⁸⁶ Rutile on the other hand is potentially cheaper to produce which can effectively reduce the production costs of DSSC and has superior light scattering characteristics, which is a beneficial property from the perspective of effective light-harvesting.⁸⁷ N. Park et.al. showed that dye-sensitized solar cells based on rutile exhibit photovoltaic characteristics comparable to those of conventional anatase based solar cells.⁸⁷ A combination of the rutile and anatase may result in a hybrid semiconductor with both the characteristics of both polymorphs.

2.6 Synthesis of TiO₂

TiO₂ liquid phase preparation procedures include coprecipitation ⁸⁸, solvothermal ⁸⁹, hydrothermal methods ⁹⁰, microemulsion ⁹¹, electrochemical synthesis and sol-gel method. ⁹² Sol-gel process involves the chemical transformation of a liquid (the sol)

into a gel state and with the subsequent post-treatment and transition into a solid crystalline oxide material. Sol-gel method is one of the most popular methods used to synthesise TiO₂, because it results in the formation of very pure and homogeneous nanoparticles at low temperatures. It also allows the introduction of other solid phases into the TiO₂ matrix to form composites, as well as dopant species to form TiO₂-doped materials. ⁹³ Depending on the type of TiO₂ precursor used, TiO₂ can be produced by means of alkoxide and non-alkoxide sol gel routes. ⁹³ In the non-alkoxide route, inorganic salts such as nitrates, chlorides, acetates, carbonates, are used and an additional step of removal of the inorganic anion is required. ⁹⁴ In the alkoxide route, metal alkoxides like titanium ethoxide, titanium isopropoxide and titanium n-butoxide are used as precursors. This method involves the formation of a TiO₂ sol or gel, or precipitation by hydrolysis and condensation of titanium alkoxides. In order to have better control over the evolution of the microstructure the hydrolysis and condensation steps should be separated. One way to achieve this is by means of acid- catalysis to peptize the sol, therefore increasing hydrolysis rates, leading to the formation of crystalline powders from fully hydrolyzed precursors. ⁹⁵ The concentration of the acid and the temperature of the sol during hydrolysis determine the type of polymorph formed. Mild acidic conditions and low temperatures result in anatase, while concentrated acids and high temperatures lead to protonation of Ti–O–Ti bridges forming rutile. ⁹⁶ Condensation is followed by post treatment by thermal treatment (calcination) to remove the organic part and to promote crystallization either in anatase or rutile phase. TiO₂ can also be synthesized in special nanostructured morphologies like nanorods, nanowires, nanotubes, and nanoribbons.

2.6.1 Doping of TiO₂

The band gap (3.2 eV) of titania limits its use in the visible region and also photoexcited electron-hole pairs tend to recombine relatively easily in TiO₂. Much of the solar radiation reaching the Earth is in the visible region of the electromagnetic spectrum. The band gap is controlled so increase the light absorption of TiO₂ in the visible region and therefore increase the efficiency of the solar cells. Therefore, it is crucial to modulate the band gap of TiO₂ to extend its optical absorption edge to the

visible-light range. Deliberate introduction of impurities into the lattice (doping) of TiO₂ enhances its optical properties by reducing the band gap. Charge mobility is also enhanced while electron recombination is slowed down. Doping of TiO₂ is well explained **section 3.1**.

2.6.2 Electron Transport in TiO₂

Photogenerated electrons are injected into the conduction band of TiO₂ and these travel by diffusion through the film and are collected in the transparent conducting electrode (TCE). Diffusion of charge carriers is made possible by a concentration gradient in the chemical potential of the electrons. The transport kinetics of an electron in nanocrystalline TiO₂ is determined by the electron diffusion length (L) which is defined as the average displacement of an electron before recombination is called electron diffusion length and the electron lifetime before recombination (τ) ⁹⁷ as shown in the following equation:

$$L_d = (D\tau)^{\frac{1}{2}} \tag{1}$$

Where D is the electron diffusion coefficient.

L is determined by the average distance the relevant charge moves in the semiconductor and recombination/extraction from the semiconductor. ⁹⁷ Therefore it can be used to describe the competition between the diffusive transport and recombination of charge carriers in a photoelectrode and gives an insight into the performance of the DSSCs. Shorter diffusion length values results in shorter τ values suggesting an unstable charge separated state and easy charge recombination between conduction band electrons in the TiO₂ and the I³⁻ in the electrolyte. L is directly proportional to the thickness of the TiO₂ film. A long electron diffusion length (L) relative to film thickness is required for long lived charge separated state and efficient collection of the charge in photoelectrodes.⁹⁸ The TiO₂ polymorph used affects L and the electron lifetime. Rutile generally shows both shorter L and electrons and holes in rutile display exponential decays with the

lifetime of a few tens of nanoseconds, while non-exponential decays are observed in anatase, indicating the presence of multiple carrier trapping processes. ⁸⁵ The reason for the difference in the lifetimes is that anatase has an indirect band gap and therefore the direct transitions of photogenerated electrons from the conduction band (CB) to valence band (VB) of anatase TiO₂ is impossible i.e charge recombination is prevented. The different carrier lifetimes of the polymorphs suggest that anatase is more photocatalytically active than rutile and hence is frequently used in DSSCs. In anatase-rutile mixed phase TiO₂ there is band bending at the interface between anatase and rutile, since the conduction band of anatase lies at 0.2 eV above than the conduction band of rutile TiO₂. ¹⁰⁰ In such a mixed phase the electron lifetime is higher than in homogeneous phases as the charge carriers are separated due to the transfer of electrons from anatase to rutile and this delays charge recombination. ¹⁰⁰ Longer electron time in defective TiO₂ are experienced. Ideal doping of TiO₂ introduces structural defects that act as shallow trap centres ⁹⁹ that delay the electron-hole recombination, and this results in longer L values and enhanced electron lifetime.

Charge separation efficiency and the carrier lifetime are determining factors for photoelectric conversion efficiency. It is important to choose the ideal TiO₂ polymorph and optimize the thickness of the TiO₂ film and the doping concentration to achieve high photoconversion efficiency in DSSCs.

2.7 Sensitisers

In DSSCs, dye molecules are chemisorbed onto the semiconductor surface and are used to sensitize the semiconductor. Upon absorption of photon, a dye molecule gets oxidized and the excited electron is injected into the nanostructured TiO₂. There are certain criteria that a dye molecule must fulfill in order to be used as a photosensitizer in DSSCs.

 A dye molecule should absorb light photons in whole of the visible region and near IR region of solar spectra and this enhances J_{SC} of the DSSCs.

- The photosensitizer should contain anchor groups like carboxylates, sulphonates and phosphates so that it can strongly chemisorb onto oxide semiconductors surface to ensure efficient electron injection into the TiO₂ conducting band and to prevent gradual leaching by the electrolyte
- The photosensitizer species should not form aggregates which reduces the efficiency of DSSC, should be stable chemically, thermally and must be photostable.
- iv) The excited state energy level (LUMO) of the dye molecule should be higher than that of the conduction band edge of the semiconductor for efficient charge injection from dye to semiconductor.
- v) Electron transfer from the dye to the TiO₂ must also be rapid in comparison with decay to the ground state of the dye.
- vi) For efficient regeneration of dye the oxidized state of dye must be more positive in potential than that of redox electrolyte. ¹⁰¹

Initial DSSCs employed organometallic compounds such as ruthenium (II)-based dyes and the showed a remarkable success with a conversion efficiency of 7.1 %. ²¹ Different ruthenium based sensitizers such as N3, N719 and N749 (Black dye) are examples of ruthenium dyes and have showed remarkable success. The high efficiencies of the ruthenium(II)-polypyridyl DSSCs is attributed to their wide absorption range from the visible to the near-infrared regions of the electromagnetic spectrum. It is also possible to improve the optical properties of ruthenium polypyridyl systems by narrowing the HOMO and LUMO energy levels red-shifting the absorption onset. ¹⁰² The spectral response can also be enhanced in the red and near-IR region. For example trithiocyanato-ruthenium(II) terpyridyl complex was synthesized by substitution of the terpyridyl ligand by three carboxyl groups in 4,4',4"-positions yielding a black dye. ¹⁰³ This dye displays very efficient panchromatic sensitization over the whole visible range extending into the near-IR region up to 920 nm. The structures of the three common ruthenium dyes are shown in **Figure 2.9**.



Figure 2.9 Structures for benchmark sensitizersN3, N719, and Black Dye for DSSC applications.

Ruthenium-based dyes are not biocompatible and this makes them environmentally unfriendly. Moreover Ru has a very limited supply in nature leading to high production costs of DSSC. Recent developments on porphyrin-based solar cells exhibit a promising advance in finding alternative photosensitisers for DSSCs Porphyrin sensitizers have excellent light-harvesting function mimicking photosynthesis. The other advantages of porphyrin-based dyes are their rigid molecular structures with large absorption coefficients in the visible region. ¹⁰⁴ Fine tuning of the optical, physical, electrochemical and photovoltaic properties of porphyrins thus is feasible as many reaction sites, i.e., four meso and eight b positions, are available for functionalization.

2.7.1 Improving Optical Properties of Sensitisers

Although the absorption spectra of most efficient sensitizers today are between 400– 800 nm, their efficiencies are quite low in the near infrared to infrared region. Progress in the optimization of the dye component of the cell has been made through systematic variation of the ligands, metal, and other substituent groups with the aim of improving the light harvesting efficiency, reduce charge recombination, increase spectral response and improve the overall performance of DSSCs.

2.7.1.1 Extending Spectral Response of Sensitisers

Many sensitizers show strong absorption in the visible region of the spectrum, for example, porphyrins show a Soret band at 400–450 nm and Q bands at 500–650 nm. This limits regions where the DSSCs can perform photoconversion. Extending the absorption spectra of porphyrin dyes to the near infrared region is beneficial to DSSCs as it leads to an increased photocurrent and overall efficiency. To achieve extension, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels must be narrow. Band narrowing enhances electron transfer from the HOMO to the LUMO of the dye preventing dye decay. In donor–acceptor systems, the introduction of electron withdrawing groups reduces E_g by lowering the LUMO levels whereas, the introduction of electron donating groups reduces E_g by raising the HOMO levels.¹⁰⁵ Further reduction in band gap is possible by enhancing the strength of donor ¹⁰⁶ and acceptor moieties via strong orbital interactions.

Broadening the spectral response can also be achieved by extending the π conjugation of the dye molecule by introducing a highly conjugated π -extended chromophore to the dye. A spectral extension in the range 600-900 nm was observed with increasing conjugation of zinc porphyrin with either vinyl groups or pphenylene vinylene groups substituted on the β carbon the substituent was observed by Ventura and co-workers. ¹⁰⁷ Cosensitization has been explored to extend the spectral region. A zinc porphyrin-bodipy dyad sensitized solar cell demonstrated higher solar spectral coverage and an improved power conversion efficiency ($\eta = 1.55\%$) compared to that of the zinc porphyrin-sensitized cell ($\eta =$ 0.84%). ¹⁰⁷ BODIPY dyes functionalised with the more highly conjugated fluoranthopyrrole units resulted in a bathochromic shift of ca. 50 nm in the electronic absorption compared to their naphthapyrrole analogs. ¹⁰⁸ The absorption spectra of coumarin dyes with extended π conjugation were red-shifted in the visible region relative to the spectrum of a conventional coumarin dye resulting in a wide absorption in the visible region. ¹⁰⁹ This was attributed to the introduction of a methine unit connecting both the cyano and carboxyl groups into the coumarin framework which expanded the π conjugation in the dye.

2.7.1.2 Suppressing Charge Recombination

Enhanced charge separation in the dye slows down charge recombination. There are several approaches that can used to inhibit charge recombination and some of them are discussed below.

Dyad system dyes (called push–pull structures))are composed of a donor (D) and an acceptor (A) linked through a π -bridge, whereby upon photo excitation an effective intramolecular charge transfer takes place generating long lived charge separated states as shown in **Figure 2.10**. In D– π –A dye photoexcitation is followed by intramolecular charge transfer (ICT) from the donor to the acceptor moiety of the dye. This creates charge separation with the hole being left behind in the donor and the acceptor getting reduced. The hole localized on the donor unit will be spatially convenient for the electron donor to approach, facilitating the efficient dyeregeneration at a moderate but right rate compared to the ultrafast charge generation at the titania/dye interface. ¹⁰⁶ This restricts the charge recombination between the hole in the semiconductor and the reduced dye. In DSSCs, D – π –A dyes maximize the efficiency of the cell due to the combination of a high molar absorptivity with a low band gap allowing an efficient intramolecular charge transfer (ICT). ¹¹⁰ This in turn leads to long lived charge separated states and low recombination rates.

Figure 2.10 Schematic drawing of donor–p-bridge–acceptor organic sensitizers and their electron transfer processes under illumination ¹¹¹

A Mingfei *et. al.* showed that molecular engineering of organic sensitizers by increasing the length of aliphatic chains of alkoxy groups can enhance the photocurrent, photovoltage, and efficiency of DSSCs with a solvent-free ionic liquid electrolyte.¹⁰⁶ The reason for this improvement is that the long hydrocarbon chains the dye interacts laterally to form an aliphatic network, thereby increasing the distance between triiodide and electrons trapped on the TiO₂ surface and thus hindering the adverse charge recombination between photoinjected electrons and the triiodide present in the electrolytes. Schmidt-Mende *et al.* also used TiO₂ films containing hydrophobic sensitizers that contain long aliphatic chains and the recombination reaction was greatly suppressed.¹¹² The explanation was that the aliphatic network, acted like a shield, thereby preventing triiodide from reaching the TiO₂ surface.

Multiple step electron transfer dyes exhibit more than one electron transfer step. The first electron-transfer step is followed by secondary, more thermodynamically favorable electron-transfer reactions. ¹¹³ The advantage of using a two-step process, as opposed to a single (long) electron-transfer event, is the achievement of long-range charge separation. ¹¹³ This can be achieved by the use of multifunctional sensitizer dyes that exhibit multi-step electron transfer cascades. Ru(dcbpy)₃²⁺ based dyes in which the bipyridyl ligand was modified by the covalent attachment of triaryl amine based electron donating groups achieved a remarkably long (4 seconds) charge separated state lifetime. Molecular triads composed of a zinc porphyrin covalently-linked gold(III) porphyrin and bridged by a ruthenium(I1) bis–(terpyridyl) complex exhibited a two–step charge transfer process resulting in a stabilized charge separated state. ¹¹³

2.7.1.3 Slowing Decay of Sensitiser

Dye decay results in low efficiency solar cells. Constantly regenerating the dye reduces charge recombination and ensures continual generation of photocurrent. Sun and coworkers successfully synthesized a binuclear ruthenium–manganese complexes where the manganese complex act as an electron donor to a photo-oxidized photosensitizer mimicking the intramolecular photoinduced electron transfer process from oxygen evolving center (OEC) to P₆₈₀+ in the reaction center of PSII of photosynthetic plants. ¹¹⁴ The manganese cluster linked to the ruthenium bipyridyl chromophore continuously regenerates the photo-oxidized photosensitizer by intramolecular electron transfer from manganese cluster is necessary for slowing charge recombination and decay of sensitizer. These self-regenerating dyes can be very useful in DSSC to ensure one way transfer of photogenerated electrons while preventing recombination.

2.8 Electrolyte

The function of the electrolyte in DSSCs is to serve as electrically conducting medium and also regenerate the sensitizer. Most solar cells are based on liquid electrolytes that are made of an organic solvent and a redox couple (RC). The iodide/triodide (I⁻/I₃⁻) redox couple is usually used in DSSCS due its good performance. This is attributed to the favourable penetration into the nanoporous semiconductor film, very fast dye regeneration, and relatively slow recombination losses through reaction with injected photoelectrons. ¹¹⁵ However, there are negative features associated with this redox couple : (1) iodine is extremely corrosive toward metals such as copper or silver, which are used as current collectors in some DSSCs; (2) the I₃⁻ ion absorbs a significant part of visible light, stealing photons from the sensitizing dye ¹¹⁵ and hence slowing photoexcitation of the dye. The main disadvantage of the liquid electrolytes is volatility. These challenge with the I⁻/I₃⁻ liquid based electrolyte has stimulated research with the aim to find and explore new less volatile electrolyte media. These new electrolytes will help to improve the stability and solve the leakage problems associated with the

liquid electrolytes. Gel polymeric electrolytes incorporating triiodide/iodide as a redox couple are already used to substitute liquid based electrolytes in DSSCs. ¹¹⁶ The use of gel polymer electrolytes looks very promising as the efficiencies of such cells are on the rise and have reached values around 9-10% at present. Xiang et. al. used tris(2,2'-bipyridine)cobalt(II)/(III) based polymer gel electrolyte in conjunction with an organic carbazole dye in the construction of stable dyesensitized solar cells with an energy conversion efficiencies of 8.7% and 10% at 1 sun and 0.1 sun light intensity. ¹¹⁷ Research efforts are underway worldwide to find ways and means of increasing the efficiency of polymer based DSSCs. A method to improve the performance of the polymer gel based DSSCs by employing a binary mixture of iodide salts having smaller and larger cations is described by Careem et. al. ¹¹⁸. Another direction of research exploits the use of ionic liquid-based electrolytes (RTILs). RTILs have favorable properties such as thermal stability, nonflammability and high ionic conductivity, and negligible vapour pressure. The main disadvantage of ionic liquids is the high viscosity which slows down ion mobility leading to delay regeneration of the oxidized dye and an overall low efficiency of the DSSC.

2.9 Counter Electrode

The counter electrode (CE) collects electrons from the external circuit and catalyzes the redox reduction in which triiodide is reduced to iodide. The collected electrons in the CE are transmitted back into the cell. Thus the ultimate function of the CE is to return the electrons from the external load back into the "circulation" within the cell. ¹¹⁹ The CE also acts as a mirror, as it reflects the unabsorbed light from the cell back to the cell to enhance utilization of sunlight. ¹¹⁹ It is usually fabricated by sputtering a platinum layer (~200 nm) or pyrolysis of H₂PtCl₆ solution on FTO substrate. Two advantages make platinized FTO glass be well suited for the counter electrode. One is the electrocatalytic activity of the platinum which improves the reduction of I_3 ⁻ by facilitating electron exchange. Platinum is also stable towards the widely used ioidine based electrolytes and also increases light-refection due to the mirror-effect of platinized FTO. ¹¹⁹

Most of the highly efficient DSSCs are based on Pt counter electrode because they give the best performance. However, the high cost and the scarcity of platinum restricts large-scale application in DSSCs. ¹²⁰ This has prompted researchers to develop low-costing platinum-free electrodes for DSSCs. Carbon materials ¹²¹, transition metal compounds ¹²², conductive polymers ¹²³, and composites ¹²⁴ are some of the catalyst materials that have been employed in these cells. Carbon materials are the most commonly used CE materials in DSSCs. An efficiency of 9.1% was achieved by Murakami et. al when using carbon black as the catalyst for triiodide reduction. ¹²⁵ A CE made from a mixture of carbon nanotubes with titanium nitride nanoparticles gave efficiency comparable to that of conventional platinum counter electrodes. ¹²⁶ Graphene is also a promising CE material for DSSCs due to its excellent conductivity and high electrocatalytic activity. ¹²⁷ Some early transition metal nitrides (TMNs) show noble metal-like behavior due to the similarity of the electronic structure of the metal nitrides to that of noble metals. This has prompted researchers to use these TMNs as catalyst materials in CEs. MoN has superior electrocatalytic activity and a higher photovoltaic performance.¹²⁸ Transition metal carbides, like titanium carbide (TiC), iron carbide (Fe₃C) and tungsten carbide (WC), have also been studied as counter electrode materials because of their interesting physic-chemical and catalytic properties, which resemble those of noble metals.¹²⁹ Conducting polymer films also make good Pt alternatives ¹³⁰

2.10 Operation Principle of DSSC

The components of the DSSC work together to convert solar energy to electrical energy. The mechanism of dye solar cells is based on the photo electrochemical processes similar to natural photosynthesis. A schematic presentation of the operating principles of the DSSC is given in **Figure 2.11**. The solid black arrows indicate forward reactions while the dashed ones represent back reactions.

Figure 2.11 Schematic illustration of the working principle and energy level scheme of the DSSC ¹³¹

Under the irradiation of sunlight, the dye molecular becomes photo-excited. The light is absorbed by a sensitizer dye molecule, resulting in a transfer of the photogenerated from th HOMO of the sensitizing dye to the LUMO generating the dye cation (LUMO⁺). This then leads to photoinduced electron transfer PET) which is defined as a process by which excited electron is transferred from donor to acceptor.

$$S + h \rightarrow S^*$$
 (2.2)

$$S^* \to S^+ + e^- \tag{2.3}$$

For electron injection to occur, the LUMO (D⁺) of the excited dye must be higher than the conduction band potential of TiO₂, V_{CB}. ¹³² The injected electron is transported through the TiO₂ predominately by the trapping/detrapping processes. The electrons diffusing through the TiO₂ are collected at the transparent conducting oxide, and driven through the external circuit where useful work is performed. The iodide (I⁻) species in the electrolyte are then converted to triiodide (I₃⁻). The build-up of I₃⁻ at the photoelectrode creates a concentration gradient so that the ions diffuse to the counter electrode where they are reduced back to I⁻ by a catalyst layer usually platinum. ²⁹

$$I^- + 2e^- \to 3I^- \tag{2.4}$$

The original state of the dye is subsequently restored by electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide couple.

$$2I^- \rightarrow I_2 + 2e^- \tag{2.5}$$

This leads to generation of voltage which corresponds to the difference between the Fermi level of the electron in the semiconductor and the redox potential of the electrolyte. Overall the device generates electric power from light without suffering any permanent chemical transformation. The light-driven electrochemical process in DSSC is regenerative. The photocurrent obtained depends on the energy difference between the highest molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) of the sensitiser. The small energy separation between the HOMO and LUMO ensures absorption of low energy photons in the solar spectrum. Therefore, the photocurrent level is dependent on the HOMO-LUMO levels separation.

The above reactions (from equation 2.2 to 2.5) compete with recombination of photoexcited electronic charges, mainly those in the TiO₂ and the conducting electrode with either holes in the oxidized dye or more significantly with the redox species in the electrolyte. Additionally, the excited state dye can decay back to its ground state, either radiatively or nonradiatively, without injecting an electron. ¹³³ The overall photoconversion efficiency, η , for a solar cell is given by the photocurrent density measured at short-circuit (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF), and the intensity of the incident light (P_{in}). Refer to **section .2.12** for the definition of the terms: J_{sc} , V_{oc} , FF and P_{in}.

2.11 Kinetic Competition in DSSCs

Following photo absorption, dye molecules undergo rapid transition to an excited state electronic configuration. This leads to charge separation (CS) then ultrafast charge injection (fs). Ideally the photo generated electron diffuse to the back

electrode contact (ns-ms) from where it is transported via an external circuit to the counter electrode. Charge separation and electron transfer reactions enter in competition with a series of unwanted reactions which are termed back or reverse reactions that might occur within the system. The fate of the electron determines the quantum yield for photocurrent generation and thus the efficiency of the device. Electrons in excited states after photo-excitation, if not rapidly injected, easily lose the absorbed photon energy as heat through electron-phonon scattering and subsequent phonon dissipation, thus generating (thermal) loss in efficiency. ¹³⁴ All these lead to charge annihilation and are detrimental to the operation of DSSC. Therefore, for the DSSCs to effectively do photoconversion, it is critical that the forward processes i.e. electron transfer, injection of electrons and dye regeneration, are faster than any recombination (loss) of charge carriers. Figure 2.12 illustrates the kinetic competition redox processes involved in the conversion of light to electric power by DSSCs. Charge recombination to the dye cation, (Figure 2.12 a), is in kinetic competition with the desired regeneration reaction and therefore limits the charge separation yield. Efficient charge collection requires charge recombination between injected electrons and oxidised redox species in the electrolyte to be slower than transport of these species to the working and counter electrodes, respectively. It can be seen that electron transfer in the semiconductor is a very slow process (ms) with a rate almost the same as recombination. If electron transfer is too slow, recombination easily occurs. To improve the efficiency of solar cells, the electron diffusion coefficient of TiO₂ should to allow fast electron transfer. To achieve a high yield of long lived and energetic charge separated states requires careful optimisation of system design. Optimum DSSC device performance is obtained when the charge separation, electron injection and dye regeneration kinetics are fast enough to compete successfully with charge recombination and dye excitedstate decay rates.

Figure 2.12 Dynamics of redox processes involved in the conversion of light to electric power by DSSCs. b) Schematic of timescale involved in different processes in DSSC ¹³⁵

2.11.1 Charge Recombination

The performance of DSSCs is based on kinetics competition between the electron injection from the sensitizer to an electron collecting material, regeneration of the oxidized dye with redox electrolyte and unwanted back reactions of injected electrons recombining with oxidized dye molecules or oxidized species of redox electrolyte. ¹³⁶ The charge recombination of the generated electrons with the holes in the dye-sensitized nanostructured TiO₂ electrode can occur either after the electron injection or during its migration in the TiO₂ electrode on its way to the electrical back contact. Electron mobility in the semiconductor is a very slow process. During this migration, the photogenerated electrolyte species, and contaminants in the system. Studies have shown that the electron recombination lifetime is largely influenced by the characteristics of nanoporous films, especially trap site distribution and density. ¹³⁷ Deep trap states in TiO₂ become recombination centres for charges. The mesoporous and nanocrstyalline nature of the TiO₂ film

results in large surface areas for such recombination to occur as the surface is not completely covered with adsorbed dye molecules.

Recombination with triiodide is the major detrimental process in a DSSC, occurring at the interfaces between TiO₂ and electrolyte or TCO and electrolyte. This is because of the high concentration of iodide ions in the electrolyte making the electrons susceptible to recombination with these ions. Recombination of electrons with the oxidised dye molecules is minimal since this is an energetically and kinetically unfavourable process. ¹³⁸ Also the electron transfer to the oxidized dye is always competing with the dye regeneration, which is a faster process i.e., the oxidized dye is reduced by the iodide. Recombination of the injected electrons with the holes in the sensitizer or the redox couple at the TiO₂/dye interface reduces significantly the charge-collection efficiency at the counter electrode, and thereby decreasing the total efficiency of the cell. Interfacial electron transfer kinetics are critical to the function of dye sensitised solar cells. ¹³⁹ Several approaches have been implemented in the literature to inhibit charge recombination (k_{rec}). There is increase in research in modifying components of DSSCs, using alternative materials and coming up with sophisticated device architectures to reduce interfacial recombination losses. Many studies are concerned with the engineering of the photoanode interfaces in DSSCs since several important processes occur at TiO₂/dye/electrolyte interface, such as the electrons injection from dyes to the conduction band of TiO₂ and the recombination of injected electron in nanocrystalline films with electrolyte and oxidized dyes. ¹⁴⁰

2.12 Current–voltage Measurements

Current-voltage curve measurements give information on DSSC device performance. In these measurements, the lighted cell is put under a reverse bias voltage scan and the generated photocurrent recorded. The key parameters given by the curve are the short-circuit current density Jsc, the open circuit voltage Voc, the maximum power point (current iMP and voltage VMP) and the fill-factor (giving the overall efficiency of a cell.

2.12.1 Short Circuit

The short circuit current I_{SC} is the highest current that can be drawn from a solar cell. The cell voltage is at this point zero. Hence the generated power is also zero. Solar cell current is normally represented as current density, J_{SC}

$$J_{sc} = \frac{I_{sc}}{A}$$
(2.8)

where A is the effective area of the solar cell. It is a function of the solar illumination, optical properties and charge transfer probability of the cell.

2.12.2 Open Voltage

The V_{oc} is the difference in potential between the two terminals in the cell under light illumination when the circuit is open. It is the highest voltage of a solar cell at a given light intensity. It is also the potential where current flow through a solar cell is zero. It is a function of the semiconductor bandgap and charge recombination in the cell.

2.12.3 Fill Factor

The Fill Factor (FF) is a measure of quality of the solar cell as it reflects the maximum output from the device. It is calculated by comparing the maximum power to the theoretical power (PT) that would be output at both the open circuit voltage and short circuit current together (equation). In DSSCS, the practical fill factor is usually lower than the maximum possible one due to the losses during cell operation and back reactions such as dye decay and charge recombination at semiconductor/redox electrolyte interface. The most common losses are due to series resistance and shunt resistance. The series resistance reduces the fill factor and thus the efficiency of solar cell by dissipating power in the resistances. ¹⁴¹

$$FF = \frac{P_{max}}{P_{theo}} = \frac{V_M \cdot I_M}{V_{OC} \cdot I_{SC}}$$
(2.9)

2.12.4 Power

The generated power P of a solar cell can be calculated by the following formula:

$$P = V \cdot I \tag{2.10}$$

The calculated power can be also plotted versus the applied potential. The resulting power curve exhibits a power maximum P_{max} . The multiplication of V_{OC} by J_{SC} results in the maximum power output possible to be achieved for the DSSC.

2.12.5 Efficiency

The efficiency of a solar cell is defined as the ratio of maximum electrical energy output to the energy input from the sun. It is expressed by:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{SC \cdot V_{OC} \cdot FF}}{P_{in}}$$
(2.11)

Efficiency is dependent on Isc, Voc and FF, and therefore to obtain overall high efficiency all these three parameters must be optimised. The internationally recognized standard condition for the efficiency measurement of solar cells is under 'AM1.5 Global' 6 solar irradiation and at a temperature of 25°C. This is derived from the path length the light has to travel through the atmosphere in order to reach the surface. The spectrum is normalized so that the integrated irradiance is 1000 W/m² (100 mW/cm²).

2.12.6 Series Resistance

Series resistance, RS in a solar cell is the result of contact resistance and charge transfer resistance in the semiconductor material. Series resistance reduces the fill factor affecting the maximum power output, while excessively high value of RS can also reduce the short-circuit current. Voc is not affected by RS because the current flow is zero. The short circuit current is also unaffected by RS. An approximation of the series resistance can be determined from the slope of the IV curve at the open-

circuit voltage point. The series resistance RS can be estimated by the inverse of the slope near the open circuit potential.

2.12.7 Shunt Resistance

RSH can be estimated by the inverse slope near the short circuit current I_{SC} . It is mainly caused by leakage current through the cell caused by impurities or defects in the manufacturing process. The lower the RSH the more the slope of the I V curve increases near the short circuit current. This leads also to a smaller open circuit potential V_{OC}. Power maximum, fill factor, and efficiency are negatively affected by small shunt resistances.

2.12.8 Incident Photon to Charge Carrier Efficiency (IPCE)

Incident Photon to Charge Carrier Efficiency (IPCE) is defined as the ratio of the number of incident photons to the number of charge carriers generated and is a function of the excitation wavelength. In DSSCs it measures the ability of the cell to generate current as a function of the wavelength of the incident monochromatic light.

$$IPCE = 1240 \times \frac{I_{SC}}{\lambda \phi}$$
(2.12)

where, I_{SC} is the short circuit current (mA/cm²), λ is the wavelength (nm) and Φ is the incident radiative light flux (W/m²).

For DSSC, the term is defined as:

$$IPCE = LHE \times \phi(inj) \times \eta(coll)$$
(2.14)

where, LHE(λ) is the light-harvesting efficiency for photons at wavelength λ , Φ (inj) is the electron injection quantum yield for the excited sensitizer to the semiconductor oxide conduction band and η (coll) is the fraction of injected charges that is able to reach the back contact.

CHAPTER 3 SYNTHESIS CHARACTERISATION AND THEORETICAL CALCULATION OF Ce-DOPED TIO2 FOR DYE SENSITISED SOLAR APPLICATION

Abstract

A series of Ce-doped TiO₂ with Ce content ranging from 0.1 to 1 mol % were successfully synthesized by an acid catalyzed sol-gel method, and its performance as the photoanode of dye-sensitized solar cells (DSSCs) was investigated. Materials were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), Energy dispersive spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), diffuse reflectance and UV-Vis spectroscopy. Ce doping resulted in a red shift in the absorption of the TiO₂ indicating narrowing of the band gap. The band gap first narrowed with increase in concentration of dopant up until 0.9 % dopant concentration. After this optimum doping concentration the band gap widens again. The electronic structure properties of cerium-doped TiO₂ were investigated using density functional theory (DFT) with plane wave basis sets and pseudo-potentials. DFT calculations showed that Ce doping introduces Ce4f impurity states located just below the conduction band resulting in band gap narrowing. Ce content (0.9%) doped TiO₂ photoanodes improve the performance of DSSCs with a conversion efficiency of 2.11% compared to 0.21% for the one with a pure TiO₂ under 1 sun, AM1.5.

Keywords: Ce-doped TiO₂; DFT; computer modelling; band gap; DSSCs

3.1 Introduction

Dye-sensitized solar cells (DSSCs) are an attractive potential source of renewable energy due to their eco–friendliness, ease of fabrication, and cost effectiveness. ⁵⁸

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A typical DSSC constitutes a photoanode and counter electrode (CE) with a redox electrolyte filled in between. The photoanode is usually a sintered porous film of sensitised semiconductor nanoparticles deposited on a transparent conducting substrate. The CE is generally a platinum coated conducting substrate. Titanium dioxide (TiO₂) is the semiconductor widely used in DSSCs where it serves as a scaffold for dye anchoring, electron transport, and electrolyte diffusion. The mesoporous structure gives a high surface area for higher dye loading.¹⁴² TiO₂ also has a low energy difference between its conduction band and the lowest unoccupied molecular orbital (LUMO) of most successful commercial dyes, providing an enthalpic driving force for electron injection.¹⁴³

The major drawback of TiO₂ is its broad band gap of 3.2 eV limiting its use in the visible region. The photo-excited electron-hole pairs tend to recombine relatively easily in TiO₂ because of the broad band gap resulting in low photoconversion efficiency of the DSSCs. In a semiconductor-based DSSCs the photogenerated electron-hole pairs need to be separated and transferred to the surface of the semiconductors ¹⁴⁴ and then injected into the dye. This charge separation should be long enough to efficiently convert solar energy into electrical energy. To enhance the efficiency of the DSSCs, the band gap of TiO₂ need to be modified to extend its optical absorption edge to the visible-light range and also decrease the rate of electron-hole recombination.

Photoactivity enhancement can be done by intentionally introducing dopant ions into pure intrinsic TiO₂ to modify the band gap or to act as charge separators of the photoinduced electron–hole pair. Different elements enhance TiO₂ nanoparticles with diverse properties. It is important therefore to have an insight into the nature of the defects so that they can be manipulated to suite a particular application. An ideal dopant for DSSC application is one that eliminates deep traps (which act as recombination centres), while introducing new states close to conduction band (CB), enhancing both short circuit current density (Jsc) and open circuit voltage Voc. ⁹⁹ Also the dopant should decrease the recombination rate of holes and electrons and enhance electron mobility. The correct balance between the CB energy, charge transport and recombination rate has to be found to obtain an optimally working

DSSC. Doping of TiO₂ can be anionic or cationic. Anionic doping involves replacing the O²⁻ anion with a non-metal dopant. Nonmetals like N 145 , S 146,147 and C 148 introduces energy states in the band gap resulting in band gap narrowing and a red shift of the absorption band edge. Cationic dopants are typically metals and they substitute Ti⁴⁺. It is crucial to select an appropriate metal dopant and also to establish its optimum doping level as these dopants sometimes result in localised d-levels deep in the band gap of TiO₂ which then serve as recombination centers for photogenerated charge carriers ¹⁴⁹ and impede carrier transport. Different metals enhance the photoactivity of TiO₂ in diverse ways. Zhou et. al observed a reduced energy band-gap of Li-doped TiO₂ resulting in easier transfer of photogenerated electrons from conducting band of nano-TiO₂ to TCO surface, leading to an enlarged short current. ¹⁵⁰ Alkali earth metals consist of electrons which can be easily donated to TiO₂ resulting in a p-type semiconductor. ⁹⁹ Mg²⁺-doped TiO₂ possess negatively shifted conduction band, indicating an upward shift of conduction band and Fermi level (E_f) resulting in an improved open-circuit photovoltage. ¹⁵¹ Ca was incorporated into TiO₂ films by the hydrothermal method, resulting in an enhanced electron mobility and higher charge collection efficiency than that in the undoped TiO₂ films. ¹⁵² Transition metals doping introduces d and f orbital electrons, which increases the absorption characteristics of TiO2 and reduces the recombination rate of electronhole pairs. Zn²⁺ donates excess negative charge carriers which increase the electron carrier density and thereby increase the photocurrent. ¹⁵³ Pt enhances the charge separation of the electrons and holes by serving as an electron sink and facilitating interfacial electron transfer to dioxygen or other electron acceptors. ¹⁵⁴

Among the lanthanides, cerium (Ce) is a potentially good dopant to improve optical properties of TiO₂ and enhance photovoltaic efficiency. As an electron scavenger Ce removes electrons from electron-hole recombination sites,¹⁵⁵ increasing the flow of electrons and enhancing the efficiency of DSSC. Cerium ions (Ce³⁺/Ce⁴⁺) act as multi-electron energy levels, and variable valence states leading to different optical properties.¹⁴³ It is has been reported that Ce induces unoccupied 4f states just under the TiO₂ conduction band ⁹⁹ to efficiently contribute to transport. The Ce 4f level plays an important role in interfacial charge transfer and elimination of electron-hole recombinations. ¹⁵⁶ The Ce⁴⁺/Ce³⁺ redox property is reported to effectively stabilise

the separation of electron-hole pairs in the DSSCs thus reducing the recombination rates.¹⁵⁷ In this work, cerium ions are doped in the TiO₂ nanocrystalline photoanode, with the aim to improve DSSC performance. To fully understand the effect of doping on the electronic structure computational modeling was performed. From this information insight on the impurity levels introduced by Ce doping and on the nature of doping sites was gained.

3.2 Materials and Instrumentation

Titanium Isopropoxide (TIP) Ti[OCH(CH₃)₂]₄, Nitric acid (HNO₃), cerium nitrate hexahydrate, flourine doped tin oxide (FTO)-coated glass substrate (10 per square, thickness 120m) and absolute ethanol (CH₃CH₂OH), were as supplied by Aldrich chemicals Ltd. The ruthenium complex dye ruthenizer 535-bis TBA, iodolyte Z-100, Ti-Nanoxide T/SP and platisol T were purchased from Solaronix (Aubonne, Switzerland). Energy dispersive spectroscopy (EDS) was done on a Jeol JSM-5600 scanning electron microscope coupled to an EDX spectrometer, FTIR was performed on Spectrum 100 FTIR spectrometer, Raman analysis was recorded using a Bruker Vertex 70 Ram II Raman spectrometer exciting laser 800 nm, TG analysis was carried on a TGA 4000 Thermogravimetric analyzer and TEM images were obtained from an FEI G2 SPIRIT transmission electron microscope. The samples were further characterized using X-ray diffraction (XRD) with Cu K irradiation Bruker Discovery D8), X-ray photoelectron spectroscopy (XPS) (VG ESCALAB 220i-XL) employing a monochromatic AI KR1 source (1486.6 eV) and UV-Vis diffuse reflectance spectroscopy (UV- 2450 UV-Vis spectrophotometer) using 150 mm integrating sphere. Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. The instrument was operated in negative ion mode using an m/z range of 400–3000 amu. The voltage of the ion sources were set at 19 and 16.7 kV for ion sources 1 and 2, respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and kV, respectively. The spectra were acquired using alpha-cyano-4-9.7 hydroxycinnamic acid as the MALDI matrix, using a 337 nm nitrogen laser.

3.3 Preparation of Doped and Undoped TiO₂

TiO₂ nanoparticles were prepared by an acid catalyzed sol-gel method. TiO₂ sols were prepared by dropwise addition of an ethanolic titanium isopropoxide (TTIP) solution, into 50 mL of distilled water (4 °C) adjusted to pH 1.5 with nitric acid under vigorous stirring at room temperature. After continuously stirring for 24 h, the resulting transparent solution was evaporated using a rotary evaporator at 50 °C and dried in the oven (70 °C) overnight. The obtained powder was calcined at 450 °C for 2 h under air. Ce-doped TiO₂ samples were prepared according to the above procedure in the presence of the cerium nitrate hexahydrate to give a doping level from 0.1 to 1 % in molar ratio. The appropriate amount of cerium salt was added to the distilled water before hydrolysis of TTIP and the remaining procedures were the same as described above.

3.4 Cell Fabrication

TiO₂ paste was applied onto clean FTO substrates by doctor blading to create a 0.25 cm² working area and sintered at 500°C. These TiO₂ coated substrates were then sensitised with the dye for 24 hours. The cathode was prepared by brush coating a Pt catalyst onto an FTO substrate. This was followed by calcination at 380 °C for 20 min and cooling in ambient temperature to 70 °C. A sandwich model solar cell was assembled by first placing a transparent counter electrode on top of a working electrode. In the sealed solar cells, the electrodes were separated using a thermoplastic thin film as a spacer. The electrolyte was then injected into the cell and two binder clips used to hold the electrodes together.

3.5 Computational Detail

The plane-wave-based density functional theory (DFT) calculation was performed using the CASTEP program with the core orbitals replaced by norm-conserving pseudo- potentials, and a kinetic energy cutoff of 600 eV. All the electronic structures and the optical absorption spectra are calculated on the corresponding optimized crystal geometries. The generalized gradient approximation (GGA) with
the PBE exchange correlation functional was adopted. 24 and 96 atom supercells were used. In order to model bulk TiO₂, the doping effects were modeled by replacing one Ti atom with one doping atom. For the 24 atom supercell this gave a stoichiometric formula of Ti_7CeO_{16} corresponding to a doping concentration of 12.5%. In the 96 supercells after doping the stoichiometric formula was $Ti_{31}CeO_{54}$ corresponding to a doping concentration of 3.13%. In addition, Ce interstitial substitution was done. To minimise error, the doping atom was placed close to the centre of the supercell. Pure TiO₂ was calculated as a comparison.





Figure 3.1: a) Undoped TiO₂, Ce substituted TiO₂, Ce interstially substituted TiO₂ Undoped TiO₂, Ce substituted TiO₂

3.6 Results and Discussion

3.6.1 FTIR Analysis

FTIR spectra of synthesized titania nanomaterials are shown in **Figure 3.2**. Both doped and undoped nanoparticles show absorption peak 1,627 cm⁻¹ and in the range 3470–3240 cm⁻¹, mainly corresponding to –OH stretching vibration of hydroxyl group chemisorbed/physisorbed on different active sites on TiO₂ surface. Bands observed at 557 cm⁻¹ and 543 cm⁻¹ corresponds to Ti-O vibrations. On cerium

incorporation this peak is shifted to lower wave number, indicating formation of Ti– O–Ce bond. ¹⁵⁸ There is no indication of Ce–O bond vibration.



Figure 3.2: FTIR Spectra of Undoped and Ce-doped TiO₂

3.6.2 XRD and TEM Analysis

Figure 3.3 shows the XRD patterns of pure and Ce doped TiO₂. The diffraction peaks corresponding to the (101), (004), (200), (211) and (204) reflections as noted, indexed within the anatase tetragonal TiO₂ crystal structure. The peak at 27.8 ° indicates TiO₂ in the rutile phase. ¹⁵⁹ The characteristic XRD peaks of cerium oxide are not detected from the samples indicating that, if present, individual clusters of this phase should be very smaller, or confirming that nearly all Ce was incorporated into the TiO₂ structure. From the XRD patterns it was observed that Ce doping influences the size, crystallinity and phase transformation retardation of the nanoparticles.

The crystallite size is estimated with the Scherrer equation from the full width at halfmaximum of the (101) diffraction (Table 3.1).

$$D = (\kappa \lambda) / \beta \cos\theta \tag{1}$$

Where D is the average crystallite size, λ is the wavelength of the x-ray radiation, k is the Scherrer's constant (κ = 0.9). β is x-ray diffraction peak and θ is the fullwidth at half maximum(FWHM).

	Band gaps of TiO ₂ Nanoparticles				
Sample	Crystal size	Lattice	Phase	A/R	Band
	(nm)	strain	content (%)		gap
		0.0074		0.45	
0–Ce	24.21	0.0074	A(75.95), R	3.15	3.27
			(24.05)		
0.1–Ce	15.55	0.0115	A(39.16),	0.64	2.97
			R(60.84)		
0.3–Ce	14.96	0.0139	A(42.60),	0.74	2.91
			R(57.39)		
0.5–Ce	13.31	0.0123	A(44.98),	0.82	2.89
			R(55.02)		
0.7–Ce	12.93	0.0135	A(48.31),	0.93	2.87
			R(51.68)		
0.9–Ce	10.04	0.0179	A(100)		2.85

Table 3.1: Effect Of Ce Doping on Crystal Size, Phase Content, and

The crystal size decreased with an increase in Ce content and lattice strain as shown in **Table 3.1**. This is evidence of grain growth inhibition in the samples containing Ce, indicating that Ce ion doping restrains the growth of particle size. The ionic radius of Ce^{3+/}Ce⁴⁺ (1.03/0.93 Å) is larger than that of Ti⁴⁺ (0.68 Å) and therefore we inferred that the Ce ions with large size reside interstitially in the crystal lattice or stay at the particle surface or the grain boundaries. ¹⁶⁰ Theoretical studies on Ce doped TiO₂ by Anderson et. al reported that doping the outermost surface layer with Ce results in negative doping energies and hence the Ce dopants are located predominantly on the anatase surface. ¹⁶¹ Also the vacancy energy of formation is almost always lower for the surface than for the bulk. ¹⁶¹ The dopants on the surface or grain boundaries then interact with these surface/grain boundaries, forming Ce–O–Ti bonds which induce slight stress in the particle lattice. ¹⁶² This results in decreased surface energy/grain boundary energy and consequently grain growth inhibition. The decreased crystalline size is also due to the presence of the lanthanide ions, which are less reactive than the titania precursor species, and slow down the condensation and crystallization of the titania. ¹⁵⁷ The decrease in particle size results in an increase to the surface area of the samples, with a corresponding increase in the photoactivity of the doped TiO₂.

Ce doping also influences the crystallinity as indicated by the broadening of the width of the (101) plane diffraction peak with increase in Ce doping amount. This broadening shows that some of the dopant ions might have been incorporated in substitutional or interstitial sites of TiO₂, leading to reduction in crystallinity. ¹⁶³ The broadened profile also confirms the decrease in particle size ¹⁶⁴ as the amorphous grain boundary region, becomes more disordered if cerium sits on these regions, inhibiting crystal growth. ¹⁶⁵ The amorphous characteristics develop also due to the creation of large concentration of oxygen defects therefore degrading the crystallinity.

The dopants produce lattice deformation which suppresses the transformation of TiO_2 from anatase to rutile phase. The weight fractions of anatase and rutile shown in Table 1 were calculated using the method of Spurr and Myers,

$$fa = (1 + 1.26lr/la) - 1, fr = (1 - fa)$$
⁽²⁾

and $A/R = (f_a/f_r)$, where f_a and f_r are anatase and rutile mass fraction and I_a and I_r are the integrated intensities of the most intense peaks of anatase [101] and rutile [110], respectively.

The peak intensity of the plane at (110) decreased with increase of Ce content, with suppression of the transformation of TiO₂ from anatase to rutile phase at 0.9 % Ce. It has been reported that the the anatase-to-rutile transformation is slowed down when anatase nanoparticles are doped with a cation of valence > +4, but favored when the valence < +4. ¹⁶⁶ Based on this report, it can be said that Ce³⁺ dopants are more predominant in samples with Ce content of < 0.5 % and promoted the anatase-to-rutile transformation. The charge states of the dopant (cerium) in the TiO₂ nanoparticle are dependent on the calcination temperature with temperatures above 300 °C causing oxidation of Ce³⁺ to predominantly Ce^{4+ 164}. In this experiment a calcination temperature of 500 °C was used to anneal all samples and probably promoted the oxidation of Ce³⁺ to Ce⁴⁺ in samples with low Ce content. As the Ce content increases, most of the dopant exists on the grain boundaries and become more susceptible to oxidation. The concentration of Ce⁴⁺ increases leading to the inhibition of the anatase to rutile transformation.



Figure 3.3: XRD Spectra of Undoped and Ce-doped TiO₂

The TEM images (**Figure 3.4**) showed that the synthesized samples are composed of nano-sized nearly spherical crystalline nanoparticles. 0–Ce TiO₂ nanoparticles had an average diameter range of 33 nm, and the size and crystallinity of the nanoparticles decreased with an increase in Ce which is consistent with the XRD results. These smaller crystallites are more aggregated a common phenomenon with nanoparticles and it occurs immediately the particles are formed.



Figure 3.4: TEM images of a) 0 % TiO₂, b) 0.1 % Ce TiO₂, c) 0.3 % TiO₂, d) 0.5 % TiO₂ ,e) 0.7 % TiO₂ and f) 0.9 Ce % TiO₂

3.6.3 Elemental Analysis

Figure 3.5 shows the EDX spectrum for undoped TiO₂ sample showed titanium and oxygen peaks, characteristic of titania. Ce doped titania revealed additional Ce peaks, confirming the doping of cerium in the samples.



Figure 3.5: EDS spectra of (a) TiO₂ b) Ce doped TiO₂

3.6.4 TOF-SIMS Analysis

The distributions of Ce species on the surface of Ce/TiO₂ semiconductor observed by TOF–SIMS images are presented in **Figure 3.6**. In the ToF–SIMS spectrum of Ce/TiO₂ in positive polarity, the most intense peak at m/z = 139 was attributed Ce. The peak confirmed that the nanoparticles were doped with Ce. The most intense peaks at m/z = 64 in negative polarity correspond to at TiOH⁻. From the depth profiles measured (**Figure 3.7**), Ce is uniformly distributed on the surface of the TiO₂ nanoparticles, indicating that Ce ions are energetically more favourable to situate on the TiO₂ surface.



Figure 3.6: Fragments of (a) positive ion mass spectrum and (b) negative mass spectrum



Figure 3.7: TOF–SIMS image of TiO₂

3.6.5 XPS Analysis

XPS measurement was carried out to understand the change of surface chemical bonding as well as the electronic valence band position of Ti and Ce in the TiO₂ and 0.9 Ce nanoprticles. The XPS spectra for 0 Ce and 0.9 Ce (**Figure 3.8**) showed photoelectron peaks of Ti and O with the Ti $2p_{3/2}$ peak at 459.07 eV representing Ti⁴⁺ in the tetragonal structure. ¹⁶⁷ The intensity of the Ti $2p_{1/2}$ peak at 464.27 eV corresponding to Ti^{3+ 168} decreased indicating that Ti in 0.9 Ce was predominantly in the tetravalent state. The XPS spectrum for 0.9 Ce is shown in Figure. 5c and has additional XPS of Ce 3d peaks at around 870 and 890 eV which were ascribed to Ce $3d_{5/2}$ and $3d_{3/2}$ arising from spin–orbital coupling. ¹⁶⁹ The multiple peaks at 870 and 890 eV arise from the coexistence of Ce³⁺ and Ce⁴⁺ oxidation states.¹⁷⁰

Figure 3.8b shows the O 1s XPS spectra of the nanoparticles. As shown, two peaks at 527.4 and 529.4 eV were observed on the 0.9 Ce nanoparticles, which were attributed to the lattice oxygen and the O^2 ⁻ ion in the TiO₂ crystal structure respectively. ¹⁵⁷ This indicates the presence of more oxygen defects at the interface of doped nanoparticles of doped nanoparticles.



Figure 3.8: High-resolution XPS spectra of Ti 2p (a), O 1s (b), and Ce 3d for 0.9 Ce

3.6.6 Raman Analysis

The Raman spectrum of undoped titania (**Figure 3.9**) shows the typical spectrum of anatase TiO₂ with the following vibrational bands: $2 E_g$ bands 148 cm⁻¹ and 198 cm⁻¹, $2 B_{1g}$ bands at 396 cm⁻¹ and 514 cm⁻¹ and an E_g band at 640 cm⁻¹ arising from the vibration of the anatase structure. ¹⁶² Ce-doped titania also showed an additional band at 467 cm⁻¹ which is an E_g of the rutile phase. This observation indicates that the Ce doped titania is a mixture of anatase and rutile phases. With an increase of Ce content, the position of the lowest frequency E_g Raman band shifts towards higher wavenumbers and their intensities decrease. This is can be attributed to the reduction of particle size in the Ce-doped samples. When the grain size decreases

to the nanometer scale, the vibrational properties of materials are influenced significantly. ¹⁷¹ We attribute this to phonon confinement. As the particle size decreases, the phonon is increasingly confined within the particle. ¹⁷² An increase in Ce content leads to particle growth inhibition as observed in the XRD patterns. The contraction of the nanoparticles results in a decrease in vibrational amplitude and consequently a decrease in the intensity of the Raman bands. ¹⁷³.



Figure 3.9: Raman Spectra of TiO₂

3.6.7 Optical Properties

Figure 3.10 is the the diffuse reflectance spectra of the TiO₂ samples. It depicts the onset of the absorption edge of the Ce-doped TiO₂ to be red-shifted compared with the undoped TiO₂ indicating that longer wavelengths of light have been absorbed. Yan *et. al.* proposed that the degree of photon penetration into TiO₂ particles is the most likely explanation for its enhanced optical absorption property we observed. ¹⁷⁴ The quantity of photons reaching the core of a spherical particle depends on the size of the particles. ¹⁷⁵ The small crystals allow a greater number of scattered

photons to penetrate the particle. The TEM images show that the crystallite size of TiO_2 decreased with an increased cerium content. This allowed for more photon penetration and therefore enhanced the optical activity in the doped nanoparticles due to their small sizes (compared to the undoped ones). From the XPS spectra we observed that the energy levels of Ce^{4+/}Ce³⁺ were introduced into the band-gap of TiO₂, accounting for the observed red-shift.



Figure 3.10: Diffuse reflectance spectra of the TiO₂ nanoparticles with different Ce doping amount

The respective calculated band gap values are summarized in **Table 3.1**. These results indicate a decrease in the band gap with a corresponding increase in Ce content up to a doping percentage of 0.9% (optimum doping content). The trend of the decreasing band gap with an increasing dopant level indicates that a greater number of free electrons are now available for charge conduction. Ce doping results in the introduction of Ce 4f levels below the conduction band or above the valence band as shown by DFT calculations (**section 3.6.9**). This level takes part in interfacial charge transfer, whereby charge is transferred between the impurity and

conduction bands of TiO₂,inducing the red shift. For pure TiO₂, the electron transition from O-2p to Ti-3d states is responsible for the onset of optical absorption. Here, it is the cerium-induced Ce-4f states at the conduction band minimum of TiO₂ that are responsible for the red shift of the optical absorption edge and thereby reduce the optical band gap energy. At 2% Ce content, the position of the absorption peak showed a blue shift indicating an increase in the band gap. This may be due to all states close to the conduction band being populated by charge carriers from the impurities atoms, therefore the electron needs additional energy to be promoted from the valence band to the conduction band. This phenomenon can be well explained by the Burstein-Moss shift (an increase in the optical band gap with increasing doping level). ¹⁷⁶



Figure 3.11: Plot showing optical band gap of the TiO₂ nanoparticles with different Ce doping amount

3.6.8 DSSC Performance

The current–voltage curves of the DSSCs based on the TiO₂ and Ce doped films are shown in **Figure 3.12**, with the photovoltaic parameters summarized in **Table 3.2**. Ce content (0.9%) doped TiO₂ photoanodes improve the performance of DSSCs with a conversion efficiency of 2.11% compared to 0,21% for the one with a pure TiO₂. For 1 Ce the efficiency dropped to 1.52% due to the increase in the band gap. The increased *J*_{SC} in the Ce-doped photoanode is due to the following reasons. The incorporation of an additional 4f energy level in the band gap allowed for visible light activity in TiO₂, resulting in an improved photoconversion of the DSSCs. The alignment of the conduction band and the LUMO of the dye led to an improved driving force of injected electrons from the LUMO of the dye to the conduction band of TiO₂, increasing *J*_{SC}. ¹⁷⁷

Another effect of Ce doping is the reduction of the recombination rate of holes and electrons by creating impurity levels which acted as shallow traps reducing charge recombination. Theoretical studies by Anderson et. al showed that the improved catalytic properties of the Ce doped TiO₂ also partially arose from the facilitated creation of oxygen vacancies ¹⁷⁸ triggered by the Ce dopant, and is further enhanced when dopant concentration is increased. In addition the charge carriers and the electron density increased, resulting in an accelerated transfer rate of electrons in the Ce-doped TiO₂ thin films. ¹⁷⁹ Further, the increased electron density caused by the Ce-doped TiO₂ improved the fill factor of the solar cell which also contributes to J_{sc} enhancement. Doping inhibited the growth rate of the TiO₂ particles, resulting in small sized particles with a high surface area for dye loading. Sufficient surface coverage of the TiO₂ film surface by dye molecules increased the number of photogenerated electron and electron-hole pairs, consequently increasing the Jsc and overall light conversion efficiency. The incorporation of Ce in TiO₂ inhibited the anatase-to-rutile phase transition, reducing rutile instigated charge recombination.⁹⁹ From the electronic structure investigation we established that cerium is a shallow level dopant, in other words, it introduces shallow trap states into the semiconductor. An increase in the shallow trap density enhances electron mobility ¹⁸⁰ while retarding charge recombination, and consequently boosts the Voc.

Sample	J₅c (mA cm ^{−2})	V _{oc} (V)	FF <i>(%)</i>	PCE (%)
TiO ₂	0.79	0.51	52.27	0.21
0.1 Ce	2.84	0.59	63.8	1.08
0.5 Ce	3.3	0.67	62.2	1.54
0.9 Ce	7.69	0,67	49.5	2.11
1 Ce	4.34	0.61	58.8	1.52

Table 3.2:Photovoltaic characteristics of the DSSC based on TiO2 and
Ce doped TiO2 photoanodes

 J_{sc} : short circuit current density; V_{oc} : open circuit voltage; η : overall energy conversion efficiency; *ff*: fill factor.



Figure 3.12: Current–voltage curves of DSSC under illumination AM1.5

3.6.9 Electronic Structure Investigation

Density functional theory (DFT) calculations were carried out to understand theoretically the values of the band gap energy. The effect of doping on the electronic properties is shown by the band structures and projected density of states (PDOS) in Figure 3.13. The band gap for undoped TiO₂ was 2.06 eV, which we underestimated due to the well-known shortcoming of the exchange-correction functional in describing excited states. ¹⁸¹ The band structures for undoped TiO₂ (Figure 3.13a) revealed that the valence band (VB) and conduction band are composed predominantly of O2p orbitals and Ti3d orbitals respectively. Substitutional doping of Ce into TiO₂, resulted in a decrease of the band gap to 1.751 eV (**Figure 3.13c**). This makes the absorption edges of the doped TiO_2 shift to the visible region. These results are in accordance with the UV-Vis and DRUV-Vis results, which showed a red shift of Ce doped samples and narrowing of band gaps. The PDOS of the doped TiO₂ nanomaterials (Figure 3.13d) also showed additional 4f electronic states located at the bottom of conduction band. Weiguang et. all also found that the Ce 4f states introduced by the Ce dopant were located at the bottom of conduction band. ¹⁸² Electrons hope form VB to holes introduced by Ce 4f. Light excites electrons in a step-up band. Ce provides free holes which act as electron traps and slow down the recombination rate. From the band structures of Ce doped TiO₂, we concluded that Ce is a shallow level impurity, as it introduces defects with levels either very close to the conduction or valence bands. This dopant is also a donor, as it inserts states just below the conduction band, and its Fermi level is closer to the conduction band.





Figure 3.13: Band structures for a) Undoped TiO₂, c) Ce doped TiO₂ and PDOS for b) Undoped TiO₂, d) Ce doped

3.7 Conclusion

Cerium was doped in the TiO₂ nanocrystals. Ce doping influences the size, crystallinity and phase transformation retardation of the nanoparticles. The cerium ions probably exist at grain boundary or on the surface of TiO₂ nanoparticles and inhibit nanoparticle growth the anatase phase is also stabilized. The UV–vis reflectance spectra showed that cerium doping shift in the absorption spectra to the visible region and lower the bandgap up until 0.9 % dopant concentration. The oxidation states; Ce³⁺ and Ce⁴⁺ coexist in the nanoparticles. The band structures for doped TiO₂ indicated that the Ce 4f level is responsible for the band gap narrowing. DSSCS based on Ce doped semiconductor showed an increased Jsc than the one made from pure TiO₂. This was attributed to the improved driving force of injected electrons from the LUMO of the dye to the conduction band of TiO₂, high dye loading, accelerated transfer rate of electrons and reduced charge recombination.

CHAPTER 4

PREPARATION OF GRAPHITISED/TiO₂ NANOCOMPOSITES PHOTOANODES FOR DYE SENSITISED SOLAR CELLS

Abstract

Electrophoretic deposition (EPD) was used to deposit graphitised/TiO₂ nanocomposites onto an FTO electrode for application as photoelectrode in dyesensitized solar cells (DSSCs). Enhanced power conversion efficiency (PCE) of 2.25% was observed for the 0.5 wt% graphene oxide/TiO₂ (GO/TiO₂) based DSSC which was higher than that of the conversion efficiency of pure TiO₂ nanoparticles (i.e. 0.52%). Graphene oxide led to high migration of photoinduced electrons to the conduction band of the collection electrode and inhibition of charge carriers recombination resulting in enhanced photoconversion efficiency. A GO content above 0.5 % resulted in a reduced transparency leading to a decrease in the PCE. 0.5 wt % GO/0.9 Ce–TiO₂ Ce based DSSC showed a slightly enhanced efficiency of 2.45%. 0.5 rGO/TiO₂ based DSSCs had a high efficiency than 0.5 rGO/TiO₂ due to improved conductivity of rGO nanosheets and suppressed recombination of charge carriers.

Keywords: graphitised /TiO2 nanocomposites, electrophoretic deposition, DSSCs

4.1 Introduction

Titanium dioxide (TiO₂) is the semiconductor widely used in DSSCs due to its suitable band gap for electron injection from most successful commercial dyes. It is also stable compared to other metal oxides and nontoxic. To increase the photoconversion efficiencies of DSSCs effort has been exerted to prepare TiO₂ with a suppressed rate of recombination of charges. Carbonaceous substances e.g. graphene oxide, can be used as an anchor of TiO₂ to form a hybrid nanocomposite electrode with good synergistic properties. Graphene oxide (GO), is a single

monomolecular layer of graphite consisting of hydrophilic oxygenated graphene sheets (graphene oxide sheets) bearing oxygen functional groups on their basal planes and edges. GO is prepared by oxidizing graphite. ¹⁸³. Dimiev *et. al.* concluded that the formation mechanism of GO from graphite is in 3 steps. ¹⁸⁴ In the first step conversion of graphite into a stage-1 graphite intercalation compound (GIC). The second step is conversion of the stage-1 GIC into oxidized graphite. This is then converted into GO after exposure to water, which involves hydrolysis of covalent sulfates and loss of all interlayer registry. Graphene oxide sheets can be used as a good anchor for TiO₂ to enhance its photocatalytic activity. Chen et al observed an enhanced visible light activity with wavelengths longer than 510 nm graphene oxide/TiO₂ composites. The incorporation of GO into TiO₂ also increased the short-circuit current density and photoelectric conversion efficiency.

(GO) contains distort sp² in-plane bonding and the oxygen containing groups act as scattering centers and affect the electrical, optical properties and charge carrier ability of GO. ¹⁸⁵ Repairing the sp² aromatic structure can be achieved by reduction of GO to produce reduced graphene oxide (rGO) which bears considerably less remaining oxygens and is closer to pristine graphene. Chemical reduction using reducing agent such as hydrazine, ¹⁸⁶ natural reducing agents such as lemon juice and vinegar ¹⁸⁷ and hydrothermal reduction using supercritical water ¹⁸⁸ have been demonstrated to be effective for this purpose. rGO has been explored for different applications in DSSCs. In photoanodes rGO scaffolds can act an electron collector and transporter ⁶², as an interfacial layer to enhance charge-transfer performance and enhance photoinduced charge transport, ⁶³ to reduce the back-transport reactions ⁶⁴, improve the conductivity of the TiO₂ nanoparticle film ⁶⁵ and recently as transparent conductive films as an alternative to indium tin oxide (ITO). In rGO/TiO2 nanocomposites, rGO improves the quantum efficiency of TiO₂ and also increases the electron transport within the film. ¹⁸⁹ The introduction of rGO to TiO₂ also contributes to reducing the resistance of the surface and the interface of the photoelectrode ¹⁹⁰ resulting in enhanced mobility of the electrons in the TiO₂ layer. rGO has a large specific surface area (2630 m²/g) and thus, it can enhance the dyeloading and increase the photogenerated electrons.¹⁹¹ Su et. al. reported on enhanced solar to electrical energy conversion efficiency of 4.74% for DSSC with

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the rGO–TiO₂-modified photoanode compared with the photoanode of DSSC composed with unmodified TiO₂ (2.19%). ¹⁹² This improved solar conversion was attributed to better charge collection efficiency of rGO, which reduced the back electron transfer process. rGO also results in DSSCs with lower internal resistances leading to a high current density. ¹⁹³ However, the addition of excess rGO reduces the transparency of the photoelectrodes, which reduces photon capture abilities of the dye, slow down charge mobility and lead to the enhancement of charge recombination and a decrease of photoelectric conversion efficiency of DSSCs. It is therefore important to determine an optimal amount of rGO in the composites.

In this study, the effect of the GO and rGO content in graphitised/TiO₂ nanocomposites on the DSSC performance was investigated by adjusting the ratios of graphene to TiO₂ in the paste. Electrophoretic deposition was used to deposit the nanocomposites onto conductive glass substrates The DSSC performance initially increases with a maximum power conversion observed at 0.5 % GO content and then decreases with increasing GO content of the composites. An rGO content of 0.5 % gave an improved efficiency. Ce TiO₂/rGO and Ce TiO₂/GO based cells had higher efficiencies than the undoped TiO₂ graphitised nanocomposites.

4.2 Experimental

4.2.1 Materials and Instrumentation

Titanium Isopropoxide (TIP) Ti[OCH(CH₃)₂]₄, Nitric acid (HNO₃), sulphuric acid, hydrochloric acid, hydrogen peroxide (30 %), potassium permanganate(KMnO4; 97%), hydrazine (35wt% solution in water), cerium nitrate hexahydrate, graphite powder, flourine doped tin oxide (FTO)-coated glass substrate (10 per square, thickness 120m), absolute ethanol (CH₃CH₂OH) and graphite powder, <20 µm, synthetic were as supplied by Sigma Aldrich chemicals Ltd. The ruthenium complex dye ruthenizer 535-bis TBA, iodolyte Z-100, Ti-Nanoxide T/SP and platisol T were purchased from Solaronix (Aubonne, Switzerland). Energy dispersive spectroscopy (EDS) was done on a Jeol JSM-5600 scanning electron microscope coupled to an EDX spectrometer, Raman analysis was recorded using a Bruker Vertex 70 Ram II

Raman spectrometer exciting laser 800 nm, and TEM images were obtained from an FEI G2 SPIRIT transmission electron microscope. The samples were further characterized using X-ray diffraction (XRD) with Cu K irradiation Bruker Discovery D8). Photo-electrochemical data were measured using a 450 W Xenon light source that was focused to give 1000 W/m² (the equivalent of one sun at air mass 1.5) at the surface of the test cell. The applied potential and measured cell current were measured using a Keithley model 2400 digital sources meter.

4.2.2 Synthesis of Graphene Oxide

GO was prepared by a modified Hummer's method. ¹⁹⁴ Graphite powder (5 g) was mixed with sulphuric acid (115 mL) and sodium nitrate (2.5 g). The precursors were stirred for 30 mins to form a uniform paste. The flask was then put in an ice bath and potassium permanganate (15 g) was slowly added to the mixture. The mixture first became green due to the formation of the oxidizing agent MnO_3^+ . The temperature was raised to 35 °C and stirring continued for 30 mins. Water was then added slowly and mixture stirred vigorously to prevent effervescing. The temperature was raised to 98 °C and stirring continued for 30 mins until a homogeneous suspension was obtained. The slurry was diluted with 400 mL water and 30 % H_2O_2 (50 mL) to reduce manganese and the colour changed to bright yellow. The mixture was filtered by vacuum filtration, washed with plenty of deionized (DI) water and centrifuged to remove impurities. Further purification of the product was achieved by dialysis in DI water for 5 days and then the product was dried at 70 °C overnight.

4.2.3 Reduction of Graphene Oxide

GO (3 mg/mL) was dispersed in water in an ultrasonic bath for 1 h. Hydrazine hydrate solution (1 μ L for 3 mg GO) was added dropwise to the GO solution and the suspension heated under reflux at 85 °C for 12 h under vigorous stirring to get a black precipitate of RGO. Subsequently, the resultant RGO was retrieved from the suspension by a centrifuge (4000 rpm, 3 times), washed thoroughly with DI water then the product was dried at 70 °C overnight.

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4.2.4 Preparation of Graphitised/ TiO₂ Nanocomposites

The appropriate amount of GO or rGO was dispersed in absolute ethanol (100 mL) in an ultrasonic bath for 1 h until the solution became clear and no precipitate present. The solution was then chilled to $\approx 5^{\circ}$ C in an ice bath. TiO₂ sols were prepared by dropwise addition of an ethanolic titanium isopropoxide (TTIP) solution, into the chilled GO and rGO solution under vigorous stirring. After continuously stirring for 24 h, the greyish-black precipitate was harvested by centrifugation (5,000 rpm, 30 min) and washed with ethanol several times to remove undecorated TiO₂ particles. The obtained powder was dried in the oven (70 °C) overnight and calcined at 500 °C for 2 h under air. Graphitised Ce-doped TiO₂ samples were prepared according to the above procedure in the presence of the cerium nitrate hexahydrate to give an optimised doping level from 0.9 % in molar ratio. The appropriate amount of cerium salt was added to the distilled water before hydrolysis of TTIP and the remaining procedures were the same as described above. Finally, 6 samples of different GO content (0.1 wt%, 0.3 wt%, 0.5 wt%, 0.5 wt% 0.9 Ce and 0.7 wt% in the hybrid) and 0.5 wt% rGO and 0.5 wt% rGO 0.9 Ce were prepared.

4.2.5 Deposition of nanocomposite on FTO

To deposit the nanocomposites on FTO, electrophoresis was used. FTO substrates were sonicated using an ultrasonic cleaner in deionized water for 15 mins, then in acetone for a 10 more mins. They were further sonicated in isopropanol, acetonitrile for 10 mins in each and finally in tertbutyl alcohol for 30 mins to remove organic contaminants. These substrates were then masked with mica tape to create a 025 cm^2 working area. The suspension for EPD consisted of 120 mg graphitised/TiO₂ sample in 80mL absolute ethanol, and stirred with a magnetic stirrer overnight. This mixture was ultrasonically dispersed in icy water for 15 mins before electrophoresis. The electrophoretic cell contained two conducting substrates of dimensions 2.5 x 2.5 cm, one was used as the cathodic substrate and the second (masked substrate) was used as anode. The standard distance between the electrodes was 20 mm. The optimized applied deposition voltage and time were 15V and 5 min respectively.

4.2.6 Cell Fabrication

Graphitised/TiO₂ nanocomposite coated FTO substrates were sensitised with the dye for 24 hours. The cathode was prepared by brush coating a Pt catalyst onto an FTO substrate. This was followed by calcination at 380 °C for 20 min and cooling in ambient temperature to 70 °C. This electrode was then sensitized in ruthenizer 535bis TBA. A sandwich model solar cell was assembled by first placing a transparent counter electrode on top of a working electrode. In the sealed solar cells, the electrodes were separated using a thermoplastic thin film as a spacer. The electrolyte was then injected into the cell and two binder clips used to hold the electrodes together. The efficiency of the fabricated cells was evaluated using simulated AM1.5 sunlight with an output power of 100 mW cm⁻².

4.3 Results and discussion

4.3.1 SEM Analysis of Electrophoretically Deposited Films

An EPD time of 5 min resulted in a thin uniform nanocomposite film on the FTO substrates. The thickness of the film on FTO increased with increasing applied potential and deposition time as can be seen from **Figure 4.1**. Films deposited for 40 minutes showed cracks. These results show that film thickness is tunable by varying the deposition time.







Figure 4.1: SEM images of nanocomposite film on FTO substrates at lower magnification deposited at (a) 5 mins, (b) 20 mins and (c) 40 mins

4.3.2 FTIR Analysis

The FTIR spectrum of GO (**Figure 4.2**) showed a number of absorption bands confirming successful oxidation of graphite: carboxyl C=O (1723 cm⁻¹), epoxy C–O (1204 cm⁻¹), carboxyl C-O (1415 cm⁻¹), alkoxy C–O (1049 cm⁻¹), hydroxy –OH (3391 cm⁻¹) groups and C-OH stretching at 1070 cm⁻¹.¹⁹⁵ The peak at 1590 cm⁻¹ was attributed to a C=C bond (aromatics functional group, skeletal vibrations from unoxidized graphitic domains). These results confirmed the functionalisation of graphite with oxygen molecules to form carbonyl group, carboxylic group, and epoxy group. The broad band at 3349 cm⁻¹ was attributed to stretching vibration of the hydroxyl group (OH) and from ambient atmospheric moisture in the sample. For rGO the intensities of the peaks indicating oxidation were reduced indicating that GO was partially reduced to rGO.



Figure 4.2: FTIR spectra of graphene oxide and reduced graphene oxide

In addition to the GO peaks, the spectra of rGO-TiO₂ and GO-TiO₂ (**Figure 4.3**) showed strong absorption around 564 cm⁻¹ which was attributed to the vibration of Ti–O–Ti bonds in TiO₂, indicating the formation of TiO₂-GO nanocomposite. The formation of Ti–O–C bonds (760 cm⁻¹), indicated the firm connection between graphene and TiO₂. ¹⁹⁶ The intensities of absorption bands of oxygen-containing functional groups such as C-O, C=O were reduced. This is because during the TiO₂ grains nucleate and grow in C-OH sites on the GO lamellar by the way of heterogeneous nucleation. ¹⁹⁷



Figure 4.3: FTIR spectra of graphene oxide and graphitised/TiO₂ nanocomposites.

4.3.3 XRD Analysis

XRD patterns of graphite, GO and rGO nanosheets are presented in **Figure.4.4**. The characteristic peak (002) of graphite at 26.43° with an interlayer distance of graphite powder was 0.334 nm. With chemical oxidation, this 2 θ peak shifted to 11.13° corresponding to the (001) diffraction peak of GO and layer-to-layer distance (*d*-spacing) of about 0.774 nm. The increase in interlayer spacing was due to the presence of functionalities in the basal plane of GO along with absorbed water molecules. Also, during oxidation, Na intercalates in the graphite layers, leading to an increased interlayer distance and making it easy for the layers to be exfoliated into individual graphene oxide sheets upon exposure to sonication in water and in solvents. The XRD pattern of the rGO powder sample, yielded only a peak at 26.56°, with an interlayer distance of rGO is 0.442 nm, which is fairly close to that of graphite powder (26.43°). The narrowing in the interlayer spacing of rGO is due to the removal of the oxygen-containing groups. The 2 θ peak of rGO was broader than the

ones for graphite and GO, which can be attributed to the amorphous nature of the GO sheets. The mean dimension of an ordered stack of graphene oxide sheets that are oriented perpendicularly to the diffracting plane was calculated from the width of the X-ray diffraction peak using the Debye–Scherrer equation, and was found to be 5.2 nm. This size corresponds to about 6 stacked graphene oxide sheets.



Figure 4.4: XRD patterns of a) graphite and b) GO and RGO

Figure 4.5 shows the XRD patterns of GO, rGO and GO-TiO₂ composites. The diffraction peaks at 25.5°, 38.4°, 48.0°, 53.9°, corresponding to the (101), (004), (200), (211) and (204) reflections were indexed to the anatase tetragonal. The peak at 27.8° indicates TiO₂ in the rutile phase and this peak diminishes with increase in GO content. This showed that an increase in GO content suppressed the transformation of TiO₂ from anatase to rutile phase. ¹⁹⁸ The (002) and (100) diffraction peaks of GO totally disappears in the nanocomposites possibly due to the low content of GO loading, or the relatively low diffraction intensity of GO and rGO. ^{199, 198} The existence of carbonaceous materials in the nanocomposites was clearly elucidated by TEM and Raman analysis.



Figure 4.5: XRD patterns of graphitised/TiO₂ nanocomposites

4.3.4 TEM Analysis

TEM analysis revealed that GO and rGO were made of nanosheets as shown in **Figure 4.6**. The oxidation of graphite to GO changes the hybridization of the stacked graphene sheets from sp² to sp³, generating defects that manifest as clear wrinkles in the nanosheets. Reduction restores the hybridization as the wrinkles disappear in rGO.





Figure 4.7 shows the TEM images of the TiO₂ nanoparticles incorporated with graphitised nanosheets, which confirmed successful formation of graphitised/TiO₂ nanocomposites. From FTIR spectra of GO, it was observed that GO sheets possess oxygen-containing groups, such as epoxide, hydroxyl, carbonyl, and carboxylic groups. Therefore, titanium alkoxides, can be readily grafted onto the surface of GO through chemical adsorption at the molecular level. ²⁰⁰ The high calcination temperature of 500 °C favoured the nucleation of the TiO₂ on the carbon surfaces. During calcination, the TiO₂ nanoparticles formed on the GO surface. The TEM images showed that the surface of GO nanosheets was packed, with uniformly dispersed TiO₂ nanoparticles indicating that the aggregation of TiO₂ was well prevented during the preparation process. The graphitic structures prevented the TiO₂ nanoparticles agglomeration and enabled their good distribution on the graphene.²⁰¹ Pre–chilling the titanium mixture in an ice bath reduced the rate of the hydrolysis rate of the titanium precursor (TTIP), promoting the homogeneous growth of TiO₂ onto GO. ¹⁹⁹







Figure 4.7: TEM images of (a) 0.1% GO, (b) 0.3% GO , (c) 0.5% GO, (d) 0.7% GO and (e) 0.5% GO-0.9 Ce.

4.3.5 Elemental Analysis

Elemental analysis results showed a decrease in C/O atomic ratio in GO compared to the starting material, graphite. The decrease is due to the functionalization of graphite by oxygen containing groups and water molecules trapped in the hydrophilic GO particle. The C/O ratio increased in rGO, indicating that many oxygen atoms were removed by the chemical reduction method. The reduction of GO also resulted in the incorporation of nitrogen from the reducing agent (hydrazine Hydrazine readily reacted with the epoxide functional groups to form the hydrazine alcohols), which were mainly responsible for the incorporation of nitrogen. ²⁰²

Sample	%C	%Н	%N	%S	C/O ratio
Graphite	95.4	5.8			
GO	56.5	3.2	0.0	9.3	0.55
rGO	85.2	4.5	1.8	4.5	0.35

Table 4.1:CHNS Results of Graphite, GO and RGO

4.3.6 Raman Analysis

The Raman spectrum of graphite (**Figure 4.8**) exhibited 3 peaks: the G-band, a primary in-plane vibrational mode at 1605 cm⁻¹ which is due to the doubly degenerate E_{2g} vibrational mode at zone center ²⁰³, the D and 2 D at 1358 cm⁻¹ and 2722 cm⁻¹ respectively. The D band comes as a breathing mode of k-point phonons of A_{1g} symmetry. ²⁰⁴ The broadening of the D and G bands of GO compared with those of graphite is possibly due to the loss of lattice symmetry as a result of the change in hybridisation of the sp² carbon networks of pristine graphite to sp³ by the strong oxidation implying a higher degree of structural disorder ²⁰⁵. The G band position is highly sensitive to the number of layers present in the sample. **Figure 4.8 d** compares the G band position of graphite, GO and rGO. These spectra have been normalized to better reveal the spectral shift information. There is an increase in the number of layers from graphite to GO as shown by shifting of the G band position for a graphene oxide layer. ²⁰⁶

The band shape of the 2D peak is also used to determine graphene layer thickness of graphitic materials. For graphite, the 2D band was observed to be a single

symmetric peak while in GO it broadens and split into an increasing 3 peaks (2551 cm⁻¹, 2708 cm⁻¹ and 2859 cm⁻¹). These results also confirmed the increase in the number of layers in GO. The band splitting of the 2D band going from graphite to multilayer GO arises from symmetry lowering that takes place when increasing the layers of graphene in the sample. ²⁰⁶ Reduction of GO resulted in partial restoration to sp² hybridisation as shown by the narrowing of the G band in the Raman spectrum of rGO. A slight blue shift of the G band of rGO, and restoration of symmetry of the 2D band indicated a decrease in the rGO layers.



Figure 4.8: Raman Spectra of (a) GO and graphite, (b) GO and graphite (c) rGO and (d) normalised spectra for GO, rGO and graphite

The typical modes of anatase were observed in the Raman spectrum of the composites (**Figure 4.9**), i.e., the $E_{g(1)}$ peak (148 cm⁻¹), $B_{1g(1)}$ peak (394 cm⁻¹), $E_{g(2)}$ peak (637 cm⁻¹), and the $A_{1g} + B_{1g(2)}$ modes centered at 512 cm⁻¹, respectively. The two characteristic peaks at about 1,328 and 1,602 cm⁻¹ for the graphitized structures were also observed.



Figure 4.9: Raman spectra of graphitised/TiO₂ nanocomposites

4.3.7 Optical Properties

Figure 4.10 shows the UV-Vis light absorption spectra of GO before and after reduction. Two kinds of characteristic features were observed in the UV-Vis spectrum of GO: peaks at 230 nm corresponding to a π - π * plasmon transitions of the aromatic C=C bond. ²⁰⁷ The other peak was at 309 nm corresponding to n- π * plasmon transitions of C=O bond. Partial restoration of electronic conjugation and sp² hybridisation within the carbon structure was evidenced by a bathochromic shift of λ_{max} . The enhancement of the light absorption of rGO in the whole spectral region

increased significantly compared to GO. Since rGO is capable of absorbing visible light, it is better suitable for DSSC application.



Figure 4.10: UV-vis spectra of GO and rGO

4.3.8 DSSC Performance

Figure 4.11 shows typical I–V curves of the various graphitized TiO2 based DSSCs, and **Table 4.2** shows a summary of the photovoltaic parameters. The photoconversion efficiency (PCE) value of the cells initially increased when 0.1 wt% of GO was used with the maximum PCE of 2.25 % observed with the 0.5 wt% GO. After that, the PCE value of the cells decreased again with the increase of the concentration of GO in the composite electrode. A GO content above 0.5 % reduced the transparency of the photoanodes resulting in reduced photon capture abilities of the dye. This led to the decrease of PCE of the DSSCs. The PCE of all the GO/TiO₂ based DSSCs was higher than that of TiO₂ based DSSC (i.e. 0.52%). The enhanced PCE of the composite based DSSCs was due to an increased active surface area for photoconversion, enhanced electron transfer kinetics in the anode and reduced

recombination rate of the electrons with the holes. In the composites, GO acted as a platform for support, scaffold, or a 2D planar substrate for anchoring the TiO₂ nanoparticles ⁷⁰. In this way, GO offered a mediator pathway for the transfer of electrons between the TiO₂ nanoparticles resulting in a stable charge separated state and slow charge recombination between conduction band electrons in the TiO2 and the I₃ in the electrolyte. GO also served as an efficient electron-transport channel between dye molecules and the TiO₂ nanoparticles in the DSSCs due to the formation of a GO–TiO₂ Schottky barrier junction. ²⁰⁸ This barrier improved the interface contact between dye and TiO₂ resulting in enhanced injection efficiency of electrons from the dye to the TiO₂ nanoparticles in the photoanode. The intimate contact between TiO₂ and GO also accelerated the rate of transfer of photogenerated electrons on TiO₂ to GO, thus reducing recombination ¹⁹⁹ and lengthening the lifetime of the charge carriers in the nanocomposite. 0.5 wt % GO/0.9 Ce-TiO₂ based DSSCs showed a slightly enhanced efficiency when compared to the GO/TiO₂ based DSSCs. In the GO/0.9 Ce-TiO₂ based DSSCs, Ce doping reduced the recombination rate of holes and electrons by creating oxygen vacancies ¹⁷⁸ and impurity levels which acted as shallow traps. Ce doping also increased the charge carriers and the electron density resulting in an accelerated transfer rate of electrons in the Ce-doped TiO₂ thin films. ¹⁷⁹

Sample	Jsc	Voc	FF (%)	PCE (%)
TiO ₂	0.45	0.37	52.2	0.52
0.1 GO	0.51	0.55	57.1	1.59
0.3 GO	0.67	0.56	44.3	1.69
0.5 GO	0.73	0.65	45.2	2.25
0.7 GO	0.49	0.54	57.1	1.73

Table 4.2:	Photovoltaic characteristics of the DSSC based on TiO ₂
	graphitised/TiO ₂ nanocomposites photoanodes

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0.5 GO 0.9 Ce	0.98	0.61	45.2	2.45
0.5 rGO	6.57	0.36	33.3	2.57
0.5 rGO 0.9 Ce	6.57	0.35	35.2	3.85



Figure 4.11: Current–voltage curves of GO/TiO₂ nanocomposite based DSSCs

rGO based DSSC showed an improved PCE when compared to GO based devices (**Figure 4.12**). Oxidation of graphite introduced oxygen containing groups onto the surface of GO. The attached oxygen groups and lattice defects on GO served as strong scattering centres that affect the electrical transport of the nanosheets. ¹⁸⁵ The restoration of the conjugated network of the graphitic lattice for rGO as confirmed by UV-vis resulted in the recovery of electrical conductivity. The improved conductivity of rGO further enhanced electron mobility, suppressed recombination

of charge carriers, resulting in an increase in PCE. The conduction band (CB) of anatase TiO₂ and the work function of rGO are very close; 4.2 eV and 4.42 eV respectively. ¹⁹⁹ The proximity of energy levels made it easy for photogenerated electrons to transfer from the TiO₂ CB to the rGO, thus stabilizing charge separation and slowing down electron-hole recombination. A slight increase in the open circuit voltage (Voc) was observed for all the DSSCs based on the composites. The Voc is determined by the difference between the Fermi level in the illuminated semiconductor and the Nernst potential of the redox couple in the electrolyte. ²⁰⁹ The results from **Table 4.2** show that the introduction of GO and or rGO into the TiO₂ nanoparticles had little influence on the Fermi level of the TiO₂ nanostructures. The short-circuit current density (J_{sc}) values of the nanocomposite based cells are greater than the TiO₂ based cell. The enhancement of J_{sc} was attributed to the faster electron kinetics and the improved interface contacts in dye/rGO/TiO₂ in the DSSCs. 210 Also, the hybridisation of TiO₂ increased the active surface area for photoconversion leading to an increment of photocurrent density and the photoconversion activity of the DSSC.



Figure 4.12: Current–voltage curves of rGO/TiO₂ nanocomposite based DSSCs
4.4 Conclusion

GO/TiO₂ nanocomposites were synthesised using a sol-gel method and deposited electrophoretically onto FTO electrodes for application as photoelectrodes in dyesensitized solar cells. TiO₂ nanoparticles were homogeneously anchored onto the GO sheets with close interfacial contact. This close contact was proposed to enhance the mobility of photogenerated electrons on TiO₂ to GO, leading to efficient separation and suppressed recombination time of charge carriers. However the DSSCs had low FF. Rsh needs to be improved and the Rs reduced to obtain a higher fill factor.

CHAPTER 5 FABRICATION OF AgWN FLEXIBLE ELECTRODE BASED DYE SENSITISED SOLAR CELLS

Abstract

A silver wire network (AgWN) transparent conducting polyethylene terephthalate (PET) substrate was fabricated as used as an indium tin oxide (ITO) alternative in DSSCs. The transmittance of the AgWN network was 82 % which is comparable to ITO substrates. Titanium oxide (TiO₂) films on the AgWN/PET substrates were obtained using the electrophoresis method. These substrates were sensitised and used to fabricate a dye sensitised solar cell. The transmittance of the AgWN with TiO₂ film in the visible domain reaches 48%. From the measured current–voltage or I-V characteristic under AM1.5 illumination of the formed DSSC using AgWN substrates, an open circuit voltage (Voc) of 0.377 V, a short circuit current (Isc) of -0.0067 mA and a fill factor (FF) 25.7 % with an efficiency of 0.00862 % were obtained from a cell of 0.075 cm² working area. The stability of the cell improved when a room temperature ionic liquid electrolyte was used.

Keywords: silver wire network transparent conducting electrode, ITO alternative, electrophoresis deposition, room temperature liquid electrolyte

5.1 Introduction

Indium tin oxide (ITO) substrate which acts as a current collector used in most DSSCs exhibits an ideal transparency and resistivity at room temperature. ²¹¹ However, ITO glass electrodes have the following disadvantages: they are expensive, brittle and crack down easily due to exposure to the sun. These electrodes make it difficult for DSSCs to be incorporated in flexible structures. Flexible DSSCs have an advantage of easy installation on buildings with flat or curved surfaces because of their light weight and flexible nature. These DSSCs can

be coated to backpacks for on-the-go recharging of portable gadgets such as cellphones. These cells would be adaptable to different shapes of surfaces and light weight to enable them as a mobile power source for portable electronic devices. Cost reductions can be achieved by using flexible transparent substrates for both the photoanode and counter electrodes. With these substrates the DSSC production cost could be cut down by 35 %. ²¹²

To lower the costs of the DSSCs even further effort has been devoted to the investigation of novel ITO–free anodes. Metal nanowire network is the next generation conducting material with the potential to replace ITO in flexible transparent conducting electrodes (TCE). The use of cheaper metal substrates TCEs is desirable in large scale DSSC devices since it will allow for continuous roll-to-roll processing. S. Kiruthika *et. al.* successfully fabricated highly interconnected Cu wire networks on polyethylene terephthalate (PET) substrates with a transmittance of 75%, as alternatives to the commonly used tin doped indium oxide (ITO) based electrodes. ²¹³ These wires had a good conductivity but very susceptible to oxidation drastically affected their conducting abilities. S. Kiruthika *et. al.* also fabricated a gold metal wire network (AuWN) to serve as a TCE with a transparency comparable to ITO. ²¹⁴ An ITO–free, flexible organic solar cell was also been fabricated using the Ag wire network by R Gupta et al. ²¹³ The advantages of these 1 dimensional (1D) conducting networks include tunable optical, plasmonic and excellent electrical properties. ²¹⁵

The restriction of high temperature sintering treatments is a major factor responsible for the relatively low conversion efficiency of plastic based DSSCs. Conducting polymer substrates are good candidates for flexible DSSCs, but require a fabrication process designed in a temperature range below 150 °C. This is due to the thermal instability of these substrates at higher sintering temperature (450–550 °C) of the TiO₂ electrodes. Thus, some alternative techniques have to be employed to improve the contact of TiO₂ film with the substrate for the fabrication of DSSCs on plastics with improved efficiencies. Effort has been made by research groups to come up with a method that does not involve high sintering temperatures of the TiO₂ electrodes. Yamaguchi *et al.* improved the efficiency of plastic DSSCs by using the

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compression method without heat treatment of the plastic substrates. ²¹⁶ In this method a TiO₂ paste was applied onto an ITO-PEN film by doctor-blade coating, an efficiency of 7.4% under 1 sun irradiation was achieved. Dürr *et al.* developed the lift-off process where the TiO₂ layer was first applied to a thin gold layer on a glass substrate. ²¹⁷ After sintering, the TiO₂ layer was removed from the glass by dissolving the gold layer. The TiO₂ layer was then transferred onto an ITO-coated PET film by application of high pressure. In this process, Dürr *et al.* achieved an efficiency of 5.8% under 100 mW cm⁻² (1 sun).

In this project TiO₂ thin films on silver wire network polyethylene terephthalate (AgWN/PET) transparent conducting substrates were obtained using the electrophoresis deposition (EPD) method. Electrophoretic deposition (EPD) is an electrochemical deposition of charged particles with an applied electric field in a suspension containing the particles, electrolyte, additives, and solvent.²¹⁸ The setup for EPD is shown in Figure 5.1. It is a two-step process. First the charged particles suspended in a liquid migrate towards an electrode under the effect of an electric field (electrophoresis). In the second step, the particles deposit on the electrode forming a relatively dense and homogeneous compact film. The movement and deposition of the particles is influenced by the charge on the particles, the electrophoretic mobility of the particles in the solvent, and the applied electric field. ²¹⁹ When conducting EPD, particles must be electrically charged to permit film formation in an electrical field and also for stabilization of the suspension. Studies have shown that a small iodine, acetone and water additive can charge TiO₂ nanoparticles in an alcohol solvent via the adsorption of generated protons. ²²⁰ The concentration of particles should be kept relatively low to favour good dispersed particle suspension.



Figure 5.1: Schematic diagram of electrophoresis deposition process

EPD is suitable for depositing TiO₂ on AgWN transparent conducting electrodes to avoid disrupting the wire network. This is because EPD produces a closely packed network of TiO₂ nanoparticles which minimizes the distance of electron travel between injection from the dye and collection by the FTO substrate. ²²¹ Since EPD results in interconnected crystalline network of TiO₂, calcination is not necessary as such it is attractive for preparing TiO₂ films on flexible plastic substrates that cannot tolerate high temperature calcination. Research has reported the use of EPD to prepare TiO₂ films for DSSCs. Miyasaka and Kijitori fabricated DSSCs at low temperature with EPD-TiO₂ film, obtaining 4.3% efficiency with an incident solar irradiance of 23mWcm⁻². ⁴² The downfall of EPD is the formation of micro-cracks at the film surface when the solvent evaporates. To reduce the cracks of TiO₂ film in this research study, a multiple EPD method was employed. Huge microcracks in the one-step process deposited films are wider and deeper than those of the two-step ones. These results suggest that the second EPD could fill the cracks produced in the first EPD to form a better quality microstructure photoanode. ²²² We investigated the use of AgNW network substrate as a TCE for the photoanode of DSSC .Cells with an efficiency of up to 0.00862 % were fabricated. These cells degraded very rapidly when iodine/triodide electrolyte was used. PCE of was achieved with room temperature ionic liquid based electrolyte.

5.2 Experimental

5.2.1 Experimental details

P-90 TiO₂ nanoparticles (Merck), absolute ethanol (commercial alcohols, Canada) isopropyl alcohol (IPA), acetonitrile (ACN), tert-butyl alcohol (t-BuOH), iodine 99.8% (I₂, Qualigens fine chemicals, India), were used as received without further purification. The ruthenium complex dye ruthenizer 535-bis TBA, flourine doped tin oxide (FTO)-coated glass substrate (10 per square, thickness 120m), iodolyte Z-100, Ti-Nanoxide T/SP and platisol T were purchased from Solaronix (Aubonne, Switzerland). Acrylic resin was bought from Ming Ni Cosmetics Co. (Guangzhou, China), non-conductive. The surface morphology was characterised using SEM Nova NanoSEM 600 instrument (FEI. Co., The Netherlands. Composition of the films was studied using with an EDAX Genesis instrument (Mahwah, NJ) attached to the SEM column. The XRD patterns were recorded in a Bruker-AXS Microdiffractometer (model D5005) with Cu K α radiation (λ = 1.5406 Å) from 20° to 70°. Optical properties of dye and films were measured using a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrophotometer. The efficiencies of the cells were obtained using a solar simulator The C-V measurements were performed using Keithley 4200 semiconductor parameter analyzer under standard global AM 1.5 solar conditions to get the photoefficiency of cell.

5.2.2 Fabrication of AgWN TCE

The fabrication process of the AgWN TCE is illustrated in **Figure 5.2**, which is a lowcost method based on a self-forming crackle template and lift-off technique. The method includes crackle template formation, conductive layer (silver) deposition and removal of the sacrificial layer. PET substrates were cut into 2.5 by 2.5 pieces and cleaned with soap water, DI water and ethanol, dried with in a stream of N₂ gas. These substrates were then subjected to ozone cleaning in a UV/Ozone Pro Cleaner (Bioforces NanoScience) for 30 minutes. A commercially available acrylic resin dispersion (Ming Ni Cosmetics Co.,Guangzhou, China) was then pipetted onto the clean substrates. This layer was used as a sacrificial crack template. The dispersion was spin coated on the substrate at 1000 rpm for 120 seconds, followed by the deposition of silver metal with a thickness of 100 nm by physical vapour deposition system (Hind High Vacuum Co., India) onto the template. The final stage involved the removal of the acrylic resin template with chloroform. These AgWN network derived TCEs were used for the fabrication of photoelectrodes of DSSCs.



Figure 5.2: Fabrication of AgWN TCE.

5.2.3 Electrophoretic Deposition of TiO₂ onto AgWN TCE

TiO₂ was electrophoretically deposited onto AgWN flexible substrates. AgNW network substrates were cleaned by immersing in acetone for 5 mins and dried in a stream of nitrogen gas (N₂). These substrates were then masked with mica to create a 025 cm² working area. The suspension for EPD consisted of 120m g TiO₂ in 80mL absolute ethanol, and stirred with a magnetic stirrer overnight and ultrasonically dispersed for 15 mins before electrophoresis. The electrophoretic cell contained two conducting substrates of dimensions 2.5 x 2.5 cm, one was used as the cathodic substrate and the second was used as anode. The electrodes were immersed vertically in a 100 ml beaker containing the suspension. The standard distance between the electrodes was 20 mm. For some experiments a charging solution

containing 2 ml acetone, 12.6 mg iodine in 50 ml ethanol solution containing 2 ml acetone and 1 ml distilled water was prepared. For experiments with both solutions, prior to electrophoresis the EPS was added to the CS and sonicated in icy water for 15 mins. Various applied fields and deposition times were investigated to determine the optimum EPD conditions for uniform nanocrystalline TiO₂ films. A two-step electrodeposition method was carried out using an electrodeposition voltage of 10 V time per step: for 10 mins and 1 mins drying intervals in between the steps. The nanotitania films were dried in air for 30 mins.

5.2.4 Assembly of DSSCs

TiO₂ coated AgWN, TCEs were used as anodes in DSSCs. They were sensitised in ruthenizer 535-bis TBA dye for 12 h and washed with ethanol to removed loose dye particles. Pt catalyst was deposited by brush coating. This was followed by calcination at 380 °C for 20 min and cooling in ambient temperature to 70 °C. A sandwich model solar cell was assembled by first placing a transparent counter electrode on top of a working electrode. In the sealed solar cells, the electrodes were separated using a thermoplastic thin film as a spacer. The electrolytes was injected into the cell and two binder clips used to hold the electrodes together. FTO substrate was used for comparison.

5.3 Results and Discussion

5.3.1 FESEM Analysis

FESEM and transmission mode microscopy (**Figure 5.3**) showed that cracks formed interconnected network of AgWN all over the substrate. The crack width is in the range $3-20 \mu m$ and the crack spacing, $50-200 \mu m$. The superior crackle contained channelling cracks dividing the plane into polygonal adjacent cells.



Figure 5.3: (a) FESEM image and (b) transmission mode microscopy image of AgWN substrate.

FESEM images of TiO₂ films deposited on FTO substrates with and without charging solution are shown in **Figure 5.4**. In EPD without charging solution, deposition was slow and a thin film was visible when the voltage was increased to 10 V with 20 mins deposition time. The TiO₂ films were homogeneous and only deposited on the AgWN conductive part leaving the non-conductive part clean (**Figure 5.4 a**). In solution with CS, the TiO₂ film was visible even at 5V, and at 10 V the film covered the non-conductive part of the TCE, and showed cracks (**Figure 5.4 b**). The fast deposition was due to the enhanced charging of TiO₂ with iodine and acetone that resulted in increased electrophoretic mobility of the particles in the solvent (**Figure 5.4 c**). The rest of the EPD experiments were conducted without a charging solution. An increase in the electrodeposition voltage and deposition time resulted in high packing density of film and then formation of cracks in the film at 50 min. The film was grown to be thick on the silver nanowires to protect them from contact with electrolytes and avoid redox chemical corrosions by iodide ions. ²²³





Figure 5.4: FESEM images of TiO₂ coated TCEs at a) 15V, 20 mins, without CS b) 15 V, 20 mins with CS and c) 15 V 40mins with CS

High magnification images (**Figure 5.5**) of the film show a relatively uniform mesoporous structure, highly desirable for photovoltaic application. The porous nature is due to the void regions (inter spheres) which are created during EPD. Porosity enhances the efficiency of DSSCs as there is a very high surface area, which is very important for dye loading. ²²⁴ Some AgWN substrates with TiO₂ were calcined at 220 °C to investigate the effect of temperature on the morphology of the films and DSSC performance. There is no morphological difference between the calcined and the uncalcined TiO₂ films. The uncalcined film also exhibited a compact TiO₂ interconnected surface morphology (**Figure 5.5 a**). These results confirmed that no calcination is required for an interconnected TiO₂ network after EPD which is highly desirable for plastic electrodes.





Figure 5.5: High magnification FESEM images of TiO₂ coated TCEs (a) uncalcined and (b) calcined

5.3.2 EDS Analysis

The EDS spectra of TiO₂ substrates is shown in **Figure 5.6**. The spectra show peaks for Ti and O which are characteristic of TiO₂. Sn and Ag are from FTO and AgWN substrates respectively. Sensitised TiO₂ showed an increase in the intensity of carbon peak due to the adsorption of dye onto TiO₂.



Figure 5.6: EDS spectra of a) AgWN, b) TiO₂ on AgWN and c) sensitised TiO₂ on AgWN

5.3.3 XRD Analysis

The XRD spectra of TiO₂ on FTO showed peaks indexed to the 101, 004 and 211 planes of TiO₂ in anatase form (**Figure 5.7**). The film on FTO was also predominantly anatase with the 101 plane as the preferred orientation of TiO₂. Samples deposited at different deposition times and deposition voltages resulted in the same XRD spectra. This confirms that the preferred orientation of anatase on AgNW is 101. The diffraction peaks corresponding to the (101), (004), (200), (211) and (204) reflections, indexed within the anatase tetragonal TiO₂ crystal structure were observed in the XRD spectrum for TiO₂ on FTO substrate



Figure 5.7: XRD spectra of a) AgWN and TiO₂ on AgWN and b) FTO and TiO₂ on FTO

5.3.4 Optical Properties

The transmittance of the AgWN network was 82 % throughout the whole spectrum (from 300 to 1000 nm) as shown in **Figure 5.8**. FTO films showed superior optical transmittance than AgWN network in the visible region of the electromagnetic spectrum. The transmittance spectrum can boost the application of transparent Ag electrodes in solar cells through utilization of the very broad solar spectrum wavelength range.



Figure 5.8: XRD spectra of a) AgWN and TiO₂ on AgWN and b) FTO and TiO₂ on FTO

5.3.5 DSSC Performance

Figure 5.9 gives the measured current–voltage (I-V) characteristic of the DSSC performed at AM1.5 illumination. Table 5.1 summaries the photovoltaic parameters of the DSSCs

Cell	TCE	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
1	AgWN	0.38	0,089	25.7	0.0086
2	AgWN	0.072	0.026	30.5	0.00057
3	FTO	0.61	4.44	57.8	1.57
4 (RTIL)	AgWN	0.51	0,79	52.3	0.21

 Table 5.1:
 Photovoltaic parameters of the DSSCs

AaWN	0.50	0.85	52.3	0.23
/ grint	0.00	0,00	02.0	0.20
	AgWN	AgWN 0.50	AgWN 0.50 0,85	AgWN 0.50 0,85 52.3

From cell 1 an open circuit voltage V_{oc} of 0.38 V and a short circuit current I_{sc} of - 0.0067 mA with an efficiency of 0.0086 % were obtained from a cell is of 0.075 cm² working area. However, a relatively rapid degradation of the DSSC as a function of time was noticed. The instant the electrolyte was injected into the AgWN TCE based DSSCs, colour change was detected. Within 1 min, the electrolyte layer had become colourless, signifying the complete reduction of I_3^- to I^- and the subsequent oxidation of metallic Ag to release Ag⁺ ions. The overall reaction is represented by the following equation:

$$2Ag(s) + I_3^- \to 2Ag^+ + 3I^-$$
 (1)

The oxidation of Ag resulted in pitting corrosion as corrosion gaps appeared on the wire network ²²⁵. The bottoms of these gaps tend to be deprived of oxygen, and this promoted further growth of the gaps into the metal until the entire network was destroyed. The annihilation of the wire network which is the path for photogenerated electrons halts the photoconversion process rendering the cell 'dead'. Also the reduction of the tri-iodide into iodide decreased the number of charge carrying species in the electrolyte and also led to inferior device performance. A room temperature ionic electrolyte based DSSC showed improved PCE of 0.11%. These cells were very stable compared to the cells with iodine based electrolyte. The wire network was not affected. However, the fill factor of this cell was low indicating a high extent of electrical and electrochemical losses. These losses resulted from both the series resistance (Rs) and shunt resistance (Rsh). Rs in the solar cell is as a result of contact resistance and charge transfer resistance in the semiconductor material. Low shunt resistance provides an alternate current path for the photogenerated current causing a loss of the photogenerated electrons, resulting in significant power loss. Rsh needs to be improved and the Rs reduced to obtain a higher fill factor. This can be done by increasing the density of the AgWN on the PET therefore reducing the polygonal adjacent cells in between the wires which can act as alternative routes for electron transfer. Mechanical pressing of the TiO_2 layer after EPD should be done to improve adhesion of the nanoparticles with the substrates and contact between the nanoparticles. The cells prepared using the conventional method for fabricating DSSCs showed an efficiency of 1.57%.





5.4 Conclusion

Silver wire network transparent conducting polyethylene terephthalate substrates with a transmittance of 82% were fabricated and used as indium tin oxide alternative in DSSCs. TiO₂ films were deposited on the using the EPD technique. This method proved to be suitable for depositing TiO₂ on polymer flexible electrodes that do not stand high calcination temperatures. It also resulted in a crystalline porous TiO₂

structure which is critical for increasing surface are for dye loading. From the I-V characteristic measured at AM1.5 of the formed DSSC, an efficiency an open circuit voltage Voc of 0.377 V and a short circuit current lsc of -0.0889 with an efficiency of 0.00862 % were obtained from a cell is of 0.075 cm² working area. These results show that AgWN network substrates can be used as photoanodes of DSSCs. However, the cells degrade rapidly due to the corrosion of the AgWN network by iodine. The AgWN was stable in RTIL based electrolyte. This research study will open up possibilities for future optimisation studies of protecting the wire network from corrosion by the iodine species and possibly the use of iodine free electrolytes and room temperature ionic liquids. Further work should evaluate how the addition of nitrogen corrosion inhibitors like tert-butylpyridine (TBP) ²²⁵ can improve the corrosion resistance of AgWN in the presence of the electrolyte. Possibly metals that demonstrate stability in the presence of a iodine based electrolytes such as platinum, titanium and tungsten can be used to fabricate the wire network TCE. If the efficiency increases, the metal crackle network can reduce the use ITO substrates and the overall costs of DSSCs.

CHAPTER 6 FABRICATION OF GOLD NANOFIBER TRANSPARENT CONDUCTING ELECTRODE

Abstract

Transparent conducting gold nanofiber (AuNF) transparent conducting electrodes were fabricated by using a low-cost electrospinning process and used as photoelectrodes for DSSCs. TiO₂ was deposited on these electrodes by using the electrospray method. DSSC using AuNF as transparent electrodes have a power efficiency of 0.52%, compared to devices made with FTO electrodes (1.48%). DSSCs.

6.1 Introduction

Transparent conductive films are the key component of DSSCs. TCEs in DSSCs use transparent conducting oxides (TCOs), owing to their high electrical conductivity and optical transparency. One of the most widely used TCOs are indium tin oxide (ITO) and fluorine doped indium tin oxide (FTO) owing to their high transparency, low sheet resistance and ideal resistivity at room temperature. ⁴⁹ It also shows low transparency in the NIR region. In addition to the above disadvantages, FTO-based devices suffer from current leakage due to FTO structural defects. ⁵² To address these shortcomings and lower the costs of DSSCs much effort has been devoted to the investigation of novel indium tin oxide (ITO)–free electrodes. These alternatives should exhibit comparable sheet resistance to ITO at high transmittance and be cheap. Other interesting characteristics could be high flexibility, and lightweight so that they are compatible with flexible substrates of DSSCs.

Carbon nanotube networks, graphene, metal wire networks, conducting polymers, metal mesh and silver nanowires are emerging alternative conducting materials for ITO. Continuous metal thin films can be good substitutes for ITO since metals have a high free-electron density, and therefore show the highest conductivity among materials at room temperature. However, bulk metals are highly reflective in the visible range and do not function well as a transparent electrode. Decreasing the thickness of the metals to the nanometer range can make them more transparent enhancing their optical and conductivity properties. ²²⁶ This is one of the reasons metal nanowire transparent conducting film which consist of a web of interconnected nanowires of high-conductivity materials have comparable conductivity with the traditional TCF, ITO. ²²⁷ However the percolation critical density of nanowires (NWs) is usually lower than that of other competitive 1D nanomaterials such as CNTs. ²²⁸ This is because most solution processing methods of NWs result in short wires dramatically reducing their aspect ratios. Electrospinning method has been used to obtain long continuous nanofibers (NFs) with high aspect ratios and good conductivity. ²²⁹ The ultrahigh aspect ratios nanofibers result in high transmittance at low sheet resistance. ²³⁰ Wu et al. fabricated copper nanofibers with ultrahigh aspect ratios of up to 100 000 and fused crossing points with ultralow junction resistances, which resulted in high transmitance at low sheet resistance, e.g., 90% at 50 Ω /sg. ²³⁰ Ostermann demonstrated the use of nanofibrous mats of transparent conducting oxides (TCOs) as nanostructured electrodes for DSCs. ²³¹ The nanofibers were obtained by electrospinning suitable inorganic precursors and polymers, followed by calcination to remove the polymer.

Electrospinning provides a simple and versatile method for generating ultrathin fibers from a variety of materials that include polymers, composites, and ceramics. ²³² It is cheap, fast and allows deposition of TCFs on both glass and plastic substrates. It results in uniform diameter and long continuous NFs which cover the entire surface to ensure uninterrupted migration of electrons through the TCF. The loss of photogenerated electrons in the 1 dimension (1D) conductive film is much lower than in random networks. Also, electrospinning is conducted at room temperature with atmosphere conditions further reducing the production costs of nanofiber transparent conducting films (NF–TCFs). The density of the nanofiber networks can be easily controlled by adjusting the deposition time of the electrospinning process. In 1 dimensional (1D) NFs, the charge carriers transport primarily is unidirectional along the fibers. The NF network has a longer conduction path compared with random network which helps in slowing down the recombination of electrons and holes. Additionally, the large scattering of the metal nanofibers can

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enhance the solar cell performance due to an effective increase in the light absorption path length in the active layer. ²³⁰

Figure 6.1 shows a schematic illustration of the basic set up or electrospinning. It consists of three major components: a high-voltage power supply, a spinneret (a metallic needle), and a collector (a grounded conductor) usually a metal screen, plate, or rotating mandrel.



Figure 6.1: Schematic diagram of set up of electrospinning apparatus. ²³³

In electrospinning, a solid fibre is generated as the electrified jet (composed of a highly viscous polymer solution) is continuously stretched due to the electro-static repulsions between the surface charges and the evaporation of solvent. ²³² When the electric field applied reaches a critical value, the repulsive electrical forces overcome the surface tension forces. Eventually, a charged jet of the solution is ejected from the tip of the Taylor cone and an unstable and a rapid whipping of the jet occurs in the space between the capillary tip and collector which leads to evaporation of the solvent, leaving a polymer behind. ²³⁴

In this study electrospinning was used to deposit Au nanofibers on glass substrates which were then used as TCEs for DSSCs. Transparent conducting substrates made of a thin Au film were used as a comparison. The AuNF transparent conducting electrode based DSSCs had an efficiency of 0.5%.

6.2 Experimental

6.2.1 Materials and Instrumentation

TiO₂, powder (synthesis and characterization in chapter 3), flourine doped tin oxide (FTO)-coated glass substrate (10 per square, thickness 120m), Polystyrene average Mw ~192,000 and DMF were used as supplied by Aldrich chemicals Ltd. The ruthenium complex dye ruthenizer 535-bis TBA, iodolyte Z-100, Ti-Nanoxide T/SP and platisol T were purchased from Solaronix (Aubonne, Switzerland). Energy dispersive spectroscopy (EDS) was done on a Jeol JSM-5600 scanning electron microscope coupled to an EDX spectrometer, FTIR was performed on Spectrum 100 FTIR spectrometer, Raman analysis was recorded using a Bruker Vertex 70 Ram II Raman spectrometer exciting laser 800 nm and TEM images were obtained from an FEI G2 SPIRIT transmission electron microscope. The samples were further characterized using X-ray diffraction (XRD) with Cu K irradiation Bruker Discovery D8). Photo-electrochemical data were measured using a 450 W Xenon light source that was focused to give 1000 W/m² (the equivalent of one sun at air mass 1.5) at the surface of the test cell. The applied potential and measured cell current were measured using a Keithley model 2400 digital sources meter.

6.2.2 Preparation of AuNF-TCE

Glass substrates were cut into 2.5 by 2.5 pieces and cleaned with soap water, DI water and ethanol, dried with in a stream of N₂ gas. The process for fabricating AuNF TCEs was based on templating polymer nanofibers on glass substrates. In the first step, polymer nanofibre templates were prepared by means of electrospinning polystyrene (PS) onto a piece of quartz glass. Quartz was used as the substrate due to its transparency in the UV region. These substrates were cut into 2.5 by 2.5 mm pieces and cleaned with soap water, DI water and ethanol and then dried with a stream of N₂ gas. PS polymer was dissolved in DMF to make solution with an optimised concentration of 20 % by mass (m/v). The polymer

solution was stirred for 2 h in order to obtain homogeneous solutions after which it was placed in a medical syringe whose nozzle was flattened with tip diameter of 0.5 mm. A copper electrode was connected to a high voltage power supply, which can generate DC voltage up to 30 kV. The glass substrate was then placed on a flat metal plate with aluminium foil was placed below serving as a grounded counter electrode to collect the fibres. The polymer solution was forced through the syringe needle at 0.2 ml/h via a syringe pump (WZS-50F2, Zhejiang University Medical Instrument Co., Ltd, China). The voltage controlled by the high voltage power supply was performed at of 20 kV. The distance between the nozzle to target was 10 cm. The as-spun polymer layer was then used as a sacrificial template for the fabrication of AuNF–TCEs. A thin layer of Au metal (100 nm thick) was then deposited onto the template by sputtering using a Quorum (Q150RS) sputtering device. The final stage involved removal of the polymer template by soaking the glass substrates in DMF leaving the AuNF transparent conducting network. A gold layer TCF was used as a comparison. This Au film did not form a close contact with the glass substrates, and extra care was taken when handling these gold coated substrates.



Figure 6.2 Fabrication of AuNF-TCE

6.2.3 Electrospray Depostion of TiO₂ on AuNF-TCE

The fine dispersion of synthesised nanocrystalline TiO_2 nanoparticles in EtOH without surfactants and additives was electrosprayed directly onto AuNF substrates for DSSC photoelectrodes (**Figure 6.3**). AuNF substrates were first cleaned in acetone and then dried under a stream of N₂ gas. These substrates were then masked to create a working are of 0.25 cm². 1 wt% of titanium dioxide suspension

in ethanol was prepared, stirred for 2 h and loaded into a 10 ml syringe. The suspension was then pumped at flowrate of 5 ml/hr by using syringe pump. The input voltage of 20 kV was applied at the nozzle tip and counter electrode. Electrosprayed particles were deposited directly onto AuNF conducting films placed on the grounded aluminium plate substrate which was placed at 10-20 cm from counter electrode. These substrates were then dried at 50 °C in air for 2 h.



Figure 6.3 A schematic illustrating the setup and working mechanism of the electrospray process for the fabrication of microsized aggregates of TiO₂ nanocrystallites.²³⁵

6.3 Results and Discussion

6.3.1 SEM and EDS Analysis

The morphology of the polystyrene nanofibers observed by SEM is shown in Figure 1, which revealed an interconnected web nanofibre network on the glass substrates. The fibres were relatively uniform with small variations in diameter, and an average diameter of approximately 250 nm (**Figure 6.4**). In addition, the nanofiber sheet contained no microscopically identifiable beads. The polystyrene nanofiber template

was easily dissolved by DMF, leaving only the AuNF. The AuNFs maintained the morphology of the nanofiber network after the polystyrene template was dissolved (**Figure 6.4 b**). Calcination at 240 °C in air was first used to remove the polystyrene template, however, the polymer decomposition also resulted in splintering of AuNFs as shown in **Figure 6.4 c**. This led to loss of electrical connection between the fibres and wire-to-wire contact resistances of the AuNF film. An increase in deposition time of the NF resulted in an increased thickness of the NFs and an improved density of the fibres. However an increase in thickness reduced the transparency of the films.







Figure 6.4 SEM images of (a) PS nanofiber (b) AuNF PS template removed using DMF and (c) AUNF PS template removed by calcination

The removal of the polystyrene template was confirmed by the decrease in the intensity of the carbon peak as shown by EDS images in **Figure 6.5**.



Figure 6.5 EDS spectrum of (a) PS template (b) PS template + Au film and (c) AuNF

An electrospray deposition time of 5 min resulted in a thin uniform TiO₂ film on the AuNF substrates. The thickness of the film on FTO increased with increasing deposition time as can be seen from **Figure 6.6**. Films deposited for 30 minutes showed cracks and this film is not desirable for DSSC application. These results show that film thickness is tunable by varying the deposition time. **Figure 6.6 c** shows a high magnification image of electrosprayed TiO₂ film showing nearly spherical aggregated TiO₂ nanoparticles. Junting et al also obtained TiO₂ aggregates are desirable for DSSC application as they have a high internal surface area and the desired size for light scattering so as to enhance the light harvesting of the photoelectrode film. ¹⁴¹



Figure 6.6 FESEM images of electrosprayed TiO₂ AuNF–TCE after (a) 5 minutes, (b) 15 minutes (c) 30 minutes and (d) high magnification of TiO₂

6.3.2 Optical Properties

The transmittance spectra of Au film, AuNF with template and AuNF without template exhibited transmittance maxima at 542 nm, 503 nm and 498 nm respectively (**Figure 6.7**). The bathochromic shift shown by the AuNF before and after removal of template probably was due to change in the Au film from one continuous film to a discontinuous inhomogeneous nanofiber film. An increase in transmittance was observed after the PS template was removed indicating a decrease in the film thickness. The PS nanofiber network after etching of PS template shows transmittance minimum at 560 nm attributed to the surface plasmon

in the metal islands. Surface plasmons (SPs) arise from the interaction of light with free electrons at dielectric/metal interface. When incident light interact with metallic nanomaterials, the free electrons on the metal surface oscillate, resulting in excitation of SPs, propagating along the interface or confined to the metal particles. ²³⁶ Plasmon resonance depends on the film thickness and aspect ratio of the nanomaterials. In the coalescing Au film the localized plasmons–polaritons disappear due to the formation of islands with a continuous gold layer. ²³⁷ The surface plasmon resonance in the AuNF without template enhanced the electromagnetic field at the metal/dielectric interface which in turn improved infrared transmittance. ²³⁶ For solar cell applications, the transmittance in the near-infrared range is important because a significant amount of the solar energy that falls into this region. The transmittance spectrum can boost the application of transparent Au electrodes in solar cells through utilization of the very broad solar spectrum wavelength range.



Figure 6.7 Transmittance Spectra of PS template , Au film, AuNF (before and after template removal)

6.3.3 XRD Analysis

The XRD spectrum for Au film and AuNF showed two peaks at 20 values of 38.4° and 44.5° which correspond to (111) and (200) planes of face-centered gold (**Figure 6.8 a**). ²³⁸ The preferred orientation of the TiO₂ nanoparticles on the Au film was (004) diffraction peak suggesting dominant crystal growth along the [001] direction. ²³⁹ The [001] exposed facets are desirable materials for photoanodes as they are known to show high activity and large special surface area for excellent capacity of dye adsorption. ²⁴⁰ To investigate whether the type substrate used for the TCE does affect the orientation of the nanoparticles, two other substrates were used. The TiO₂ nanoparticles were oriented along the 101 plane in the AgWN and FTO substrates (**Figure 6.8 b**). At this moment the reason for the preferred orientation depending on TC on substrate is not fully understood and hence future studies are needed to investigate this phenomenon.



Figure 6.8 XRD patterns of TiO₂ on AuNF, AgWN and FTO.

6.3.4 DSSC Performance

DSSCs with Au nanofiber networks in which template was removed by etching in DMF showed a slightly improved efficiency when compared to the DSSCs with AuNF (template removed by calcination) and Au thin film (**Figure 6.9**). The challenge with the Au film based electrodes was delamination of gold coating off the glass substrate because the film did not form a close contact with the glass

substrates. Masking the substrates to create a working area for electrospray deposition of TiO₂ and also sensitisation delaminated the Au film even more. This decreased the conductivity of the film and resulted in low PCE of the cells. Future research should look into improving the adhesion of Au film onto glass substrates. This can be achieved by UV treatment of glass before gold deposition and deposition of a thin Ti layer between glass and Au coating. The AuNF where the template was removed by annealing showed a very low efficiency of 0.000005 %. These nanofibers were disrupted during annealing and this led to loss of electrical connection between the fibres and wire-to-wire contact resistances of the AuNF film.

Sample	J₅c (mA cm⁻²)	V _{oc} (V)	FF <i>(%)</i>	PCE (%)
Au film	0.32	0.37	0.42	0.099
AuNF (destroyed)	0.38	-0.00015	-0.016	0.000005
AuNF	0.35	0.37	0.40	0.52
FTO	0.49	0.56	0.57	1.59

Table 6.1:Photovoltaic characteristics of the AuNF based DSSCs



Figure 6.9 Current-voltage curves for cells based on Au film, AuNF template removed by calcination and AuNF removed by calcination.

6.4 Conclusion

Continuous metal nanofibers were fabricated using the electrospinning process and TiO₂ films were deposited using the electrospray deposition technique. This electrode was then used as a photoanode for DSSC. The electrospinning method demonstrated to be a fast and cost effective approach in fabricating transparent conducting electrodes for DSSCs. These gold nanofiber networks are good transparent electrode materials, with performances superior to the Au film based DSSCs in terms of transmittance and DSSC performance. All of these advantages should continue to expand and open up new applications for use of AuNF based transparent conducting electrodes as alternatives fto FTO and ITO TCEs

CHAPTER 7

SYNTHESIS OF DYAD AND REGENERATIVE SENSITISERS

Abstract

The boron dipyrrin (BODIPY) chromophore was combined with a carboxy coumarin moiety to create donor–acceptor (dyad) system dyes. Regenerative dyad dyes were formed through covalently linking a porphyrin chromophore to a manganese(II) ion through bridging ligands. These chromophores and also porphyrin and BODIPY dyes were used as sensitisers for DSCCs. The effect of the anchoring group on the BODIPY dye on the efficiency of the DSSCs was investigated. The carboxyl anchoring group BODIPY based DSSCs showing the highest efficiency. The regenerative dye based DSSCs showed a photoconversion efficiency of 4.09% which was higher than the efficiency of the parent porphyrin (2.57). The enhanced efficiency was attributed to the manganese bypridine cluster in the ZnTPP–Mn bpy supramolecule acted as an electron donor to the photo-oxidized porphyrin continuously regenerating the porphyrin and preventing its decay

Keywords: BODIPY dyes, donor–acceptor systems, regenerative dyad dyes DSSCs, Manganese ion, bridging ligands, dye decay

7.1 Introduction

In DSSCs, dye molecules are chemisorbed onto the semiconductor surface and are used to sensitize the semiconductor. Upon absorption of photon, a dye molecule gets oxidized and the excited electron is injected into the nanostructured TiO₂. Initial DSSCs employed organometallic compounds such as ruthenium (II)-based dyes and the showed a remarkable success with a conversion efficiency of 7.1 %. ²¹ The high efficiencies of the ruthenium(II)-polypyridyl DSSCs is attributed to their wide absorption range from the visible to the near-infrared regions of the electromagnetic spectrum. It is also possible to improve the optical properties of ruthenium polypyridyl systems by narrowing the HOMO and LUMO energy levels. The spectral response can also be enhanced in the red and near-IR region. For example

trithiocyanato-ruthenium(II) terpyridyl complex was synthesized by substitution of the terpyridyl ligand by three carboxyl groups in 4,4',4"-positions yielding a black dye. ¹⁰³ This dye displays very efficient panchromatic sensitization over the whole visible range extending into the near-IR region up to 920 nm. However, Rutheniumbased dyes are not biocompatible and this makes them environmentally unfriendly. Moreover Ru has a very limited supply in nature leading to high production costs of DSSC.

Recent developments on porphyrin-based solar cells exhibit a promising advance in finding alternative photosensitisers for DSSCs. Porphyrin sensitizers have excellent light-harvesting function mimicking photosynthesis. The other advantages of porphyrin-based dyes are their rigid molecular structures with large absorption coefficients in the visible region. Fine tuning of the optical, physical, electrochemical and photovoltaic properties of porphyrins thus is feasible as many reaction sites, i.e., four meso and eight b positions, are available for functionalization. Porphyrins show strong absorption in the visible region of the spectrum, and this is drawback for their use in photocurrent generation as the regions where the DSSCs can perform photoconversion are limited. Extending the absorption spectra of porphyrin dyes to the near infrared region is beneficial to DSSCs as it can lead to an increased photocurrent and overall efficiency. The inferior performance of porphyrin dyes is also attributed, in part, to I₃-porphyrin complex formation that increases the concentration of redox shuttle at the semiconductor surface. This then results in fast charge interception of injected electrons by the redox shuttle, and quenching of a fraction of the photoexcited dyes before injection can occur. Fast recombination of electron in semiconductor in semiconductor with hole in the dye is another downfall of many sensitisers.

Broadening the spectral response can be achieved by extending the π -conjugation of the dye molecule by introducing a highly conjugated π -extended chromophore to the dye to form a donor-acceptor unit (dyad system). The BODIPY chromophore has been used as an effective antenna group for porphyrins and phthalocyanines to form these systems. They have a high fluorescence quantum yield, long excited lifetimes, a suitable excited state energy, good solubility in many solvents and

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excellent photostability. A BODIPY–porphyrin conjugate, with an acetylide group as bridge, has recently shown improved power conversion efficiency, η , compared to its parent porphyrin chromophore when used as a sensitizer in a DSSC.

Dye decay results in low efficient solar cells. Constantly regenerating the dye reduces charge recombination and ensures continual generation of photocurrent. To address this problem, supramolecular assemblies composed of mononuclear metal polypyridyl complexes can be utilised. These assemblies are designed to transduce energy in one particular direction. Sun and coworkers successfully synthesized a binuclear ruthenium-manganese complexes where the manganese complex act as an electron donor to a photo-oxidized photosensitizer mimicking the intramolecular photoinduced electron transfer process from oxygen evolving center (OEC) to P_{680} ⁺ in the reaction center of PSII of photosynthetic plants. ¹¹⁴ The manganese cluster linked to the ruthenium bipyridyl chromophore continuously regenerates the photo-oxidized photosensitizer by intramolecular electron transfer from manganese cluster is necessary for slowing charge recombination. These self-regenerating dyes can be very useful in DSSC to ensure one way transfer of photogenerated electrons while preventing recombination.

In this research study dyad systems were created to address the above issues. Also the problem of quick dye decay was addressed by creating self–regenerative dyes. The dyad showed an enhanced efficiency than the BODIPY dye alone. The regenerative dye based DSSCs showed a photoconversion efficiency of 4.09% which was higher than the efficiency of the parent porphyrin (2.57%).

7.2 Experimental

7.2.1 Materials and Instrumentation

The reagents used in this project were supplied by Aldrich® and were used without further purification. Thin layer chromatography (TLC) was carried out using Merck silica gel 60 PF254 plates and were viewed under ultraviolet (UV) light, while Flash chromatography was carried out using Merck silica gel 60 (particle size 0.040-0.063)

mm). NMR spectra were recorded on Bruker 400 MHz AVANCE and Bruker Biospin 600 MHz spectrometers and were referenced using solvent signals (δ H: 7.26 ppm for CDCI3, 2.50 ppm for DMSO-d6; δ C: 77.0 ppm for CDCI3, 39.4 ppm for DMSO-*d*6). Signal assignment for some structures was achieved with the aid of NMR prediction software MestRecNova. Infrared spectra were acquired on a Perkin Elmer 100 FTIR Spectrometer. UV-vis and fluorescence spectra were recorded in a 1 cm path length quartz cell on a Cary 5 spectrophotometer and a Perkin Elmer lambda 25 UV/Vis spectrometer, respectively. CV experiments were performed at a scan rate of 20 mV/s at room temperature under nitrogen. The setup is computer controlled consisting of a potentiostat VoltaLab 40. The photocurrent-voltage (*J*–*V*) characteristics of the DSSCs were measured under AM 1.5 (100 mWcm⁻²) illumination which was provided by a Keithley 2420 3A grade solar simulator calibrated with a standard crystalline silicon solar cell. All geometries of the dyes are fully optimized by means of the density functional theory (DFT) calculations using the Gaussian 09 package at the B3LYP/6-31G(d) level.

7.2.2 Synthesis of Porphyrins 5,10,15,20–tetrakis (4–carboxyphenyl) porphyrin (H₂TCPP)

The metal free porphyrin; H₂TCPP was synthesised according to a procedure. ²⁴¹ The crude product was purified by flash chromatography [on silica gel; elution with ethyl acetate – hexane (3:2)]. The free base porphyrin (1 g, 1.27 mmol) and previously dried zinc chloride (0.5 g, 3.67 mmol) were refluxed in DMF for 3 h. A decrease in the number of Q bands from four to two in the absorption spectrum indicated successful metallation. The DMF solution was then cooled to room temperature and 0.1 M HCl added to the mixture to precipitate out the product, ZnTCPP. After filtration the residue was allowed to air dry. Yield 28 %, ATR–IR (cm⁻¹): 3324 (O-H) and 1719 (C=O), ¹H NMR (600 MHz, DMSO-d6) δ 8.50 (2H, b, Ar–H), 8.31 (1H, s, Ar–H), 8.27–8.12 (5H, b, Ar–H), 7.95–7.79 (8H, m, Ar–H), 7.51 (2H, m, Ar–H), 7.35–7.25 (4H, b, Ar–H), 7.11 (2H, m, Ar–H). UV–Vis (DMF) 421, 587, 550, m/z (ES⁺) 857.2 (M⁺).



Reaction Scheme 7.1: Synthesis and metallation of H₂TCPP

7.2.3 Synthesis of 4,4-difluoro-8-[4-carboxy]-1,3,5,7-tetramethyl-4-bora-3a,4a diaza-s-indacene (COOH–BODIPY)

Under an argon atmosphere 2,4-dimethylpyrrole 1 (205 mg, 2.16 mmol) and 4formylbenzoic acid (162 mg, 1.08 mmol) were dissolved in dry CH₂Cl₂ (100 mL). Then 1 drop of trifluoroacetic acid added to the reaction mixture, and stirred for about in the dark for 24 h under an argon atmosphere at room temperature. After the complete consumption (silica gel, CH₂Cl₂) of the aldehyde, a solution of DDQ in 20 mL CH₂Cl₂ was added dropwise. The mixture was stirred for 30 min, Et₃N (3 mL) was added and BF₃·OEt₂ (3 mL) were added slowly to the mixture in an ice bath. After the mixture was further stirred for 12 h it was filtered. The reaction mixture was concentrated under vacuo and purified by flash chromatography (silica gel, CH₂Cl₂) to trap unreacted organics. The fraction was concentrated and purified by column chromatography (silica gel, 3 Ethyl acetate: 2 Hexane) and evaporated to give a dark-red solid. Yield 15 %, ATR–IR (cm⁻¹): 2932 (O-H stretch), 1688 (C=O stretch), 1270(C-O stretch). 1H NMR (500 MHz, DMSO): 8.18 (d, 2H), 7.41 (d, 2H), 6.07 (s, 2H), 2.49 (s, 6H), 1.40 (s, 6H), m/z (ES⁺) 316.11 (M⁺).

7.2.4 Synthesis of 4,4-difluoro-8-[4-hydroxycoumarin]-1,3,5,7tetramethyl-4-bora-3a,4a diaza-s-indacene (OH–BODIPY)

Under an argon atmosphere 2,4-dimethylpyrrole 1 (205 mg, 2.16 mmol) and 4hydroxybenzaldehyde (132 mg, 1.08 mmol) were dissolved in dry CH₂Cl₂ (100 mL). Then 1 drop of trifluoroacetic acid added to the reaction mixture, and stirred for about in the dark for 24 h under an argon atmosphere at room temperature. After the complete consumption (silica gel, CH₂Cl₂) of aldehyde 2, a solution of DDQ in 20 mL CH₂Cl₂ was added dropwise. The mixture was stirred for 30 min, and Et₃N (3 mL) was added and BF₃-OEt₂ (3 mL) were added slowly to the mixture in an ice bath. After the mixture was further stirred for 12 h it was filtered. The reaction mixture was concentrated under vacuo and purified by flash chromatography (silica gel, CH₂Cl₂) to trap unreacted organics. The fraction was concentrated and purified by column chromatography (silica gel, 3 Ethyl acetate: 2 Hexane) and evaporated to give a dark-red solid. Yield 18 %, ATR–IR (cm⁻¹) (cm⁻¹): 3386 (O-H stretch), 1296 (C-O-H bend). ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.10 (m, 2H, Ar*H*), 6.92 (d, *J* = 8.6 Hz, 2H, Ar*H*), 2.43 (s, 6H, 2'- and 16'-C*H*₃), 2.08 (s, 1H, 18'-CH(Ar)₃), 1.41 (s, 6H, (2x Ar(1'-C*H*₃) and Ar(17'-C*H*₃)), m/z (ES⁺) 363.2 (M⁺).
7.2.5 Synthesis of 4,4-difluoro-8-[4-amino]-1,3,5,7-tetramethyl-4-bora-3a,4a diaza-s-indacene (NH₂–BODIPY)

4-nitrobenzaldehyde was first reduced to 4-aminobenzaldehyde by using Fe powder as follows. Iron powder (2.11g, 37.7 mmol) was added to a stirred solution of 4nitrobenzaldehyde (2g, 12.6 mmol) in acetic acid at 110 °C with continued stirring. After 1 hour, TLC showed the commencement of formation of the product and the reaction was allowed to run for 12 h. The reaction mixture was then cooled to room temperature and the acetic acid removed in vacuo. Ethyl acetate was then added to the residue and the resulting mixture stirred and filtered to remove the insoluble iron powder. The residue was washed with ethyl acetate and the washings combined with the filtrate. The solvent was removed in vacuo and the crude product purified by column chromatography using hexane:EtOAc (1:1) as the eluent. Then the synthesis of the BODIPY was carried out as outlined in Section 7.2 . The target product was obtained by column chromatography on silica gel using a hexane/ethyl acetate (1:1, v:v) system as an orange solid. Yield 28 %, ATR–IR (cm⁻¹) (cm⁻¹): 2986 (N-H stretch), 1693 (N-H in plane bend), 501, 1296, 1186, 1152 (C-N-C), . m/z (ES⁺) 469.8 (M⁺).



Reaction Scheme 7.2:





Reaction Scheme 7.3: General synthesis of BODIPY dyes

7.2.6 Synthesis of Carboxy Coumarin

Carboxycoumarin was synthesised from Meldrum's acid. For Meldrum's Acid Malonic acid (5.2g, 4909 mmol), concentrated H_2SO_4 (10-15 drops) and acetic anhydride (5.1 g, 50.0 mmol) were stirred at 60 °C for 30 mins. The mixture was allowed to cool to room temperature, and acetone was added dropwise for 30 mins. The resulting mixture was stirred for 1 hour. After cooling to room temperature, the mixture was pit in a fridge to effect precipitation.

Meldrum's acid (72.1 mg, 0.5mmol) and salicyladehyde (67.2 mmol, 0.55 mmol) were put in a flask and Et₃N (0.015 mmol) and 50 µL water added. The mixture was allowed to heat under reflux for 4 h. After completion of reaction, 3 mL aqueous ethanol was added and the mixture vigorously stirred for a 2 mins. The pH was adjusted to 2 with dilute HCI. The precipitate was filtered and washed with aqueous ethanol. NMR spectrum shown in the Appendix.



Reaction Scheme 7.4: synthesis of carboxy coumarin

7.2.7 Synthesis of Donor–Acceptor Dyes

This dye was prepared by conjugating a donor carboxy coumarin an OH–BODIPY dye (acceptor) to via an ester bridge to yield a BODIPY–Carboxy Coumarin dyad (B–C dyad). Carboxy coumarin (16.6 mg, mmol) and by OH–BODIPY (51.3 mg, 0.15 mmol) were conjugated by esterification. 3 drops of HCI was added to a solution of coumarin and bodipy in THF. The mixture was heated under reflux for 4 h and then cooled to room temperature. The solvent was removed in vacuo to yield the pure product. Yield: 100%, ATR–IR (cm⁻¹) 1740 (ester C=O). NMR spectrum shown in the Appendix.



Reaction Scheme 7.4: Synthesis of B– C dyad

7.2.8 Synthesis of Regenerative Dyes

Regenerative dyes were synthesised by conjugating porphyrins and BODIPY dyes to manganese bipyridine complexes. 2,2'-Bipyridine is a bidentate chelating ligand, forming complexes with many transition metals.

7.2.9 Synthesis of 4,4'-diamino-2,2'-bipyridine

4,4'-diamino-2,2'-bipyridine (Lig 2) was synthesized from 2,2'-bipyridine (Lig 1). Hydrogen peroxide (27.5 % in water, 15 m) was added to a solution of 2,2'-bipyridine (6 g, 38.4 mmol) in glacial acetic acid (40 mL) at 75 C. After stirring for 5 h, another portion of H₂O₂ (10 mL) was added and the solution was stirred for another 8 h. The reaction was allowed to cool to room temperature and then acetone (400 mL) was added and the precipitate formed was filtered and air dried to give 90% yield of 2,2'bipyridine N,N-dioxide as white crystals. This ligand was insoluble in NMR solvents, and hence NMR analysis was not done. ATR-IR (cm⁻¹): 1253 (N–O), m/z (ES⁺) 189.1 (M⁺).

2,2'-bipyridine N,N-dioxide was nitrified to give 4,4'-dinitro-2,2'-bipyridine N,Ndioxide (Lig 3). Concentrated sulphuric acid (98%, 7.2mL) was added to 2,2'bipyridine N,N-dioxide (1.5 g, 8 mmol). The mixture was cooled to 0 °C and fuming nitric acid (90%, 2.5 mL) was added and the mixture was heated under reflux for 20h. The mixture was cooled to room temperature and then poured onto ice-water mixture at -40 °C. A bright yellow precipitate formed and the solution was filtered and the yellow precipitate collected and washed with 3 x 25mL of water and allowed to air dry. ATR–IR (cm⁻¹): 1510 (NO₂), 1340 (NO₂) and 1290 (N–O) cm⁻¹, ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.68 (d, J = 3.42 Hz), 8.58 (d, J = 7.32 Hz) and 8.36 (dd, J = 2.93 Hz).

The reduction of 4,4'-dinitro-2,2'-bipyridine N,N-dioxide was done using hydrazine hydrate and Pd/C (10%) as catalyst according to a procedure by Kavanagh et.al. The yellow precipitate washed with 6 x 30 mL cold water to remove hydrazine hydrate, then soaked in water (80 mL) and left at 4 °C overnight. The white powder was collected by vacuum filtration, washed with cold water and dried at room temperature to give 4,4'-diamino-2,2'-bipyridine (Lig 4). ATR-IR (cm⁻¹): 3450 (NH₂) and 1635 (NH) cm⁻¹, ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.01 (d, J = 4.88), 7.52 (s), 6.43 (d, J = 3.91)



Reaction Scheme 7.5: Synthesis of 4,4'-diamino-2,2'-bipyridine

7.2.10 Synthesis of Manganese bypridine complex

The precursor complex Mn(II)(bpy)(NH₂)₂Cl₂.2H₂O, (Mn bpy cpx) was prepared by refluxing manganese(II) chloride tetrahydrate solution in methanol together with a molar equivalent of 4,4'-diamino-2,2'-bipyridine ligand for 6 h. After the solution

was cooled to room temperature, a crystalline solid was obtained by filtration, washed with cold methanol, and dried for 4 h in vacuum at 40 °C. Mn (II) is paramagnetic, therefore this complex could not be observed on ¹H NMR. ATR–IR (cm⁻¹): 3450 (NH₂) and 1635 (NH) cm⁻¹, m/z (ES⁺) 531.35 (M⁺).



Reaction Scheme 7.6: Synthesis of Mn bpy cpx

7.2.11 Synthesis of Porphyrin Bipyridyl Regenerative Dye (H₂TCPP–Mn bpy)

N–ethyl–N'–(dimethylaminopropyl)carbodiimde hydrochloride (EDC.HCl) (11.5 mg, 0.06mmol) and N,N'–didisopropylethylamine (22 μ l, 0.125 mmol)) were added to a solution of H₂TCPP, (chromophore) (34.24 mg, 0.4mmol) and Mn bpy cpx (18.20 mg, 0.05 mmol) and 1-hydroxybenzotriazole hydrate (HOBt.H₂O) (8.11 mg, 0.06mmol) in dry dimethylformamide ((3mL) and stirred for 36 h at room temperature under nitrogen. The solvent was removed in vacuo. ATR–IR (cm⁻¹): 3334 (N-H stretch asymmetric), 3180 (N-H stretch symmetric), and 1688 (N-H bend), m/z (ES⁺) 1012.5 (M⁺).



Reaction Scheme 7.7: Synthesis of ZnTCPP-Mn bpy

7.3 Fabrication of DSSCs

TiO₂ paste was applied onto clean FTO substrates by doctor blading to create a 0.25 cm² working area and sintered at 500°C. These TiO₂ coated substrates were then sensitised with each of the synthesised dyes 24 h. The cathode was prepared by brush coating a Pt catalyst onto an FTO substrate. This was followed by calcination at 380 °C for 20 mins and cooling in ambient temperature to 70 °C. A sandwich model solar cell was assembled by first placing a transparent counter electrode on top of a working electrode. In the sealed solar cells, the electrodes were separated using a thermoplastic thin film as a spacer. The electrolyte was then injected into the cell and two binder clips used to hold the electrodes together.

7.4 Results and Discussion

7.4.1 FTIR Analysis

The FTIR spectra of OH–BODIPY, NH₂–BODIPY and COOH–BODIPY are shown in **Figure 7.1** OH–BODIPY exhibited an OH vibration peak at 3344 cm⁻¹, NH₂– BODIPY showed amine characteristic peaks at 2986 (N-H stretch), 1693 cm⁻¹ (N-H in plane bend). The peaks 2932 (O-H stretch), 1688 cm⁻¹ (C=O stretch), 1270(C-O stretch) were observed in COOH–BODIPY. The B-F vibration was observed at 1525 cm for all the BODIPY dyes.



Figure 7.1 FTIR spectrum of BODIPY dyes

The successful conjugation of the OH–BODIPY to the carboxy coumarin was confirmed by the ester C=O peak at 1740 cm⁻¹ (**Figure 7.2**).



Figure 7.2 FTIR spectra of COOH coumarin, OH–BODIPY and B–C dyad

The infrared spectra of compound the ligands are shown in **Figure 7.3**. The 2,2 – bpypidine based absorption peaks were observed at 836, 775, 732, and 695 cm ⁻¹ and were almost all present in all the ligands, with Lig 2 having the most intense peaks. In the spectrum for Lig 2, the peak at 1253 cm-1 indicated an N–O stretching vibration confirming the successful synthesis of the ligand. The N–O stretching vibrations in Lig 3 occurred near 1494 cm⁻¹ (asymmetrical) and 1354 cm⁻¹ (symmetrical). The N-H stretch at 3447 N-H in-plane-bend at 1628 cm⁻¹ indicated the reduction of Lig 3.



Figure 7.3 FTIR spectra of ligands

The successful amide conjugation of ZnTPP to Mn bpy cpx was indicated by the following FTIR peaks 3334 (N-H stretch asymmetric), 3180 (N-H stretch symmetric), and 1688 (N-H bend) which are characteristic of amide bond (**Figure 7.4**).



Figure 7.4 FTIR spectrum of ZnTPP, Mn bpy cpx and ZnTPP–Mn bpy cpx

7.4.2 Photophysical Properties

Free base and metallated poprhyrin chromophores exhibited intense Soret bands at ca. 420 nm. In ZnTCPP the 4 Q bands Qx(0,0), Qy(0,0), Qx(1,0) and Qy(1,0) are reduced into 2 Q bands, [Q(0,0) and Q(1,0)] indicating the degeneracy of the X and Y components of the excited state (**Figure 7.5**). The electronic spectrum of all bodipy dyes showed intense absorption bands at ca.500 nm attributed to the lowest energy spin-allowed $\pi - \pi^*$ transition of the BODIPY moiety. Absorption bands of lower intensity in the 280–380 nm region attributed to higher energy $\pi - \pi^*$ transitions of the Bodipy group were also observed.



Figure 7.5 UV–vis spectra a) H₂TPP and ZnTPP and b) BODIPY dyes

The absorption spectrum of carboxycoumarin in methanol showed a maximum absorption band at 288 nm and 320 nm due to the $\pi - \pi^*$ transition (**Figure 7.6**). The spectrum of the dyad showed a sum of the constituent parent chromophores indicating that the BODIPY and coumarin moieties in the conjugate do not show significant ground state interactions. ²⁴² Also the absorption band of the coumarin dye is blue-shifted by 20 nm indicating extended π –conjugation. ¹⁰⁷ The spectral response was enhanced in the visible and infrared regions as shown by the appearance of additional bands at 423, 557 and 593nm. The band at 423 nm was attributed to the intramolecular charge transfer (ICT) from the donor to the acceptor, providing efficient charge-separation at the excited state.



Figure 7.6 UV-vis spectra of OH BODIPY, COOH coumarin and B-C dyad

The electronic spectrum of NH₂ bpy ligand gave an absorption band at 272 nm attributed to ligand centred $\pi \rightarrow \pi^*$ transitions of the bpy ligand. ²⁴³ The Mn bpy complex showed a broad metal to ligand charge transfer (MLCT) absorption shoulder with λ_{max} at 300 nm which confirmed the formation of the complex. After conjugation of the complex with H₂TPP, the spectrum appear to possess only porphyrin character, but close examination of the spectrum revealed that the Soret band of H₂TPP in the conjugate showed a red shift of 9 nm compared to the parent porphyrin, while the Q bands exhibited a blue shift. The Soret band also broadened slightly due to the presence of the metal to ligand charge transfer under the Soret. ¹² These changes were also as a result of the increased conjugation of the bypyridine–porphyrin system.



Figure 7.7 UV–vis of a) Lig 4 and Mn bpy cpx and b) Mn bpy cpx, H₂TPP and H₂TCPP–Mn bpy

7.4.3 Electrochemistry of Chromophores

Energy levels of sensitizers are crucial to judge the possibilities of electron injection from the excited dyes to the conductor band of TiO₂ and dyes regeneration by the iodide/triiodide electrolyte. The electrochemical properties of these sensitizers were measured using cyclic voltammetry (CV) in CH₂Cl₂ solution containing 0.1 M TBAPF6 as supporting electrolyte. All potentials reported are calibrated with Fc/Fc⁺ as an external reference. Cyclic voltammetry results of the some sensitisers are shown in **Table 7.1**. The results obtained from these data are summarized in Table 1, showing the oxidation/reduction bands of these compounds and the HOMO–LUMO.

The LUMO for both B–C dyad and H₂TCPP–Mn bpy are more negative than the CB edge of TiO₂ (–0.5 V vs NHE), ensuring an efficient electron injection process from the excited state of the dyes into the TiO₂ electrode. In addition the ground- state oxidation potentials are sufficiently positive compared with that of the I⁻/I₃⁻redox couples (-0.42V vs NHE) indicated that regeneration of the dyes is thermodynamically feasible. In the B-C dyad, the double reduction peaks at 0.35 and ⁻0.156 V are likely to be associated with the reduction of the OH–BODIPY unit and COOH coumarin respectively. The introduction of the acceptor to OH-BODIPY resulted in a more negative HOMO and increased the LUMO energies inducing a

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faster electron injection from the dyad into CB of TiO₂. In the H₂TCPP–Mn bpy sensitiser the first reduction peak at $^{-}0.65$ V correspond to the reduction of ZnTPP Mn bpy while the second peak at 0.65 V was assigned to metal-based oxidation at (Mn ²⁺/Mn³⁺). The more negative oxidation potential for H₂TCPP–Mn bpy facilitated electron transfer from the manganese complex to the porphyrin in the conjugate. In this way regeneration of the porphyrin π -cation radical occurred upon photoexcitation of the complex.

Table 7.1:Electrochemical data for sensitisers and HOMO-LUMO gapscalculated from cyclic voltammetry

Sensitiser	E _{ox} (volts)	E _{red} (volts)	E _{номо} (eV)	E _{LUMO} (eV)	Electrochemical
					Eg(eV)
OH-BODIPY	0.33	0.053	-4.84	-5.17	0.34
COOH coumarin		0.61	-5.41		
B–C dyad	0.24	-0.16 0.035	-5.04	-4.64	0.4
Mn cpx	0.789	0.52 -0.52	-5.59	-5.32 -4.38	0.27
H₂TCPP-Mn bpy	0.58	0.69 -0.65	-5.38	-4.86 -4.15	0.52
		lated by the fo	nmula E HOMO		ox(red) + 1 80) Eox(red)

HOMO(LUMO) level was calculated by the formula E $^{HOMO(LUMO)} = -(E_{onset}^{ox(red)} + 4.80)$, $E_{onset}^{ox(red)}$ values are shown in the brackets.

Electrochemical HOMO-LUMO gap was calculated as a difference between HOMO and LUMO levels.



Figure 7.8 Current-voltage curves for cells based on Au film, AuNF template removed by calcination and AuNF removed by calcination.

7.4.4 DSSC Perfomance

The current–voltage curves of DSSCs based on the different dyes synthesised simulated AM 1.5G illumination (100 mW cm⁻²) were measured and shown in **Figure. 7.9**. The corresponding short-circuit currents (J_{sc}), open-circuit potentials (V_{oc}), fill factors (FF), and overall conversion efficiencies (η) are summarized in **Table 7.2**.

Table 7.2:Photovoltaic characteristics of the DSSC based on TiO2 and
Ce doped TiO2 photoanodes

Sample	J _{sc} (mA cm⁻²)	V _{oc} (V)	ff (%)	PCE (%)
NH ₂ BODIPY	4.44	0.61	57.81	1.57
OH–BODIPY	3.33	0,61	62.24	1.27
COOH BODIPY	7.69	0.65	49.04	2.47
COOH coumarin	0.86	0.50	52.43	0.23
BC dyad	11.5	0.67	50.32	3.89
ZnTPP	8.52	0.66	44.26	2.57
H₂TCPP–Mn bpy	12.06	0.68	49.76	4.09

COOH–BODIPY based DSSC showed the highest PCE when compared to NH_2 – BODIPY and OH–BODIPY based cells (**Figure 7.10**). These results indicate that the nature of the anchoring group has an effect on the PCE of DSSCs. The COOH anchoring group improves the binding nature of the dye with TiO₂, forms excellent adsorption geometry with the semiconductor and increases the amount of dye molecules adsorbed onto TiO₂. ²⁴⁴ As a result electron directionality from the excited dye is enhanced which facilitates electron transfer from the excited dye to TiO₂ and suppresses recombination of holes and electrons. The carboxyl group also ease the perpendicular localization of dye molecules of dye molecules onto the TiO₂ surface for efficient electron injection. ²⁴⁵. Luschtinetz et. al. conducted an investigation on the binding mode of COOH onto TiO₂ and their work suggested that the most stable adsorption configuration on the anatase TiO₂ (101) surface is that of a bidentate structure. ²⁴⁶ The bidentate model led to faster injection times from dyes to TiO₂ and hence the increase PCE for COOH–BODIPY. The OH–BODIPY showed a low PCE because the hydroxyl group has a negligible adsorption on TiO₂ surfaces.



Figure 7.10 Current-voltage curves for BODIPY based cells

The efficiency of the B–C dyad based DSSCs was higher than OH–BODIPY cells (**Figure 7.13**). The introduction of the COOH–coumarin to the OH–BODIPY broadened the spectral response of the resultant sensitizer. The HOMO energy of the dyad was more negative than the one for the OH–BODIPY and also the LUMO energy increased inducing a faster and one directional electron injection from the acceptor (COOH coumarin) into CB of TiO₂. The alignment of the conduction band and the LUMO of the dye led to an improved driving force of injected electrons from the LUMO of the dye to the conduction band of TiO₂, increasing Jsc. ¹⁷⁷ This minimized the recombination of electrons. Intramolecular photoinduced electron

transfer from the BODIPY to the coumarin (**Figure 7.12**) led to stable charge separated states that facilitated the electron injection into the TiO₂ conduction band. **Figure 7.11** shows the sequential steps for PET and CS in the dyad system.







Figure 7.12 PET in the dyad system



Figure 7.13 Current-voltage curves for COOH coumarin, OH–BODIPY and B–C dyad based DSSCs

The H₂TCPP–Mn bpy based DSSCs showed an enhanced PCE than the H₂TCPP based ones (**Figure 7.15**). Covalently linking the Mn bpy complex to the porphyrin extended the conjugation of the resulting chromophore, broadened the spectral response and improved the light harvesting properties of the DSSCs. This resulted in an improved PCE of the DSSCs. The manganese bypridine cluster in the H₂TCPP–Mn bpy supramolecule acts as an electron donor to the photo-oxidized porphyrin. The cluster continuously regenerates the porphyrin preventing its decay (**Figure 7.14**). In this way the manganese cluster mimicks the intramolecular photoinduced electron transfer process from oxygen evolving center (OEC) to P₆₈₀⁺ in the reaction center of PSII of photosynthetic plants. ¹¹⁴ Constantly regenerating the dye speeds up the rate of electron transfer from the porphyrin to the TiO₂ semiconductor, improves photocurrent generation while reducing charge recombination.



Figure 7.14 PET in and dye regeneration in H₂TCPP–Mn bpy



Figure 7.15 Current-voltage curves for H₂TCPP and H₂TPP Mn bpy based DSSCs.

7.5 Conclusion

Co–sensitisation of the boron dipyrrin (BODIPY) chromophore with a carboxy coumarin moiety to create donor–acceptor (dyad) system dyes resulted in an improved efficiency of the DSSCs when compare to the BODIPY alone The enhancement was due to the broad spectral response of the dyad system. The HOMO energy of the dyad was more negative than the one for the OH–BODIPY and also the LUMO energy increased inducing a faster and one directional electron injection from the acceptor (COOH coumarin) into CB of TiO₂.Regenerative dyad dyes were formed through covalently linking a porphyrin chromophore to a manganese(II) ion through bridging ligands. The carboxyl anchoring group BODIPY based DSSCs showing the highest efficiency. The regenerative dye based DSSCs showed a photoconversion efficiency of 4.09% which was higher than the efficiency of the parent porphyrin (2.57%). The enhanced efficiency was attributed to the manganese bypridine cluster in the H₂TCPP–Mn bpy supramolecule which acted as an electron donor to the photo–oxidized porphyrin continuously regenerating the porphyrin and preventing its decay.

CHAPTER 8 CONCLUSIONS AND FUTURE PERSPECTIVES

8.1 Conclusions

The main thrust of this research study was to design and optimise the components of the DSSCs to produce cells with improved synergistic working of the individual components. The study has shown that cerium doping in TiO₂ enhances the photoconversion efficiency of DSSC with 0.9% Ce content giving a maximum efficiency. The enhancement was attributed to band gap narrowing caused by the introduction of Ce 4f levels into the crystal structure of TiO₂. This led to improved driving force of injected electrons from the LUMO of the dye to the conduction band of TiO₂, high dye loading, accelerated transfer rate of electrons and reduced charge recombination.

The mobility of photogenerated electrons of TiO₂ was improved by anchoring TiO₂ nanoparticles onto graphitised structures to form nanocomposites. The nanocomposites were synthesised using a sol-gel method and deposited electrophoretically onto FTO electrodes for application as photoelectrodes in dye-sensitized solar cells. The close interfacial contact between the graphitised nanosheets and TiO₂ nanoparticles was proposed to enhance the mobility of photogenerated electrons on TiO₂ to GO, leading to efficient separation and suppressed recombination time of charge carriers.

One of the more significant highlight of the study was fabricating flexible ITO–free electrodes. The silver wire network transparent conducting film had a transmittance of 82% throughout the whole spectrum (from 300 to 1000 nm). EPD method proved to be suitable for depositing TiO₂ on polymer flexible electrodes that do not stand high calcination temperatures. It also resulted in a crystalline porous TiO₂ structure which is critical for increasing surface are for dye loading. From the I-V characteristic measured at AM1.5 of the formed DSSC, an efficiency an open circuit voltage V_{oc} of 0.377 V and a short circuit current I_{sc} of -0.0889 with an efficiency of 0.00862 % were obtained from a cell is of 0.075 cm² working area. These results show that AgWN network substrates can be used as photoanodes of DSSCs. However, the cells degrade rapidly due to the corrosion of the AgWN network by iodine. RTILs did not destroy the AgWN and gave an efficiency of 0.23%.

Continuous metal nanofibers were fabricated using the electrospinning process and TiO₂ films were deposited using the electrospray deposition technique. This electrode was then used as a photoanode for DSSC. The electrospinning method demonstrated to be a fast and cost effective approach in fabricating transparent conducting electrodes for DSSCs.

Co–sensitisation of the boron dipyrrin (BODIPY) chromophore with a carboxy coumarin moiety to create donor–acceptor (dyad) system dyes resulted in an improved efficiency of the DSSCs when compare to the BODIPY alone The enhancement was due to the broad spectral response of the dyad system. The HOMO energy of the dyad was more negative than the one for the OH–BODIPY and also the LUMO energy increased inducing a faster and one directional electron injection from the acceptor (COOH coumarin) into CB of TiO₂.Regenerative dyad dyes were formed through covalently linking a porphyrin chromophore to a manganese(II) ion through bridging ligands. The carboxyl anchoring group BODIPY based DSSCs showing the highest efficiency. The regenerative dye based DSSCs showed a photoconversion efficiency of 4.09% which was higher than the efficiency of the parent porphyrin (2.57%). The enhanced efficiency was attributed to the manganese bypridine cluster in the ZnTPP–Mn bpy supramolecule acted as an electron donor to the photo–oxidized porphyrin continuously regenerating the porphyrin and preventing its decay

Table 8.1 shows a summary of the photovoltaic parameters of different modified components of DSSCs.

Table 8.1:Summary of photovoltaic parameters of different modified
commponents of DSSCs

Sample	J _{sc}	<i>V</i> _{oc} (V)	FF <i>(%)</i>	PCE (%)
	(mA cm⁻²)			
TiO ₂	0.79	0.51	52.27	0.21
0.1 Ce	2.84	0.59	63.8	1.08
0.5 Ce	3.3	0.67	62.2	1.54
0.9 Ce	7.69	0,67	49.5	2.11
1 Ce	4.34	0.61	58.8	1.52
0.1 GO	0.51	0.55	57.1	1.59
0.3 GO	0.67	0.56	44.3	1.69
0.5 GO	0.73	0.65	45.2	2.25
0.7 GO	0.49	0.54	57.1	1.73
0.5 GO/0.9 Ce	0.98	0.61	45.2	2.45
0.5 rGO	6.57	0.36	33.3	2.57
0.5 rGO 0.9 Ce	6.57	0.35	35.2	3.85
AgWN	0.38	0,089	25.7	0.0086
AgWN	0.072	0.026	30.5	0.00057
FTO	0.61	4.44	57.8	1.57
AgWN (RTIL)	0.51	0,79	52.3	0.21
AgWN (RTIL)	0.50	0,85	52.3	0.23

Au film	0.32	0.37	0.42	0.099
AuNF (destroyed)	0.38	-0.00015	-0.016	0.000005
AuNF	0.35	0.37	0.40	0.52
FTO	0.49	0.56	0.57	1.59
NH ₂ BODIPY	4,44	0.61	57,81	1.57
OH-BODIPY	3.33	0,61	62,24	1.27
COOH BODIPY	7,69	0.65	49,04	2.47
COOH coumarin	0,86	0,50	52,43	0.23
BC dyad	11,5	0.67	50.32	3,89
ZnTPP	8,52	0.66	44,26	2.57
H ₂ TCPP–Mn bpy	12,06	0.68	49,76	4.09

8.2 Future Perspectives

The findings of the study provide the following insights for future research

Effort should be devoted to the investigation of novel ITO-free electrodes that exhibit comparable sheet resistance to ITO at high transmittance and be cheap. Other interesting characteristics could be high flexibility, and lightweight so that they are compatible with flexible substrates of DSSCs. AgWN exhibit these characteristics but easily corroded by iodine based electrolytes.

- Further work should evaluate how the addition of nitrogen corrosion inhibitors like tert-butylpyridine (TBP) can improve the corrosion resistance of AgWN in the presence of the electrolyte. The use of iodine free electrolytes and room temperature ionic liquids should be investigated. Metals that demonstrate stability in the presence of iodine based electrolytes such as platinum, titanium and tungsten can be used to fabricate the wire network TCE. If the efficiency increases, the metal crackle network can reduce the use ITO substrates and the overall costs of DSSCs.
- Time resolved fluorescence and laser flash photolysis studies need to be conducted in order to determine the fluorescence lifetimes and rate of electron transfer systems of the dyad and the regenerative dyes. This information would determine characteristic timescales of the PET and hence the efficiency of the dyes.
- Synthesis of regenerative dyes with more than one manganese cluster covalently linked to the chromophore. This will determine if the number of clusters affect the regeneration of the chromophore.
- Computational chemistry and quantum dynamics studies need to be done for all the components of the DSSC to investigate the synergy of these components on the device performance. Theoretical studies will also help identify dyes with broad adsorption spectra and favourable electron transfer from the photoexcited dye to the semiconductor.



Figure 8.1 ¹H NMR spectrum of OH–BODIPY



Figure 8.2 ¹H NMR spectrum of COOH coumarin



Figure 8.3 ¹H NMR spectrum of B–C dyad



Figure 8.4 ¹³C NMR spectrum of B–C dyad















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