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Mesoporous Titania Beads for use in Dye-Sensitized Solar Cells

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Abstract

A range of titanium dioxide (titania) samples provided by Huntsman Pigments and Additives were investigated for their suitability for use in various optoelectronic devices, specifically dye-sensitized solar cells (DSSCs). Five of the titania samples are 1-20 micrometre size spherical 3D porous beads made up of titania nanoparticles and a further six samples are porous titania nanoparticle clusters of no specific shape, all of which possess high surface areas from 85 to 276 m² g⁻¹. The samples were compared to commercially available nanocrystalline TiO₂ powders and paste. All of the samples were initially assessed for suitability in DSSC devices by investigating various properties such as crystal phase, particle size, band gap, morphology and N719 dye adsorption, both as a powder sample and as a sintered film, employing techniques such as powder x-ray diffraction, UV/Vis spectroscopy and scanning electron microscopy. Different methods of formulating the samples into pastes for application to a substrate were attempted and electrochemical properties of a selection of films were also compared. The more promising titania samples were formulated into dye-sensitized solar cells and cell efficiencies calculated. DSSC devices were also fabricated with low temperature (125°C) sintering of the titania layer to assess the suitability of the samples for use in devices with flexible substrates. Initial devices incorporating the Huntsman TiO₂ samples provided low efficiencies (< 0.1%). The samples were then modified with pre-sintering treatment prior to paste formulation to optimize crystallinity, particle size, porosity and surface area. The modified titania bead samples showed great promise in low temperature sintered devices, providing device efficiencies of 2.8%, more than double that of those incorporating the standard P25 TiO₂ (1.3%). After sample modification a superior solar cell performance (3.2%) was also observed in 510°C sintered devices when compared to the standard P25 TiO₂ devices (2.9%), with higher photocurrent and open circuit voltage than devices fabricated from commercially optimized TiO₂ paste. Devices were also fabricated using pre-sensitized titania in an attempt to reduce device manufacturing time. The modified samples again showed good performance, providing working devices with efficiencies comparable to the equivalent pre-sensitized P25 devices.
Declaration

I hereby declare that this thesis was composed by myself and the work presented is entirely my own except where clearly indicated in the acknowledgements, references or text. This work has not been submitted for any other degree or professional qualification.

John Mallows
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Chapter 1. Introduction

1.1 Energy Needs & Solar Solutions

1.1.1 Energy Crisis

Worldwide power requirements are increasing, rising 12% from around 16 TW to over 18 TW between 2009 and 2014, while continued use of fossil fuels is both expensive and has caused carbon dioxide levels to rise dramatically in recent history to currently high levels above 400 ppm. The need for cheaper, cleaner, renewable energy sources is therefore essential. Various alternative sources of energy are currently being implemented, such as nuclear. However due to the need for clean and renewable energy, wind, tidal and in particular solar energy are attracting great interest. While it is prudent to develop all potential renewable energy sources, solar energy shows a greater potential for future energy production than all other renewable sources. The estimated total potential of annual energy production for various renewable sources is shown in Figure 1.1. While it is unrealistic to expect to achieve the maximum realistic exploitable potential for each resource as is shown in the values, achieving just a small fraction of the potential solar resources would clearly have a huge impact on future energy solutions.
1.1.2 Solar Energy

Solar energy is an area of great potential as the sun delivers $3 \times 10^{24}$ Joules of energy to the earth each year and the annual global energy requirements of humanity are only a tiny fraction of this.\textsuperscript{[5]} The sun can be approximated as a black body which emits energy in the form of electromagnetic radiation, with a specific spectrum dependant on its temperature. The main part of the spectrum reaching the earth’s surface consists of ultraviolet, visible and infrared radiation, peaking in the visible 400-700 nm range.\textsuperscript{[6]} Some of the electromagnetic spectrum is shielded from the earth’s surface by the atmosphere. Wavelengths below 300 nm are filtered out by ozone, oxygen and nitrogen, while water vapour and carbon dioxide absorb some of...
the infra-red.\textsuperscript{[6]} The exact spectrum delivered to the earth’s surface differs depending on the position on earth it is measured. The average solar spectrum reaching the earth’s surface is normalised to an air mass factor of atmosphere of 1.5 and the integrated irradiance is 1000 Wm\textsuperscript{-2}.\textsuperscript{[6]} This is represented in the AM 1.5g spectrum as shown in \textbf{Figure 1,2}. This is replicated by a solar simulator using a Xenon arc lamp with special filters and is the standard testing condition for photovoltaic devices. For solar cell efficiency the spectrum must be defined, as for any spectrum there is an optimum band gap where efficiency has a maximum value.\textsuperscript{[6]} Solar energy is a clean, carbon free, renewable source of energy, though further research is needed to improve efficiency and operating lifetimes of devices as well as finding cheaper and easier production methods to both reduce cost and increase the range of applications.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{solar_spectrum.png}
\caption{Spectral irradiance of the AM 1.5g standard solar spectrum (red) and of an ideal solar simulator (black).\textsuperscript{[7]}}
\end{figure}
1.1.3 Photovoltaics

In 1839 Edmond Becquerel discovered the photovoltaic effect, where photons strike a semiconductor, exciting a valence electron into the conduction band, leaving a hole in the valence band. This effect can be used to generate a difference in electric potential across the interface of the junction of two different materials, inducing a flow of electrons, therefore converting light into electricity.[5] The aim of a solar cell is to generate photocurrent, the quantity of which depends on finding the optimum balance of light absorption, current generation and charge recombination.[6] Light at longer wavelengths possess less energy per photon as shown by\[ E = hv \]
where \( h \) = Planck’s constant and \( v \) = frequency). Also \( v = c / \lambda \) (where \( c \) = speed of light in a vacuum and \( \lambda \) = wavelength), showing the energy of the photon is inversely proportional to the wavelength as \( E = hc / \lambda \), therefore the light radiation must have a short enough wavelength to possess enough energy to excite an electron across the energy gap between the valence and conduction bands, or band gap, of the semiconductor. It is the number of photoexcitation events and not the amount of energy absorbed above the band gap which is the important factor in photovoltaic devices, as energy of photons above the band gap is lost through relaxation, therefore the photovoltage is determined by the band gap.[6]

1.1.4 Silicon Solar Cells

In the 1950s solid-state photovoltaic devices were developed with a junction between two doped forms of silicon, allowing for efficient, but very expensive solar cells.[3] P-doped and n-doped crystalline silicon form a simple p-n junction as in Figure 1,3. P-doped silicon has impurities introduced to create an excess of holes in the material, while n-doped silicon has an excess of electrons introduced.[5] When light of the correct wavelength strikes the semiconductor, an electron is excited into the conduction band of the semiconductor, leaving a positively charged hole behind in the valence band. The difference in electric potential at the interface of the junction causes
the charge carriers to separate and diffuse in opposite directions through the semiconductor creating a photocurrent. Crystalline silicon cells have relatively high power conversion efficiencies in excess of 25% and silicon is widely available.\textsuperscript{[8]} The certified record efficiency of a single junction crystalline silicon solar cell is 26.3%.\textsuperscript{[9][10]} The cost and energy consumption of purifying the silicon is however a major disadvantage to the technology. A relatively thick layer of silicon is also required in the device for efficient light absorption due to the indirect band gap of silicon. The cells are also difficult to recycle and the devices are large and heavy, meaning it is not suitable for use on flexible substrates or for portable devices. The colour of the device is also limited to blue and so does not look overly attractive which is an important factor when marketing the technology. This has led to various other types of solar cells being researched and produced.

![Figure 1.3. Schematic diagram of standard p-n junction in equilibrium. When a photon with energy equal to or greater than the band gap ($E_g$) strikes the semiconductor an electron is excited across the band gap to the conduction band creating an electron-hole pair. Charge separation is caused by the built in potential difference in the space charge region and the charges are transported through the conduction or valence band.\textsuperscript{[11]}](image-url)
1.1.5 Other Solar Cell Devices

Thin film solar cell technologies have good efficiencies, are cheap to produce, use less material, are easier to manufacture, are much less bulky and lighter than crystalline silicon cells and are also suitable for a range of applications such as on flexible substrates or even on windows and buildings. Thin films use a semiconductor with a direct band gap and so with a higher absorption coefficient than silicon which has an indirect band gap. Thin films also offer a reduction in the electron diffusion time due to the shorter path length, reducing the probability of charge recombination. Gallium-arsenide thin film devices offer efficiencies around 28%, though the materials are not as widely available as silicon and are toxic, limiting their use to certain applications.\textsuperscript{12,13} Cadmium-telluride based thin film solar cells give a record efficiency of 21.0%, even performing well under low levels of illumination.\textsuperscript{14,15} Copper-indium-gallium-diselenide, or CIGS, thin film solar cells also offer high efficiencies of around 21%, though they are difficult to produce and the availability of certain materials such as indium is currently decreasing.\textsuperscript{10,15,16} Alternative versions of CIGS cells using abundant, non-toxic materials are currently being developed in the form of copper-zinc-tin-sulfide (CZTS) cells and the selenide equivalent (CZTSe), though efficiencies are currently lower than the CIGS devices at 9.8%.\textsuperscript{17} Another recent material advance in solar cell technology is perovskite solar cells which incorporate a layer of perovskite structured organometallic microcrystals, typically made of methylammonium lead triiodide (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}), for light absorption and charge transport. Perovskite solar cells have developed rapidly in recent years with record efficiencies now around 22.1%.\textsuperscript{18,19,20} There are various other types of devices and materials currently being developed such as multi-junction solar cells which have high efficiencies but are expensive and difficult to produce on a large scale.\textsuperscript{10,21} Many different organic photovoltaic devices are also being looked into with efficiencies around 11%.\textsuperscript{13,22} Dye-sensitized solar cells (DSSCs) are also devices with great commercial potential.
1.2 Dye-Sensitized Solar Cells (DSSCs)

1.2.1 DSSC Overview

Efficiencies of dye-sensitized solar cells were low at just over 1%, until in 1991 O’Regan and Grätzel brought dye-sensitized solar cells (DSSCs) to prominence by employing a layer of high surface area nanocrystalline mesoporous titania with a monolayer of dye adsorbed onto its surface which absorbs visible light as a photoanode. The dye-sensitized semiconductor was placed in contact with an electrolyte, creating a photoelectrochemical cell which converts sunlight directly into electricity, now achieving certified cell efficiencies of 11.9% under solar simulator illumination and around 12% under diffuse daylight.[5][8][23][24]

In addition to direct band to band generation, it was observed that the absorption band gap of the semiconductor could be extended through addition of a dye which was sensitive to longer wavelengths, leading to multi-step photogeneration through sub-band gap excitation of the semiconductor.[5] This is due to the smaller energy difference between the ground and excited-state levels in the dye than the valence-conduction band gap in the semiconductor, meaning less energy is needed to excite an electron. The excited state must dissociate to release mobile charge carriers through electron injection into the semiconductor before recombination occurs.[6] The excited-state energy level must be higher than the conduction band energy level to drive electron injection. However if it is too high there will be greater loss of energy.[5]

Dye-sensitized solar cells differ from other photovoltaic devices as they incorporate a similar process to that used in photosynthesis, where the light absorption and charge transfer processes occur in separate regions in the cell, light being absorbed by the sensitizer dye and charge transport carried out in the semiconductor and electrolyte.[25]

Dye-sensitised solar cells are of great interest as they possess many benefits compared to other photovoltaic devices as they have relatively good efficiencies of up to 12% which is lower than some other devices, but high in relation to the cost.[26] DSSCs also perform well in low light conditions and are better under diffuse light than
a standard p-n junction device, are cheap to produce, easy and safe to manufacture, can be printed in a variety of shapes and colours so can be incorporated into buildings and windows, while also having shorter energy payback times.\textsuperscript{[27][28]} Dye-sensitised solar cells can also be produced on lightweight, flexible plastic substrates, making them suitable for a range of applications such as on clothing, bags, sunglasses, electronic devices, buildings and even cars. Flexible DSSC efficiencies (8.6\%) are low when compared to flexible CIGS devices (20.4\%),\textsuperscript{[26]} whereas CIGS devices are more expensive and require higher processing temperatures, limiting the flexible materials it can be used on.\textsuperscript{[26]} Areas being looked at to improve the flexible DSSC include titania paste preparation for easy application and also improving titania particle connections.\textsuperscript{[26]} There are various other parts of the DSSC which need to be optimized for commercial use, such as sensitizers which absorb a wider range of the spectrum, cheaper and more stable electrolytes, semiconductors with high surface area and fast electron transport properties and also improving the cell through light scattering techniques, while finding safe, inexpensive application and production methods.

It is worth noting the reported efficiencies of similar DSSC devices vary widely from group to group as slight differences in fabrication procedures and technique can greatly affect the final performance. It is therefore necessary to compare new devices and materials to standard devices fabricated in the same laboratory using the same techniques. For example, reported efficiencies of standard DSSCs incorporating the widely used P25 TiO\textsubscript{2} nanoparticles, N719 dye and I/I\textsubscript{3} redox electrolyte system commonly vary from as little as 1\% to around 11\% in the literature depending on fabrication methods and how well the materials in the cell are optimized.\textsuperscript{[29][30][31]}
1.2.2 DSSC Configuration

DSSCs normally consist of a fluorine-doped tin oxide (FTO) coated glass conducting plate coated with a porous film of TiO$_2$ nanoparticles which has a monolayer of sensitizer dye adsorbed onto it, making it sensitive to visible light (Figure 1, 4.). A photon excites an electron from the dye’s ground state to its excited state,$^{[32]}$ the electron is then injected into the conduction band of the TiO$_2$ at a very fast rate of around 10 ps, effecting charge separation and oxidising the dye.$^{[26]}$ The electron then diffuses through the semiconductor layer to the anode which is connected, via the load, to a platinum coated cathode. The oxidised dye is reduced by an iodide electrolyte, which in turn is then reduced at the cathode.$^{[33]}$ The cell is regenerative as there is no overall chemical change. The hole left behind by the electron in the conduction band can be thought of as a positive charge carrier which travels in the opposite direction to the electron, diffusing through the electrolyte, or hole transport material. The photocurrent is a function of the band gap and spectrum meaning the photocurrent is related to the amount of light which is absorbed. Incomplete absorption of light, reflected light and light which passes straight through the cell all reduce the photocurrent in photovoltaic devices such as dye-sensitized solar cells.$^{[6]}$ The maximum photovoltage generated is equal to the energy difference between the semiconductor Fermi level under illumination and the redox potential of the electrolyte.$^{[8]}$
Figure 1. DSSC Configuration with circuit connecting dye-sensitized TiO$_2$ coated working electrode (photoanode) to platinum coated counter electrode (cathode) via an external load. The electrodes are separated by a redox active electrolyte.

### 1.2.3 Electron Transfer Processes

A number of necessary electron transfer processes take place in a dye-sensitized solar cell to convert incident light into electric current (Figure 1.5). For the initial light absorption to occur the incident light must be of sufficient energy ($h\nu$) to excite an electron from the dye’s ground state (D) into an excited state (D$^*$).

$$D + h\nu \rightarrow D^*$$ \hspace{1cm} Equation 1.1.

The excited electron is then injected from the dye into the conduction band of the TiO$_2$ with a specific rate constant ($k_1$) dependant on the excited state lifetime and the energy level alignment of the excited state and the vacant TiO$_2$ acceptor states. After electron injection the dye is left in an oxidized state (D$^+$). It has been shown the photoinduced charge separation can take place in the order of a few femtoseconds, though this is generally seen in non-optimized devices with a higher density of trap states in the TiO$_2$.\[^{34}\]
\[ D^+ \xrightarrow{k_1} D^+ + e^- \]  \textit{Equation 1,2.}

The injected electron then diffuses through the TiO\textsubscript{2} to be collected at the conducting electrode. The injected electron has a determinable lifetime and diffusion coefficient which are represented as \( k_2 \) in \textit{Figure 1,5}. The oxidized dye is regenerated by the iodide (I\textsuperscript{−}) in the electrolyte which is oxidized in a two electron transfer process with rate constant \( k_3 \) into triiodide (I\textsubscript{3}−). The triiodide is then reduced back to iodide with rate constant \( k_4 \) at the platinum coated counter electrode where the platinum catalyses the reaction.

\[ 2D^+ + 3I^- \xrightarrow{k_3} 2D + I_3^- \]  \textit{Equation 1,3.}

\[ I_3^- + 2e^- \xrightarrow{k_4} 3I^- \]  \textit{Equation 1,4.}

The loss of mobile electrons and holes by several different recombination methods are factors crucial to the performance of solar cells. There are unavoidable types of recombination such as radiative recombination caused by essential processes in the cell which are the mechanisms which limit the efficiency of a perfect cell. Radiative and non-radiative decay of the excited state occurs with combined rate constant \( k_5 \) which is related to the excited state lifetime and is in competition with the rate constant of electron injection.

\[ D^+ \xrightarrow{k_5} D + h\nu \]  \textit{Equation 1,5.}

There are also avoidable types of recombination where injected electrons can recombine with oxidized dye molecules with rate constant \( k_6 \), meaning this reaction is competing with the regeneration of the dye by the electrolyte (\textit{Equation 1,6.}).\textsuperscript{[3]} Injected electrons diffuse through the semiconductor as conducting electrons and can also react with the oxidized electrolyte before reaching the counter electrode represented as \( k_7 \) in \textit{Figure 1,5 (Equation 1,7.).}\textsuperscript{[3]}

\[ D^+ + e^- \xrightarrow{k_6} D \]  \textit{Equation 1,6.}

\[ I_3^- + 2e^- \xrightarrow{k_7} 3I^- \]  \textit{Equation 1,7.}
For the cell to function efficiently, the processes of electron injection, diffusion and regeneration of the dye and electrolyte must be kinetically more favourable than the loss charge transfer processes.\textsuperscript{35} Recombination reduces the photovoltage and photocurrent in solar cells, while resistance between the point of charge separation and the external circuit can reduce the photovoltage.\textsuperscript{6}

\textbf{Figure 1.5.} Energy level diagram of DSSC highlighting electron transfer processes in cell under illumination.
1.2.4 Solar Cell Characteristics

The external quantum efficiency ($\eta$) of any solar cell is the amount of electrical power output of the cell ($P_{\text{out}}$) in terms of the optical power entering the cell ($P_{\text{in}}$):\(^\text{[6]}\)

$$\eta = \frac{P_{\text{out}}}{P_{\text{in}}} \quad \text{Equation 1.8.}$$

Solar cells are tested under standard conditions using the AM 1.5g spectrum with incident light intensity ($P_{\text{in}}$) of 1000 W m\(^{-2}\) which is equal to 100 mW cm\(^{-2}\). The cells are tested by applying an external bias (V) to the cell and measuring the current generated under illumination across a voltage range. The current density (J) is then calculated and a J-V curve is produced (\textit{Figure 1.6}). $P_{\text{out}}$ can be calculated using certain cell characteristics which can be derived from the J-V curve. The short circuit photocurrent density ($J_{\text{SC}}$), measured in mA cm\(^{-2}\), is found at the point on the J-V curve where the photovoltage is zero. The open circuit photovoltage ($V_{\text{OC}}$) is found at the point on the J-V curve where the photocurrent is zero. The fill factor (FF) is the ratio of the actual maximum output of the cell to the theoretical output of the cell, where $J_{\text{MP}}$ and $V_{\text{MP}}$ are the parameters at which the actual output of the cell is at its maximum.

$$FF = \frac{J_{\text{MP}}V_{\text{MP}}}{J_{\text{SC}}V_{\text{OC}}} \quad \text{Equation 1.9.}$$

The product of the short circuit photocurrent density, open circuit photovoltage and fill factor is the electrical power output of the cell.

$$P_{\text{out}} = J_{\text{SC}}V_{\text{OC}}FF \quad \text{Equation 1.10.}$$

The efficiency (%) of a dye-sensitized solar cell can therefore be calculated using \textit{Equation 1.11}.

$$\eta \,(\%) = \left(\frac{J_{\text{SC}}V_{\text{OC}}FF}{P_{\text{in}}}\right) \times 100 \quad \text{Equation 1.11.}$$

The device is also tested in the dark to confirm the short circuit photocurrent density is zero with no illumination.
Various forms of resistance to the flow of photogenerated current exist within the DSSC device and can be estimated from the J-V curve. The characteristic resistance ($R_{CH}$) is the output resistance of the device at its maximum power point. The characteristic resistance can be estimated as the inverse of the slope of the linear line through the maximum power point which can be further estimated from Equation 1,12.\[^{36}\]

$$R_{CH} = \frac{V_{MP}}{J_{MP}}$$

Equation 1,12.

There are also two main forms of parasitic resistance which cause loss of power and therefore reduce efficiency. The series resistance ($R_S$) is the resistance to current flow...
through the materials, interfaces and contacts within the device and can be estimated as the inverse of the slope near the point of open circuit photovoltage. A high series resistance can lower the fill factor and also the photocurrent. The resistance against alternate current pathways in the device is the shunt resistance ($R_{SH}$). The shunt resistance can be estimated as the inverse of the slope near the point of short circuit photocurrent. A low shunt resistance can lead to power loss from the device as the photocurrent finds alternate pathways other than through the junction resulting in a lower fill factor and photovoltage. The actual series and shunt resistance values are divided by the characteristic resistance to normalize the resistive effects of both which are seen in the non-ideality of the fill factor in device operation.\cite{36,37,38}
1.3 DSSC Components

1.3.1 Substrates

A range of substrates are suitable for manufacturing DSSCs. The most common substrate used is glass coated with a thin layer of a transparent conducting oxide (TCO). The TCO layer collects the current and transports it to the electrode contact while the glass both supports the cell and seals it from the air. The most frequently used TCO’s in solar cells are fluorine doped tin oxide (SnO$_2$: F or FTO) and indium tin oxide (In$_2$O$_3$: Sn or ITO) which both offer high conductivity and transparency. A range of sheet resistances are available though as the conductance of the TCO film increases, the transparency decreases so a compromise must be reached. FTO films offer higher thermal stability than ITO films and so are generally preferred for use in standard DSSCs due to the high processing temperatures involved.$^{[39]}$ The conducting glass substrates used in DSSCs not only make up around a third of the total cost of the devices and are relatively heavy but are also very rigid which limits the widespread commercial use of the devices.$^{[40]}$

Alternative transparent conducting substrates such as ITO/PET are of great interest as they are both flexible and lightweight. Unfortunately substrates such as this cannot survive temperatures in excess of 150°C.$^{[40]}$ Other substrates which offer flexibility such as metal foils and other TCO coated plastic substrates are also available however these do not offer the same transparency or thermal stability as the glass substrates. As standard DSSCs adopt high temperature sintering of the titania layer in excess of 500°C it is necessary to develop effective low temperature sintering of the titania layer below 150°C while maintaining device efficiency to enable widespread commercial application of DSSCs for use on flexible substrates. New substrates such as high temperature stability polymers and flexible glass are currently being developed to expand the range of substrates available and therefore expanding the range of potential applications.
1.3.2 Sensitizer Dye

The sensitizing dye is crucial to cell efficiency as it absorbs the visible light, initiates charge separation and drives electron injection into the TiO$_2$ conduction band, while also influencing electron transfer at the dye-electrolyte interface. The structure of the dye can be tuned to improve light absorbing properties, improve electron injection, and to control loss electron transfer processes such as recombination of injected electrons with the oxidised dye or recombination of electrons with oxidised electrolyte.$^{[33]}$ A good sensitizing dye must be able to be adsorbed onto the semiconductor through anchoring groups. Carboxylate or phosphonate groups which are capable of covalently bonding to the semiconductor are generally used and play a key role in both anchoring the dye molecule to the surface and carrying out electron injection into the semiconductor.$^{[33][41]}$ Only dye molecules which are in direct contact with the semiconductor surface can carry out sensitization by electron transfer, so for greatest efficiency a densely packed monolayer of dye should be adsorbed on the semiconductor surface.$^{[5]}$ The dye must have optimum absorption overlap with the solar spectrum for efficient light absorption, have the excited state energy level correctly aligned with that of the conduction band of the semiconductor to allow efficient electron injection, and have correct alignment of the ground state energy level with that of the redox potential of the electrolyte, allowing the dye to be regenerated. It is also important the dye is capable of prolonged photocurrent generation, and stays anchored to the semiconductor for a long period, giving the cell a longer lifetime.$^{[33]}$

Polypyridyl ruthenium (II) complexes are among the most effective sensitizer dyes as they are highly stable in oxidised state Ru (III) and have favourable electrochemical properties which can be tuned to increase efficiency.$^{[42]}$ Excitation of ruthenium complexes via photon absorption is of metal to ligand charge transfer (MLCT), which involves a transition from a 4d orbital of the metal to a π* orbital of the ligand. Ligand centred charge transfer (LLCT), which involves a transition from a π orbital of the ligand to a π* orbital of the ligand, are also exhibited in ruthenium based dyes. The MLCT-type is more effective as it occurs in the visible part of the spectrum unlike the π-π* transition.$^{[35]}$ Successful examples of this type of dye include
N719 which is often used as the standard dye when comparing devices (Figure 1,7). The dye adsorbs to the semiconductor through one, two or three of its carboxyl groups. There are various other types of sensitizers including organic dyes and porphyrins which are being developed to increase factors such as light absorption and stability, but many still have a narrow absorption range or toxicity and stability issues or are difficult or complicated to synthesize.\textsuperscript{[26][44][45][46]}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{molecule.png}
\caption{Molecule of N719 dye (Ru in +2 oxidation state), (TBA = tetrabutylammonium).}
\end{figure}
1.3.3 **Electrolyte**

When charge separation occurs an excited electron is injected from the dye into the TiO$_2$ leaving a hole. When the dye is regenerated with an electron from the electrolyte, the positively charged hole moves in the opposite direction to the electron. The electrolyte can be thought of as a hole transport material. The electrolyte must contain a redox active couple to regenerate the dye.$^{[33]}$ An iodide/triiodide couple is often used which is formed in a low viscosity solvent, typically acetonitrile or valeronitrile. The iodide reduces the oxidised dye, so becomes oxidized itself and forms triiodide, which diffuses and is reduced at the cathode.$^{[47]}$ A thin layer of platinum is formed on the counter electrode to catalyse the triiodide reduction. The properties of the electrolyte can alter the cell efficiency and kinetics therefore the electrolyte can be optimized for the cell.$^{[28]}$ Additives such as 4-tert-butylpyridine have been shown to decrease the recombination of electrons in TiO$_2$ with triiodide by preventing triiodide access to the TiO$_2$ surface and/or by complexation with iodine in the electrolyte hence increasing solar cell performance.$^{[48]}$ Lithium ions also have an effect on the kinetics of charge transfer but have also been shown to decrease thermal stability of devices by degrading the sensitizer.$^{[49]}[50]}$ Different redox couples are also available for use in liquid electrolytes such as redox active cobalt complexes for which the redox potential can be tuned, though the larger complexes reduce the diffusion rate of the electrolyte.$^{[51]}$

Industrial scale issues with liquid DSSCs have been encountered due to problems sealing the device and losing iodine from the electrolyte which has led to the development of solid-state hole transport materials where the liquid electrolyte is replaced with a polymer, or more commonly a small molecule which is able to penetrate the pores in the semiconductor.$^{[26]}$ Spiro-OMe-TAD is an example of an organic solid state hole transport material which may offer better long term stability.$^{[26]}$ Recombination is increased as it is more difficult for the solid state hole transport material to infiltrate the porous titania network while also adding grain boundaries for the positive holes to diffuse through, lowering the overall cell efficiency. Also the solid
state hole transport materials performance in devices can be affected by various factors such as morphology of the semiconductor.[52]

1.3.4 Semiconductor

Semiconductors for use in dye-sensitized solar cells require a high surface area, must be a good electron acceptor and have high charge transport mobility to reduce electron transport resistance. The semiconductor should also have a wide band gap, be chemically stable, widely available and of relatively low cost.[3] Many metal oxides such as TiO$_2$, SnO$_2$, ZnO, SrTiO$_3$ and Nb$_2$O$_5$ among others have been investigated for use as semiconductors in dye-sensitized solar cells with TiO$_2$ found to be the most versatile of these. TiO$_2$ is also widely available at low cost as it is already mass produced for use as a pigment in the paint industry.

The mesoporous structure of semiconductors such as TiO$_2$ can increase the surface area available for chemisorption of the dye by more than a thousand times that of a planar structure as it acts like a sponge, allowing more dye molecules to be adsorbed on the surface and still be in contact with the electrolyte, allowing for greater absorption of photons.[5][26] The porosity of the mesoporous structure can also be optimized by varying the particle size while the pore size between particles can often be optimized to suit the dye to be adsorbed.
1.4 Titania (TiO$_2$)

1.4.1 Titania for use in DSSCs

Titania is polymorphous, existing in three distinct crystal phases; anatase, rutile and brookite. Brookite is a rare form of titania and is of no commercial interest. The rutile phase is often used as a white pigment in paints and other materials due to its higher refractive index making it appear whiter and like anatase, possesses a tetragonal crystal structure. Anatase which has a band gap of 3.2 eV, which is slightly higher than rutile, is the phase most of interest for photovoltaic applications due mainly to the higher band gap and lower refractive index, and can be converted to the more stable, tightly packed thermodynamic phase of rutile when exposed to temperatures above 600°C.[53] Phase stability is also dependant on crystal size, as nanocrystalline materials tend to have lower melting points and lower transition temperatures than their macrocrystalline versions. Smaller crystal sizes have higher surface areas and particle aggregation which affects the crystal growth.[54] With equal particle size, anatase is the thermodynamically stable phase at crystal sizes below 11 nm, brookite is the most stable at crystal sizes between 11 and 35 nm, while rutile is the stable phase at crystal sizes above 35 nm.[55] Changes to the chemical composition, structure and surface morphology of the titania can each alter its properties, meaning it can be optimized for use in DSSCs.[8] The anatase titania can be produced in various morphologies with benefits for dye-sensitised solar cells because factors such as surface area, pore size, porosity, particle size, shape and orientation all affect processes in the cell such as the rate of electron transport and recombination at the semiconductor-electrolyte interface, which are two competing processes in the cell.[16] The surface of the titania is covered with hydroxyl groups, which through a dehydration reaction with the carboxyl anchoring group of the sensitizer dye form a covalent bond via an ester linkage with the dye.[56][57] A TiO$_2$ film thickness of around 12 μm is optimum, minimising the path length required for electron collection, while maximising the surface area and also minimising charge recombination.[5][57] Multi-layer titania structures are often employed in dye-sensitized solar cells, for example, using a compact layer of titania
through TiCl₄ pre-treatment of the substrate surface to reduce recombination at the anode-electrolyte interface, then a mesoporous layer for high dye adsorption, followed with a layer of larger light scattering particles which cause the photons to take a longer path through the semiconductor, increasing the chances of absorption. Different multi-layer structures have been attempted to optimize the device structure. However more complicated structures add extra stages in production, increasing cost and lowering potential for commercialization. As well as high surface area a high level of crystallinity in the titania is desirable to prevent recombination of electrons and holes at defect sites in the material.\[59\]

1.4.2 Titania Morphologies

Mesoporous nanocrystalline titania (Figure 1,8,) has a wide band gap of around 3.2 eV. While the nanoparticles may cluster together due to electrostatic forces there are no connections between the small particles prior to high temperature sintering. TiO₂ only absorbs up to 388 nm, making it invisible to most of the visible and I.R part of the solar spectrum. The sintered film is transparent as the nano sized particles do not scatter light. As there is no light scattering the absorption path length is relatively short meaning fewer photons are absorbed. Larger particles are sometimes added as scattering centres to lengthen the absorption path length. It was also observed that layers of organized TiO₂ particles showed much greater cell efficiencies than layers of randomly orientated nanocrystals. Nanocrystalline films have a high surface area but low electron diffusion rates compared to the 1D structures due to the more random diffusion path. There are also more grain boundaries which increase the probability of recombination and lower the electron lifetime.\[53\][65]
Figure 1.8. SEM image of nanocrystalline P25 TiO₂ powder.

More ordered nanoparticle morphology can offer a more direct path for charge transfer, reducing recombination, which in principle can be achieved by growing 1D titania nanotubes, nanowires or nanorods onto the substrate (Figure 1.9).\(^6\) The process can also reduce the number of grain boundaries for electrons to cross, either between nanoparticles, or between cracks or growth defects in the nanoparticle layer. This can however reduce the overall surface area which severely effects the photocurrent.\(^7\) As the 1D structures have much lower porosity it is more difficult for the electrolyte to penetrate the titania network than in nanocrystalline mesoporous films, therefore increasing resistance for the charge transfer at the dye-electrolyte interface, leading to lowering of the photovoltage.\(^8\) Growing 1D nanostructures directly onto the substrate also offers problems in manufacturing on an industrial scale as the growth must be controlled so all the structures are vertically aligned to the substrate. If the structures are randomly aligned or possess growth defects the electron diffusion path is more random and grain boundaries are introduced increasing recombination.\(^8\) The random alignment of TiO₂ nanotubes has also been shown to provide a light scattering effect within the film.\(^9\) One of the key problems with the 1D structures is that any increase in surface area to enhance dye loading simultaneously decreases pore size and porosity making it difficult for the electrolyte
to be in contact with the dye.\textsuperscript{[16]} Thin films using a mix of 1D structures and nanocrystalline particles have been produced to try and achieve the high surface area provided by the nanoparticles along with the increased electron lifetime, diffusion coefficient and shorter diffusion length associated with the 1D structures, however the efficiencies are still relatively low, highlighting the importance of high surface area for dye sensitization.\textsuperscript{[16]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{SEM images of oriented rutile TiO$_2$ nanorod film grown on FTO substrate (a) top view, (b) cross-sectional view, (c) and (d) tilted cross-sectional.\textsuperscript{[70]}}
\end{figure}

3D titania nanostructures such as sub-micrometre sized spherical beads or microspheres (\textit{Figure 1,10.}) have various different pores, between nanoparticles and between beads, allowing for high dye adsorption while still allowing the electrolyte to successfully diffuse throughout the mesoporous structure.\textsuperscript{[16]} The beads can also be sintered at higher temperatures to improve interparticle connections between the nanocrystals within the bead, improving electron transport.\textsuperscript{[71]} Titania beads have
shown better electron diffusion lengths, diffusion coefficients and longer electron lifetimes when compared to nanocrystalline films due to the tightly packed interconnected particles within the bead.\textsuperscript{16,66} The pore size between particles and the pore size between beads can be optimized depending on the size of the dye to be adsorbed, also the size of the beads can be optimized to scatter light at the correct wavelength. A more recent feature of dye-sensitized solar cells is the addition of a layer of submicrometer sized particles, which are used to scatter the light in the red and near infra-red part of the electromagnetic spectrum which have wavelengths around 600-1000 nm.\textsuperscript{71} Mesoporous titania beads of the correct size can also scatter the light, while offering a high surface area for dye adsorption and are therefore multifunctional.\textsuperscript{65} The specific surface area of beads is significantly larger, commonly around 125 m\textsuperscript{2} g\textsuperscript{-1}, when compared to standard nanocrystalline P25, which has a surface area around 48 m\textsuperscript{2} g\textsuperscript{-1} when measured under BET methods.\textsuperscript{72} 3D hollow mesoporous TiO\textsubscript{2} spheres of submicrometer diameter and in larger 1-3 \textmu m diameter size have been shown to achieve multifunctional high surface area and efficient light scattering, thus improving device performance.\textsuperscript{73,74} Other morphologies can also be obtained such as hexagonal nanoplates, 2D nanosheets, nanoribbons and nanoleaves among others.\textsuperscript{75,76,77,78}
1.4.3 Titania Deposition Techniques

There are various methods of depositing titania onto a substrate. The titania is generally made into a paste, which is then printed onto the desired substrate by either the ‘doctor blading’ technique or printing the paste using a screen printer and a mask of the desired shape (Figure 1.11). The film is then heated to attach the titania to the substrate. Titania has hydroxide groups at its surface, so when heated onto a treated substrate (i.e. FTO glass) with hydroxide groups at its surface, a dehydration reaction progresses connecting the titania to the substrate.[57][80] Titania is generally sintered onto glass substrates at temperatures over 450°C, burning off all organic molecules and enabling good particle interconnection.[27] Flexible dye-sensitized solar cells are of great interest as they can be easily manufactured on roll-to-roll printing lines and greatly extend the range of potential applications, but flexible dye-sensitized solar cells
cannot withstand temperatures much in excess of 150°C due to the lower melting point of the plastic substrates, therefore resulting in poor connections between the titania particles, lowering rates of electron transport through the semiconductor which can lower efficiencies.\textsuperscript{[57][72][81]} The use of higher pressures, microwave sintering, electrodeposition, UV irradiation and chemical sintering have been explored, however these can result in higher costs and other problems when up scaling the process to industry, such as more waste and hazardous procedures.\textsuperscript{[69][71][80]}

![Figure 1.1. Screen Printer with mask containing holes to apply paste to substrate.](image)

### 1.4.4 Titania Paste formulation

The characteristics of the titania paste is of great importance to the production and performance of DSSCs.\textsuperscript{[80]} The titania powder can be easily dispersed in water or other non-viscous solvents. Acetic acid can be added and adsorbed on the titania surface to reduce aggregation of the titania particles.\textsuperscript{[82]} Paste synthesised with nanocrystalline titania powder using water as a solvent show much less long-term stability than \(\alpha\)-terpineol based pastes due to the more viscous solvent.\textsuperscript{[82]} Water is still
used in the initial stages of paste formulation to initially disperse the particles and promote surface coverage of hydroxyl groups on the titania, enabling the dehydration reaction used to sinter particles together or to the substrate.[82] Various polymer binding agents can be added to the paste providing porosity in the film which are fully burned out during sintering. It was found the best combination of solvent and binding agents for a paste with uniform dispersion used α-terpineol and ethyl cellulose, while using two different molecular weights of the ethyl cellulose further increased efficiency.[83][84] Additional additives can be added to the paste to fine tune the TiO₂ conduction band edge which affects the dye adsorption and electron injection.

1.4.5 Titania Film Sintering

Sintering of the TiO₂ film is a key stage in the fabrication of dye sensitized solar cells. Standard DSSCs are typically sintered at temperatures in excess of 450°C to ensure both complete removal of any organics and binders present in the paste and to create strong interparticle connections between the TiO₂ nanoparticles in the film.

Thermal analysis reports in the literature of TiO₂ films formed using the standard α-terpineol and ethyl cellulose paste show the α-terpineol solvent evaporates between 60–214°C and is an endothermic process. The ethyl cellulose binder begins to exothermically decompose into CO₂ and H₂O between 210°C and 320°C with full combustion of any remaining carbonaceous material observed at 450°C.[85][86] It is important that all residual organics are removed from the film as the degradation products will occupy vacant sites at the TiO₂ surface hindering dye adsorption.[87] The organic binder is used to control the porosity of the film, increase the viscosity of the paste and to improve particle interconnections allowing for large scale uniform films with good adhesion to the substrate.[88][89]

In an effort to ensure uniform films a heating programme (as described in experimental chapter) which gradually increases the temperature is usually employed.
The purpose of the gradual heating is to minimise any stress within the film, allowing slow evaporation of the solvent and to ensure full degradation and combustion of the binder. As the ethyl cellulose binder does not decompose until around 450°C the gradual heating is not necessary prior to this stage in the heating as the binder prevents cracking in the film. Many examples in the literature now omit the gradual heating programme and still produce crack free films.\cite{85,90} As the temperature increases the TiO$_2$ nanoparticles develop stronger connections. An optimum temperature is reached (~510°C) and held for a period of time to ensure all organics are removed and the strong interparticle connections have been developed without decreasing the surface area for dye loading which would occur at higher temperatures. The films are then allowed to cool gradually to minimise cracking and are generally immersed in dye-baths when they have cooled to around 80°C to minimise adsorption of molecules from the air which can occupy adsorption sites.

Unfortunately, such high temperature processing techniques are typically limited to rigid glass substrates which are not suitable for large scale roll-to-roll processing. As the flexible substrates require much lower processing temperatures it is essential to select suitable solvents and binders which can be removed at the required temperature. The ethyl cellulose binder, for example, is not suitable for use in low temperature devices as it is not degraded during sintering and is soluble in the dye-bath solution resulting in the film peeling from the substrate.\cite{88} Use of additional additives in the paste such as metal peroxides have been shown to decompose exothermically in the film at slightly lower temperatures than the binder combustion occurs, releasing oxygen and heat into the film which help to fully decompose the binder at lower temperatures of around 300°C which is a suitable temperature for certain foil substrates.\cite{85} As many plastic substrates cannot withstand temperatures in excess of 150°C and it is difficult to remove many binders at this temperature research has mainly focussed on the production of binder free pastes for low temperature (<150°C) thermal sintering, though it has been shown that binder free pastes exhibit higher levels of cracking and peeling from the substrate than films incorporating binders.\cite{85,89} Studies of binder free P25-TiO$_2$ films sintered at temperatures ranging from 25°C to 600°C show no change in dye loading but show a higher photocurrent in devices with increasing temperature due to the improved interparticle connections in
the film, though comparative films with binders show higher efficiencies provided the temperature was sufficient to remove the binder.\[^{[88][89]}\] Less viscous solvents such as water or ethanol are often employed in pastes for low temperature application due to their lower boiling point. The aim is therefore to produce films with no cracking, good adhesion to the substrate, strong interparticle connections and no residual organics which can be processed using temperatures below 150°C and so are suitable for flexible plastic substrates and large scale roll-2-roll processing.

### 1.5 Titania Production

#### 1.5.1 Titania Synthesis Routes

There are various routes for synthesizing nano-TiO\(_2\) including flame synthesis by TiCl\(_4\) oxidation and inert gas condensation among others.\[^{[91][92][93]}\] The standard P25 TiO\(_2\) nanoparticles are prepared by gas-phase flame synthesis where the final phase (usually around 80:20 mix of anatase and rutile) is controlled by the flame conditions.\[^{[94][95]}\] Wet chemistry routes offer more control over structure and composition, while also using lower temperatures.\[^{[96]}\] The typical synthesis route for titania nanoparticles in the laboratory is the sol-gel method which is a simple low cost technique. This involves a hydrolysis or polycondensation reaction of a titanium precursor such as a titanium alkoxide or titanium tetrachloride with a suitable solvent such as water or alcohols to produce a colloidal solution. As the solution dries an inorganic gel-like network is formed with the titanium centres connected with oxide or hydroxide bridges. Final calcination removes any liquid providing nanocrystalline TiO\(_2\). A similar alternative synthesis route is the hydrothermal method where the titanium precursor is added to water and the solution heated to precipitate out the TiO\(_2\). The precipitate is then filtered and further calcined if required. Aggregates can then be broken down by grinding or ball-milling to leave individual nanoparticles. The size,
morphology, crystallinity and phase of the nanoparticles depends on the ratio of
titanium to solvent, the nature of the solvent, the initial reaction temperature, pH, the
final calcination temperature and also the use of any templates or other additives.
Initial heating provides enough energy for the atoms to organize into the kinetically
metastable anatase phase where the 101 plane is the most thermally stable. Further
heating (above 700°C) leads to formation of the thermodynamically stable rutile phase
where the most thermally stable surface is the 110 plane. The nanocrystalline TiO₂ can
be formed into various morphologies such as 3D mesoporous spheres which were
previously discussed by simply adjusting the reaction conditions.

Nanotubes can be grown directly on substrates via a hydrothermal reaction.
These often employ pre-formed seed layers on the substrate however it is also possible
without the seed layer. A titanium precursor such as potassium titanium oxide oxalate
dehydrate (PTO) is dissolved in water and an organic compound such as diethylene
glycol (DEG) is then added, where the ratio of water to DEG controls the final
morphology. The solution is placed on the substrate and heated in an autoclave at
temperatures high enough to drive hydrolysis forming TiO₂ nanocrystals. The organic
compound serves as a capping agent, binding to a particular crystal plane, i.e. the 110
plane which is in the x-axial direction, therefore promoting growth along the y-axial,
i.e. the 001 plane. The temperatures are then increased to remove the organic capping
agent leaving vertically aligned titania nanotubes around 16 µm tall and 300 nm
wide.[97] Similar methods are used to produce other morphologies in solution which
can then be deposited on substrate. Altering the heating conditions, pH of solution,
addition of capping agents, binders and dispersants among other things all have an
effect on the final morphology.

The current methods of synthesizing the bead structures involve hydrolysis of
a titanium precursor such as titanium (IV) tetraethoxide, followed by solvothermal
treatment, providing ~10 nm size primary particles which floc together to form
spherical bead structures of variable size with surface area ~110 m²g⁻¹ which is
measured using nitrogen sorption analysis.[98] Other similar methods have been
attempted using titanium (IV) isopropoxide, providing 18 nm particles, producing
beads with a surface area of 89 m²g⁻¹.[71] An alternative method of synthesizing
mesoporous beads is simply mixing titanium (IV) isopropoxide with acetone, heating at 200°C for 12 hours, filtering, washing with ethanol and drying at 60°C to provide mesoporous 550-1050 nm diameter spheres made of 12 nm anatase nanoparticles with a specific surface area around 138 m²g⁻¹.[79] Lower surface areas may be due to the larger primary particles increasing the pore size but reducing the number of pores, while the extent to which the primary particles have aggregated will also affect surface area. There are many other similar procedures which produce similar products. The slight changes in reaction procedures cause differences in the resulting properties of the final products. The commercially available starting materials such as TiCl₄ are initially obtained through purifying ilmenite ore or titanium slag via the chloride or sulphate process.
1.5.2 Sulphate Process

Titanium is recovered from naturally occurring deposits mainly in the form of the mineral ore Ilmenite. The Ilmenite, with theoretical formula FeTiO$_3$ is then typically converted to titanium dioxide using either the sulphate or chloride process.\(^{[99]}\) The sulphate process is the main process used by Huntsman Pigments and Additives in Europe and is outlined in *Figure 1,12.*

\[
\begin{align*}
\text{Ilmenite (FeTiO}_3\text{) ball-milled to fine powder} \\
\text{Concentrated Sulphuric acid added and heated with water to 100°C} \\
\text{Scrap Iron added to reduce all ferric iron to ferrous iron} \\
\text{Mixture concentrated and filtered to remove any solids} \\
\text{Mixture cooled below 15°C to crystallize out FeSO}_4\cdot7\text{H}_2\text{O which is then removed by filtration} \\
\text{Nano TiO}_2\text{ nuclei in H}_2\text{O formed using either Mecklenburg or Blumenfeld method added to mixture} \\
\text{Hydrolysis of mixture at 96°C causes precipitation of TiO}_2\cdot_n\text{H}_2\text{O micelles with size dependant on amount of nuclei added} \\
\text{Precipitate filtered and washed with water} \\
\text{Ti}^{3+}\text{ and sulphuric acid added to leach out remaining iron} \\
\text{Solution heated to 70°C, stirred for 2 hours and washed with water to give post-leach pulp} \\
\text{Further treatment and calcination to give final TiO}_2\text{ product}
\end{align*}
\]

*Figure 1,12. Outline of sulphate process for TiO$_2$ production at Huntsman Pigments and Additives.*
The sulphuric acid digests the finely ground ilmenite according to Equation 1,13.

\[ \text{FeTiO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{TiOSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{O} \quad \text{Equation 1,13.} \]

Scrap iron metal is then added to the mixture which reduces any trivalent ferric iron (Fe\(^{3+}\)) to ferrous iron (Fe\(^{2+}\)) which is easier to remove. This is done during or immediately after digestion of the ilmenite as any remaining Fe\(^{3+}\) will be hydrolysed along with the titanium oxysulphate (TiOSO\(_4\)) and remain in the precipitate so must be removed.[100] The solution is then filtered and any solids are removed while keeping the temperature relatively low to avoid any premature hydrolysation. The concentrated solution is then cooled so the iron crystallizes out as ferrous sulphate heptahydrate (FeSO\(_4\).7H\(_2\)O) which is then easily removed leaving a black liquor solution of TiOSO\(_4\) in sulphuric acid and water along with some residual impurities such as iron and sulphates. Hydrated TiO\(_2\) micelles are then precipitated from the solution by hydrolysing the TiOSO\(_4\) as in Equation 1,14.

\[ \text{TiOSO}_4 + n_{+1}\text{H}_2\text{O} \rightarrow \text{TiO}_2\cdot n\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \quad \text{Equation 1,14.} \]

The hydrolysis is conducted at 96°C to drive the reaction however the reaction is incomplete and slow and therefore is accelerated by the addition or formation of nano-TiO\(_2\) seed crystals using either the Mecklenburg or the Blumenfeld technique. The Mecklenburg method uses a small amount (0.5 – 1.8 % by wt.) of pre-prepared anatase or rutile nanocrystals dispersed in water which is added to the reaction. The nanocrystals surface provides nucleation sites for the formation of further hydrated TiO\(_2\) nanocrystals which are then either removed from the surface to initiate secondary nucleation elsewhere in the solution or remain on the surface forming micelles with the other nanocrystals it is in contact with. These nanocrystals are connected by strong crystalline bonds resulting in a primary agglomerated particle around 5 nm in size. As the reaction continues the primary particles begin to floc together forming aggregates with sizes above 1 µm and precipitate out of the solution.[101] The Blumenfeld method involves taking a small portion of the black liquor solution and heating in the water, shifting the equilibrium to TiO\(_2\) and hydrolysing the small amount of TiSO\(_4\), hence creating its own TiO\(_2\) nanoparticle nuclei seed crystals. The rest of the black liquor solution is added and nucleation and precipitation of the hydrated TiO\(_2\) commences as
previously described. Addition of a higher concentration of the seed crystals will result in more secondary nucleation causing the primary particles to be formed from fewer crystals and hence be smaller in size. A low nucleation level of around 0.1% by wt. in Mecklenburg precipitation can provide 150nm size particles. The primary particles in the larger aggregate are held together by weaker physical bonds than the nanocrystals making up the primary particle. The use of rutile seed crystals in the precipitation has been shown to promote the formation of rutile phase nanoparticles after final calcination though it is thought the initial precipitate is in the anatase form.\textsuperscript{[101]}

After precipitation of all hydrated TiO$_2$ aggregates the precipitate is filtered and washed with water. Sulphuric acid and trivalent titanium is then added to ensure any remaining iron is ferrous, so is soluble and can be leached out. The solution is heated to 70$^\circ$C, stirred for 2 hours, filtered and washed with water to remove some of the acid and any remaining impurities. This provides a pulp of hydrated TiO$_2$ aggregates made up of smaller hydrated TiO$_2$ micelles in an aqueous solution which is around pH 2 as well as containing some sulphates and other trace impurities. This post-leach pulp is manufactured at Huntsman Pigments and Additives facility in Scarlino, Italy and is the starting point of many of the TiO$_2$ samples used in this work. The post-leach pulp can then be further treated as desired (detailed in next section), washed and then dried during final calcination to remove any water from the product as in \textit{Equation 1,15}.

\[
\text{TiO}_2 \cdot n\text{H}_2\text{O} \rightarrow \text{TiO}_2 + n\text{H}_2\text{O}
\]

\textit{Equation 1,15.}

In standard TiO$_2$ production the dried aggregates are usually put through a high energy ball milling process after final calcination to break the aggregates down into their individual nanoparticles, with the nanoparticle size being dependant on the nucleation level used during the precipitation step and also the temperatures used.
1.5.3 Huntsman Titania Synthesis

Huntsman Pigments and Additives produced a range of TiO$_2$ samples using a unique method which is described here (Patent: WO 2015/040426 A1). Some of the samples described here use different hydrolysis methods and differing crystal phase and quantities of nano-TiO$_2$ nucleation seed crystals as described in the previous section, however most variation and unique formation of the samples takes place in the treatment after processing the post-leach pulp and during final calcination as shown in Figure 1,13.

![Figure 1,13. Production process of various titania samples produced by Huntsman Pigments and Additives. (MIPA = monoisopropanolamine)](image)

Post-leach pulp (from Figure 1,12.)

- Neutralise with NH$_3$ or NaOH
- Filter and wash until sulphate level < 100 mg L$^{-1}$
- Peptize with concentrated HCl till pH 1.5
- Citric acid added (0 – 10% by wt. TiO$_2$)
- Neutralise to pH 8 with MIPA
- Cross-flow filtration

700$^\circ$C

Dry on pulsation reactor

- Sample: 5033-VP1
- 300$^\circ$C
- Sample: 5033-VP3

Stir in dopants (SO$_3$: 0 – 0.58%)
(Carbon: 0 - 0.126%)

Spray dry at 110$^\circ$C

- Sample: M712/22
- Sample: M712/21
- Sample: M712/13/1
- Sample: M712/15

Samples: ST2663/1
ST2683/1
ST2683/9
ST2688/5
The post-leach pulp, containing the precipitated hydrated TiO₂ aggregates produced in the sulphate process as previously described, is stirred while adding either ammonia or sodium hydroxide until the solution is neutralised to pH 7. The solution is then filtered and washed with water until the sulphate level falls below 100 mg L⁻¹ leaving a white cake of hydrated TiO₂. The white cake is then re-pulped in water giving a slightly runny white slurry. The pH of the slurry is lowered to pH 1.5 by the addition of concentrated hydrochloric acid. This acts as a peptising agent which introduces a positive charge to the micelle surface causing them to repel each other, becoming so small they are transparent and causing the TiO₂ aggregates to fully disperse into a colloidal sol. Lowering the pH of the slurry causes dispersion as the TiO₂ micelles flock together at the isoelectric point which is the pH value when they carry no net charge. This is around pH 5.8 for TiO₂ therefore shifting the pH further away from this point causes greater dispersion.¹⁰³ The isoelectric point of the TiO₂ in the sol can also be controlled by the addition of a dispersant such as citric acid. Addition of more citric acid lowers the isoelectric point of the TiO₂, causing flocculation of the TiO₂ micelles as the isoelectric point moves closer to the pH of the peptised TiO₂ sol. The amount of citric acid added is in the range of 0 - 10% by wt. TiO₂. Greater levels of flocculation provide larger pore sizes between nanoparticles in the final samples. The sol is then neutralised to pH 8 with addition of monoisopropanolamine (MIPA) which is a common dispersant for TiO₂ pigments.¹⁰⁴¹⁰⁵ The TiO₂ micelles now become dispersed at pH 8 as the isoelectric point was shifted to lower pH values by the citric acid. The extent to which the hydrated TiO₂ micelles in the sol are dispersed is dependent on how much citric acid was added and therefore how far from the isoelectric point the pH of the TiO₂ is after addition of the MIPA. A greater dispersion leads to a smaller pore size between nanoparticles in the final sample. The sol is then filtered using crossflow filtration where the feed sol is heated to 40°C and passed through a hollow tube with fine filter membrane walls (Figure 1,14.). The TiO₂ sol passes across the fine membrane with a positive pressure forcing any remaining impurities out with some of the water. As the aqueous sol is pumped across the membrane it stops the pores becoming blocked with solid material and so is suitable for continuous use with high solid concentrations. After passing across the membrane the sol is fed back into the initial feed sol where extra water is added to the feed sol at
the same rate as the filtrate is removed. The crossflow filtration is continued until the conductivity of the feed sol falls below 2 mS cm\(^{-1}\) indicating most of the salts have been removed from the solution. At this point the extra water addition is stopped and the TiO\(_2\) sol is concentrated to around 17% solid concentration by weight.

![Figure 14. Crossflow Filtration system at Huntsman Pigments and Additives.](image)

The concentrated sol is then spray dried at 110\(^\circ\)C using Lab Plant laboratory spray dryer (Figure 15.) to produce mesoporous TiO\(_2\) spherical beads with diameter in the size range of 1-30 µm which are formed from the individual nanoparticles. The size of the nanoparticles is controlled by the amount of nanoparticle nuclei added in the precipitation step, while the size of the ordered 3D spherical bead can be controlled through the atomizer pressure of the spray dryer. Higher temperatures during spray drying causes the bead structure to deform and produces toroidal shaped structures. There are two definitive pore sizes in the 3D bead structure; the pore sizes between the nanoparticles are related to their size as are the pore sizes between the beads. Various samples were produced at different stages of the process using a range of differing production conditions for comparison as is detailed in the following section.
1.5.4 Huntsman TiO$_2$ Individual Sample Production

A total of eleven different TiO$_2$ samples were fabricated by Huntsman Pigments and Additives in the context of this project. Three samples were produced using the full procedure described above to produce spherical micrometer sized mesoporous titania beads. **Sample M712/15** was produced by forming rutile seed crystals using the Blumenfeld method during the precipitation step in the sulphate process to produce rutile phase TiO$_2$ and a 10% citric acid level was used to lower the
isoelectric point of the sol. This was the only rutile phase sample produced; all further samples are anatase phase TiO₂. **Sample M712/21** was produced using a standard post-leach pulp manufactured at the Scarlino plant which used the Blumenfeld precipitation method to form anatase seed crystals and therefore produce anatase TiO₂ and used a 1% level of citric acid. **Sample M712/13/1** was produced by adding 1.8% by wt. anatase seed crystals using the Mecklenburg precipitation method and used a 10% level of citric acid. The 1.8% weight ratio is roughly equivalent to the nucleation level found in the standard Blumenfeld precipitated post-leach pulp used in other samples.

Two further samples of mesoporous titania beads were also produced with changes in the procedure. **Sample M712/12/1**, as is shown in **Figure 1,16**, was produced using a 1.8% nucleation level during Mecklenburg precipitation and a 10% citric acid level. The crossflow filtration step was omitted during production leaving a higher level of ions or salts in the sol which was then concentrated to 17% and spray dried. **Sample M712/22** was produced using a 0.5% nucleation level which should produce larger hydrated TiO₂ micelles during Mecklenburg precipitation. Once the sol was peptized by addition of hydrochloric acid until pH 1.5 was reached it was then concentrated and spray dried, omitting addition of any citric acid, MIPA neutralisation and crossflow filtration to produce mesoporous beads at pH 1.5. An overview of the differences in the procedure used to synthesize the different samples with a 3D spherical bead morphology is shown in **Table 1,1**.
Figure 1.16. SEM image of Huntsman Pigments and Additives mesoporous TiO$_2$ bead sample M712/12/1.

<table>
<thead>
<tr>
<th>Huntsman Titania Sample</th>
<th>M712/21</th>
<th>M712/22</th>
<th>M712/12/1</th>
<th>M712/13/1</th>
<th>M712/15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Rutile</td>
</tr>
<tr>
<td>Precipitation method</td>
<td>Blumenfeld</td>
<td>Mecklenburg</td>
<td>Mecklenburg</td>
<td>Mecklenburg</td>
<td>Blumenfeld</td>
</tr>
<tr>
<td>Nuclei Added (% wt. TiO$_2$)</td>
<td>N/A</td>
<td>0.5</td>
<td>1.8</td>
<td>1.8</td>
<td>N/A</td>
</tr>
<tr>
<td>Neutralization agent</td>
<td>NH$_3$</td>
<td>NH$_3$</td>
<td>NH$_3$</td>
<td>NH$_3$</td>
<td>NH$_3$</td>
</tr>
<tr>
<td>Peptized with HCl</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Citric acid (% wt. TiO$_2$)</td>
<td>1.0</td>
<td>No</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>pH</td>
<td>8</td>
<td>1.5</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Crossflow filtered</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Dried</td>
<td>Spray Dried (110°C)</td>
<td>Spray Dried (110°C)</td>
<td>Spray Dried (110°C)</td>
<td>Spray Dried (110°C)</td>
<td>Spray Dried (110°C)</td>
</tr>
</tbody>
</table>

Table 1.1. Overview of differences in procedure used to fabricate various samples of Huntsman Pigments & Additives TiO$_2$ micrometer sized beads.
A further six TiO₂ samples were produced prior to the peptization step of the procedure. As the flocculated micelles in the slurry were not dispersed this resulted in non-bead micrometer sized aggregated clusters of nanoparticles with no particular shape. The pore sizes between the primary particles depend on their size and the extent to which they have aggregated together, providing a range of pore sizes deviating from the average. All six samples use the standard Blumenfeld precipitated anatase post-leach pulp as used in sample M712/21. Two samples were produced using a different calcination method where the sol is dried on a pulsation reactor for around 5 minutes until dried. **Sample 5033-VP1** was produced by neutralizing the post-leach pulp, washing sulphate free and re-pulping in water. Dopants were then added (% by wt. TiO₂) and stirred into the sol in the form of 0.5437% sulphur trioxide (SO₃) and 0.021% carbon in the form of graphite. The sol was then dried on a pulsation reactor at 700°C until dry. **Sample 5033-VP3** was produced in a similar manner but using 0.4731% sulphur trioxide and 0.029% carbon as dopants and dried on the pulsation reactor at 300°C. **Sample ST2663/1**, as shown in *Figure 1,17*, was produced in the same manner as the previous two samples without adding any dopants. The sol was then concentrated to 17% solid and spray dried at 110°C using the Lab Plant laboratory spray dryer. The remaining three samples were produced in a similar manner however the neutralization of the post-leach pulp was carried out using sodium hydroxide (NaOH) where all other samples used ammonia (NH₃) as the neutralization agent. Sulphur trioxide and carbon dopants were also added in varying quantities and the pH of the sol adjusted before concentrating and spray drying. **Sample ST2683/1** had 0.58% SO₃ and 0.115% carbon added and had pH 5.45. **Sample ST2683/9** had 0.21% SO₃ and 0.126% carbon added and had pH 6.36. **Sample ST2688/5** had 0.19% SO₃ and 0.043% carbon added and had pH 8.02. An overview of the differences in the procedure used to synthesise the different samples with a non-bead morphology is shown in *Table 1,2.*
Figure 1.17. SEM image of Huntsman Pigments and Additives clustered TiO$_2$ nanoparticle sample ST2663/1.

<table>
<thead>
<tr>
<th>Huntsman Titania Sample</th>
<th>5033-VP1</th>
<th>5033-VP3</th>
<th>ST2663/1</th>
<th>ST2683/1</th>
<th>ST2683/9</th>
<th>ST2688/5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Anatase</td>
</tr>
<tr>
<td>Precipitation method</td>
<td>Blumenfeld</td>
<td>Blumenfeld</td>
<td>Blumenfeld</td>
<td>Blumenfeld</td>
<td>Blumenfeld</td>
<td>Blumenfeld</td>
</tr>
<tr>
<td>Neutralization agent</td>
<td>NH$_3$</td>
<td>NH$_3$</td>
<td>NH$_3$</td>
<td>NaOH</td>
<td>NaOH</td>
<td>NaOH</td>
</tr>
<tr>
<td>Peptized with HCl</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>SO$_3$ (%)</td>
<td>0.5437</td>
<td>0.4731</td>
<td>N/A</td>
<td>0.58</td>
<td>0.21</td>
<td>0.19</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>0.021</td>
<td>0.029</td>
<td>N/A</td>
<td>0.115</td>
<td>0.126</td>
<td>0.043</td>
</tr>
<tr>
<td>pH</td>
<td>Neutral</td>
<td>Neutral</td>
<td>Neutral</td>
<td>5.45</td>
<td>6.36</td>
<td>8.02</td>
</tr>
<tr>
<td>Dried</td>
<td>Pulsation Reactor (700°C)</td>
<td>Pulsation Reactor (300°C)</td>
<td>Spray Dried (110°C)</td>
<td>Spray Dried (110°C)</td>
<td>Spray Dried (110°C)</td>
<td>Spray Dried (110°C)</td>
</tr>
</tbody>
</table>

Table 1.2. Overview of differences in procedure used to fabricate various samples of Huntsman Pigments & Additives TiO$_2$ non-bead micrometer sized aggregated clusters of nanoparticles.
1.6 Industrial Scale

The ability to use solar energy technologies to supplement the growing energy demands of the world’s rising population is not just down to developing the photovoltaic devices and optimizing them to gain maximum efficiency, but also being able to manufacture the devices on a large scale while being cost effective. The growing requirement for ‘green’ chemistry is also of concern on a large scale as waste products need to be disposed of correctly, adding to the overall expenditure, therefore greener manufacturing methods for devices are desirable. Many devices are difficult to make, or use hazardous materials and procedures such as high temperatures and pressures, resulting in high manufacturing costs. What is required is finding the correct balance in the cost to benefit ratio, therefore solar devices which have an average efficiency but are safe, low cost and easy to manufacture are often of much greater benefit to a large marketplace than expensive, high efficiency cells. Dye-sensitized solar cells offer good efficiencies while being relatively low cost and easy to manufacture, with little waste and shorter energy payback times than other devices.

While developing manufacturing techniques to improve device performance across a range of flexible substrates is important as previously mentioned, so are developing techniques that lower the overall cost and speed production by reducing the number of steps in the DSSC fabrication process. The dye-sensitization of the titania film often takes up to 24 hours, slowing the overall production process. With this in mind various attempts have been made to eliminate this step by pre-sensitizing the titania prior to paste formulation so it can be applied directly to the substrate. Devices using pre-sensitized titania currently cannot be sintered at high temperature due to degradation of the dye and so require alternate production procedures. The lack of high sintering temperatures leads to poor interparticle connections and therefore lowers charge transport in the film. The mesoporous TiO₂ beads offer a potential solution as the interparticle connections are already formed within the bead structure and could therefore be suitable for both flexible devices and pre-sensitized titania.
1.7 Research Proposal

The various titania samples produced and supplied by Huntsman Pigments and Additives will be initially assessed for suitability for use in devices such as dye sensitized solar cells by investigating various properties such as crystal phase, particle size, band gap, morphology and dye adsorption, both as a powder sample and as a sintered film. The samples will be compared against the commercially available P25 nanoparticles which is the standard TiO$_2$ used in such devices as well as a commercially available pigmentary anatase TiO$_2$ control sample with large particle size. The most promising samples will then be formulated into pastes and fabricated into standard DSSC devices and the performance optimized using different deposition methods and compared to both control samples as well as a commercially available pre-prepared TiO$_2$ paste. The samples will also be fabricated into devices using different paste formulations and low temperature sintering of the film to assess initial suitability for use in devices incorporating flexible substrates. With a view to reducing the device manufacturing time the samples will also be pre-sensitized with dye and fabricated into low temperature sintered devices and the performance measured. Once the initial performance of the samples in devices has been investigated the aim of this work is then to modify the samples to optimize their properties to increase performance in DSSC devices, particularly for use in flexible DSSC devices which is where the current gap in the solar cell market is most prominent.
1.8 References


48. Boschloo, G.; Häggman, L.; Hagfeldt, A., Quantification of the effect of 4-tert-butylpyridine addition to I-/I3-redox electrolytes in dye-sensitized


Chapter 2. General Experimental Techniques

Various experimental techniques were employed to characterise the titania samples, both as a powder, as a film and in devices once fabricated. In this chapter the general methods used to formulate the sample into a paste, a film and into DSSC devices are detailed. The techniques used to assess crystal phase, particle size, surface area, morphology, band gap, light absorption and reflection properties, electrochemical properties and solar cell efficiencies of the samples are also discussed. All centrifuging was carried out using an Eppendorf Centrifuge 5702. Optical Microscopy was carried out using a CMEX5000 Microscope with ImageFocus software.

2.1 Paste Formulation

To transform the titania powder into a thin film it must first be formulated into a printable paste. There are various methods for formulating printable pastes from powdered titania using various solvents and binding agents. The method using \( \alpha \)-terpineol as a solvent and ethyl cellulose as a binding agent has been shown to provide a more uniform paste as the viscous terpineol solvent increases the paste stability as the solvent will take much longer to evaporate and so can be stored for longer while maintaining good dispersion of the TiO\(_2\), whereas less viscous solvents may dry out and allow aggregation of TiO\(_2\) after a few days. The ethyl cellulose is used to bind the TiO\(_2\) particles, connecting them together and bind them to the substrate and has been shown to create porosity in the film, as after high temperature (510\(^\circ\)C) sintering of the film it is burned out leaving a porous TiO\(_2\) network behind.\(^{[1][2]}\) The titania sample powder is ground in a mortar with acetic acid which imparts a positive charge on the sample surface ensuring the particles do not aggregate while grinding. Ethanol and deionised water are added to initially disperse the particles because of their low viscosity. \( \alpha \)-terpineol is then added to the already dispersed mixture and stirred with a
magnetic stirrer bar. The ethyl cellulose which is pre-dissolved in ethanol is then added and stirred. Most of the ethanol and water is then evaporated out of the mixture leaving the TiO₂ and ethyl cellulose dispersed in the more viscous terpineol solvent. All terpineol pastes are formulated in this way for all titania samples (Figure 2,1.).

![Diagram](image)

**Figure 2,1. Method for fabricating viscous titania paste, adapted from reference.**

When low temperature (125°C) sintering of the paste is required a different paste formulation is needed as the sintering temperature is not sufficient to remove the ethyl cellulose binding agent and viscous solvent from the film. For low temperature sintering pastes the titania is simply dispersed by stirring in either a 2:1 tert-butyl alcohol/water solution or in a 25% wt. ethanol solution.
2.2 Film deposition methods

Screen printing and doctor blading are the two methods used in this work for depositing the titania paste onto the substrate to form a uniform thin film. The printing screen used for all screen printing is a Nylon screen with 0.7 cm diameter circular holes containing 90T mesh and was supplied by Mascoprint. The substrate was held down by vacuum and the screen placed on top. A small amount of sample paste was placed above the hole on the screen with the substrate below, a rubber blade was swiped over the hole filling the mesh with sample paste and a second swipe to print the paste onto the substrate. The substrate was then placed on a hotplate at 125°C for 10 minutes to level the layer. Additional layers were then printed on top in the same manner followed by final sintering of the film. When using the doctor blading technique each end of the substrate was masked with a layer of scotch tape (Figure 2,2.). The tape was attached to the workbench to hold the substrate in place and any air bubbles in the tape were smoothed out ensuring a uniform layer. A drop of the titania paste was applied along the uncovered edge of the substrate and the edge of a clean glass slide swiped across the surface while pressing on the scotch tape at either side to produce a uniform layer of paste. The scotch tape was removed and the film levelled on a hotplate. The scotch tape was reapplied and the procedure repeated to achieve the desired number of layers followed by final sintering of the film as is described in the Solar Cell Fabrication section. The cooled film can then be scraped to the desired size (1 cm² film was used in this work).

![Diagram of film deposition methods](image)

*Figure 2,2. Doctor blading method, substrate masked at either edge with scotch tape, TiO₂ paste added to edge and is swiped across substrate to produce a uniform film.*
2.3 X-Ray Diffraction (XRD)

X-Ray diffraction is a highly informative technique used for characterising crystalline material, both as a powder and as a sintered film, providing information on crystal phase, purity and crystallite domain size.

The X-rays are produced by accelerating electrons to high speed and hitting them into a metal target, in this case copper. The high speed electron knocks a low energy electron from an inner orbital of the copper atom. An electron drops from a higher energy orbital to fill the space and emits a discrete quantity of energy, without mass or charge, propagated as a characteristic X-ray wave. The copper target produces X-rays with a wavelength ($\lambda$) of 1.5406 Å. As the X-rays possess a similar wavelength to the plane spacing of atoms in crystalline materials the atomic lattice planes of the crystal cause the incident X-ray beams to interfere with each other as they leave the crystal (Figure 2, 3.).

---

Figure 2, 3. Scattering of X-rays by points A & D on neighbouring lattice planes. Angle of incidence of X-rays is $\theta$. Lattice planes are separated by distance $d_{hkl}$ where $h$, $k$ and $l$ are the Miller indices for the crystal plane. Extra distance travelled by X-ray diffracted at point D = $BD + DC = 2d_{hkl}\sin\theta$. Where the extra distance equals an integral number of wavelengths ($n\lambda$) the diffracted X-rays are in phase and produce constructive interference which produces a signal picked up by the detector.\[5]
If the additional distance travelled by X-ray photons between neighbouring diffracting planes is an integral number \((n)\) of wavelengths the X-rays will produce constructive interference and the signal can be detected, producing a bright spot on photographic film known as a Laue spot. The distance travelled between diffracting planes is dependent on the angle of incidence of the X-ray beam \((\theta)\) and the lattice spacing \((d_{hkl})\), where \(h\), \(k\) and \(l\) are Miller indices defining the crystal plane. This relationship is expressed as Bragg’s law \((Equation 2.1.)\).[6]

\[
n \lambda = 2 d_{hkl} \sin \theta
\]

\(Equation 2.1.\)

As the angle of incidence of the x-ray and the detector is varied from 0-90° a Laue spot is produced for each lattice plane in a particular orientation and is used for crystal structure determination with single crystals. As powder and film samples have an effectively infinite amount of crystals in random orientations multiple Laue spots are produced, forming a ring with a cone semi-angle of 20° where each ring corresponds to a particular lattice plane in the sample. The measured intensity of the signal is plotted against the 20 angle with a sharper more intense peak indicating more crystalline material in the sample. The characteristic powder XRD pattern can then be compared to a crystal structure database for phase identification.

Peak broadening can be observed with smaller particles as slight deformations or distortions in the lattice planes can shift some of the interference signal slightly from the actual 20 value. Even if the material is perfectly crystalline it still has a finite crystallite domain size which is limited by the size of the particle, which will result in peak broadening. A perfect peak with no broadening would only be seen with a perfectly crystalline material with an infinite crystal domain size. The relationship between peak broadening in the X-ray diffraction pattern and crystallite size is summarised with the Scherrer equation \((Equation 2.2.)\) and can be used to estimate crystallite domain and potentially particle size.

\[
\tau = \frac{k \lambda}{\beta \cos \theta}
\]

\(Equation 2.2.\)
Where $\tau =$ crystallite/domain size ($\text{Å}$), $k =$ constant related to crystallite shape which is normally taken as 0.9, $\lambda =$ wavelength of incident beam ($1.5406 \text{ Å}$), $\beta =$ width of peak at half its maximum intensity (rad) and $\theta =$ Bragg angle (rad).\textsuperscript{[7]}

A small amount of the powder was mounted on an amorphous glass slide and placed in the sample holder. When obtaining diffraction pattern of films, the film was doctor bladed onto the glass slide and sintered at the relevant temperature. The glass slide was then placed in the sample holder. All Powder X-Ray Diffraction was carried out on Bruker D2 PHASER diffractometer using settings 30 kV and 10 mA. A coupled theta-2theta scan was carried out over range 5-90°, rotation speed of 8.0 rpm, step size of 0.05° and time per step of 0.45 s for all samples.

### 2.4 UV/Vis Absorption Spectroscopy

UV/Vis spectroscopy is a useful tool to measure the absorption by a sample of electromagnetic radiation in the ultraviolet and visible region of the spectrum. In absorption spectroscopy the transmittance ($T$) of light through the sample is measured. The transmittance is the ratio of the intensity of the light transmitted through the sample ($I$) compared to the intensity of the incident light ($I_0$) \textit{(Equation 2,3.)}.

\[ T = \frac{I}{I_0} \] \textit{Equation 2,3.}

The technique is usually carried out in a glass cuvette containing the sample which is fully dissolved in an appropriate solvent \textit{(Figure 2,4.)}. The proportion of light not transmitted by the sample is assumed to have all been absorbed by the sample, therefore any light scattering by the sample resulting from effects such as particle aggregation must be minimised for reliable results. The absorbance ($A$) of the sample can be calculated using the measured transmittance \textit{(Equation 2,4.)}.

\[ A = -\log_{10} T \] \textit{Equation 2,4.}
The transmittance of the sample is measured across a range of wavelengths and the absorbance plotted as a function of wavelength to produce an absorption spectrum. Each peak in the spectrum is the result of an electronic transition in the sample. The wavelength the transition occurs at and the intensity are determined by the nature of the transition.

The amount of light absorbed by the sample depends on how much of the sample it interacts with which is dependent on both the concentration ($c$) and length of the sample the light passes through ($l$). The absorbance also depends on how strongly the sample absorbs the light at each wavelength, which is referred to as the molar absorption coefficient ($\varepsilon$). This relationship is defined in the Beer-Lambert law (Equation 2.5).

$$A = \varepsilon c l$$  

Equation 2.5.
The molar absorption coefficient for a material can be found by measuring the absorbance of a dissolved sample at the desired wavelength across a range of concentrations and plotting the absorbance as a function of concentration in a Beer-Lambert plot (Figure 2.5). The gradient of the linear best-fit line gives the molar absorption coefficient with units mol\(^{-1}\) dm\(^3\) cm\(^{-1}\). If the line is not linear then the absorbance is not concentration dependant due to undissolved sample or particle aggregation. This is avoided by correct choice of solvent and using relatively low solution concentrations. Once the molar absorption coefficient for a material at a specific wavelength in a certain solvent is known the absorbance of the sample can be used to find an unknown concentration of that sample.\(^8\)

A Beer-Lambert plot was obtained to find the molar absorption coefficient (\(\varepsilon\)) for N719 in aqueous (1 M) KOH solution (Supp. Info.). N719 dye (0.0119 g) was added to 1 M aqueous solution of potassium hydroxide (0.1 L) to give a stock solution of 0.1 mM. The stock solution was diluted down into 10 ml samples of concentrations 0.01 mM, 0.02 mM, 0.03 mM, 0.04 mM, 0.05 mM, 0.06 mM, 0.07 mM, 0.08 mM, 0.09 mM, and 0.10 mM. UV/Vis absorption spectroscopy was carried out on each sample in a 1 cm cuvette using 1 M aqueous potassium hydroxide as a baseline and the absorbance maximum at 501 nm recorded, providing a value of \(\varepsilon = 1.15 \times 10^4\) mol\(^{-1}\) dm\(^3\) cm\(^{-1}\). This value can then be used to calculate dye uptake on a sample by desorbing the dye with KOH solution, measuring the absorbance of the solution and calculating the concentration of N719 from the sample.
All UV/Vis absorption spectroscopy was carried out on a Jasco V-670 series Spectrophotometer using Spectra Manager™ II software. A reference measurement of the solvent with no sample is first taken and then subtracted from subsequent measurements. Samples were fully dissolved in either ethanol or 1 M aqueous potassium hydroxide solution and then added to a 1 cm glass cuvette for measurement. The transmittance measurements of thin sample films on FTO-glass substrate were also attempted. The sample length was taken as the estimated film thickness and a blank piece of FTO-glass was used as reference for measurements. This is discussed further in Chapter 3.
2.5 Diffuse Reflectance Spectroscopy

UV/Vis Diffuse Reflectance Spectroscopy is a useful technique to measure the reflectance by a sample of electromagnetic radiation in the ultraviolet and visible region of the spectrum.

There are two types of reflection; specular reflection and diffuse reflection. Specular reflection dominates on smooth polished surfaces. The intensity of specularly reflected light is dependent on the angle which the incident light strikes the surface and is referred to as the reflectivity of a sample. Diffuse reflection occurs more on rough or dull surfaces and is the result of multiple reflections, refraction and diffraction (scattering) inside the sample, therefore the intensity of diffusely reflected light is independent of the angle the incident light strikes the surface and is referred to as the reflectance of a sample. Multiple reflections occur at the surface of small particles, therefore randomly orientated crystals in the sample film will scatter light in all directions. If the particle diameter is larger than the wavelength of the incident light, the light is reflected around the sample depending on the extent of random crystal orientation and emerges diffusely at the surface. If the particle size is equal to or smaller than the wavelength of incident light, scattering will occur and multiple scattering will produce an isotropic distribution of diffusely reflected light.

The reflectance of a sample can be measured using Diffuse Reflectance UV/Vis spectroscopy (DRS) (Figure 2,6.). Incident light is directed through an integrating sphere and onto the sample which reflects some of the light. The intensity of light which is diffusely reflected is measured by a detector at an angle from the sample which does not detect specularly reflected light. As the sample absorbs some of the light the intensity of the reflectance is reduced. The absolute reflectance ($R_\infty$) of the sample is the ratio of intensity of reflected light ($R$) to the intensity of the incident light ($I_0$) as in transmission spectroscopy (Equation 2,6.).\(^9\)

$$R_\infty = \frac{R}{I_0} \quad \text{Equation 2,6.}$$
As the absolute reflectance is difficult to measure the reflectance relative to a standard \((r_\infty)\) is measured \((Equation\ 2.7)\). A non-absorbing white reference standard is used and the reflectance of this is considered to be 100% and all sample measurements are relative to this.

\[
r_\infty = \frac{R_{\text{sample}}}{R_{\text{standard}}}
\]

\(Equation\ 2.7.\)

\[\text{Figure 2.6. Diffuse reflectance spectroscopy set-up. The incident light is directed through the integrating sphere onto the sample. Any diffusely reflected light is reflected around the walls of the integrating sphere into the detector. Baffles are placed inside the integrating sphere to eliminate any contribution from incident or specularly reflected light.}\]

The intensity of reflectance in areas of strong absorbance depends on the path length of the light through the sample as light with longer path lengths will be absorbed and the shorter path lengths reflected and detected. Differences such as particle size, refractive index of the material and the homogeneity of the film all have an effect on the reflectance of the film. Areas of weak absorbance do not absorb some of the light with longer path lengths. This results in the intensities of reflectance being relative to the wavelength and path length of the light. The Kubelka-Munk function \((f(r_\infty))\) is used
to standardise the intensity so it can be used for quantitative analysis and comparison to transmittance data (Equation 2.8.), where $K$ is the absorption coefficient and $S$ is the scattering coefficient of the sample at each wavelength.

$$f(r_{\infty}) = \frac{(1 - r_{\infty})^2}{2 r_{\infty}} = \frac{K}{S} \quad \text{Equation 2.8.}$$

Plotting $f(r_{\infty})$ as a function of wavelength results in estimated absorption spectra which accounts for the reflectance of the material at different wavelengths so is much more suitable than transmittance spectroscopy for estimating absorption properties of solid materials. The Kubelka-Munk model is a general model for a solution to the equation of radiative transfer and makes various assumptions regarding particle shape among other things and so has certain limitations on the accuracy of results.$^{[10]}$ The model also assumes an infinite sample thickness (normally at least a few mm thick) and therefore assumes no light is transmitted through the sample meaning all light not detected is assumed to have been absorbed or specularly reflected by the sample. Measurements on thin films in the order of a few $\mu$m thickness may result in some light being transmitted through the sample leading to an overestimation of the absorption intensity.$^{[11]}$

The Kubelka-Munk function can then be used to estimate the optical gap of the crystalline sample. A Tauc plot of $(f(r_{\infty}).h\nu)^{1/n}$ plotted against $h\nu$, where $h\nu$ is the photon energy (eV) and $n$ is dependent on the type of transition occurring ($n = 2$ for indirect band gap material such as TiO$_2$, $n = \frac{1}{2}$ for direct band gap materials).$^{[12]}$ The linear region of this plot indicates the absorption onset therefore extrapolating this line to the x-intercept gives the optical gap of the material (Figure 2.7.).$^{[13]}$
Figure 2.7. Example Tauc Plot for indirect band gap TiO$_2$ highlighting how the size of the optical gap is extrapolated.

All UV/Vis Diffuse Reflectance Spectroscopy was carried out on a Jasco V-670 series Spectrophotometer using Spectra Manager™ II software with ISV-723 60 mm integrating sphere unit attachment. Diffuse reflectance spectroscopy was carried out on sample films produced as previously described. A white PTFE reference was used as standard for total reflectance and the sample films measured against this over wavelength range 250-950 nm. Kubelka-Munk conversions and Tauc plots were then produced from the measured reflectance data.
2.6 Brunauer-Emmett-Teller (BET) Analysis

Brunauer-Emmett-Teller (BET) theory, which was named after those to first publish the theory, is a widely used technique to explain the multilayer adsorption of gas molecules on a solid surface.\textsuperscript{14} The method uses gas, in this case nitrogen, to determine the specific surface area of solid powders.

The experiment is usually conducted at the temperature of liquid nitrogen. The powder sample is exposed to nitrogen atmosphere at different relative pressures and the volume of gas adsorbed by the sample is measured by volumetric or continuous flow methods. The measurements are treated using the BET adsorption isotherm equation (Equation 2.9,\textsuperscript{10}) where \( P \) and \( P_0 \) are the partial vapour pressure (in Pa) of adsorbate gas in equilibrium with the surface and the saturation pressure of adsorbate gas at the temperature of adsorption (77.4 K which is boiling point of liquid nitrogen), \( V_a \) and \( V_m \) are the total volume (in mL) of gas adsorbed and the volume of gas adsorbed to produce a monolayer on the sample surface (volume measured at standard temperature and pressure), while \( C \) is a constant related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

\[
\frac{1}{V_a (\frac{P_0}{P} - 1)} = \frac{C - 1}{V_m C} \left( \frac{P}{P_0} \right) + \frac{1}{V_m C}
\]

Equation 2.9.

The measured value of \( V_a \) is input and the left side of the equation is plotted as a function of the relative pressure (\( P/P_0 \)). Measurements at a minimum of 3 different relative pressures across range of 0.05 to 0.3 are normally required to ensure linearity of the plot however single point measurements can be made using certain assumptions. Values for \( V_m \) and \( C \) can then be derived from the BET plot using the following equations (Equation 2.10, & Equation 2.11.).

\[
V_m = \frac{1}{\text{(Slope+Intercept)}}
\]

Equation 2.10.

\[
C = \left( \frac{\text{Slope}}{\text{Intercept}} \right) + 1
\]

Equation 2.11.
The specific surface area (S) (in $m^2 g^{-1}$) of the sample is then calculated from the volume of gas adsorbed to produce a monolayer on the sample surface ($V_m$) using 

Equation 2.12.,

where $N$ is the Avogadro constant ($6.022 \times 10^{23}$), $\sigma$ is the effective cross sectional area of one adsorbate molecule ($1.62 \times 10^{-19} m^2$ for nitrogen),\cite{15} $V$ is the molar volume of the adsorbate gas (in mL) and $m$ is the mass (g) of the sample.

$$S = \frac{V_m N \sigma}{V m}$$  

Equation 2.12.

All BET measurements presented in this work were carried out by Huntsman Pigments & Additives.

2.7 Effective Surface Area Analysis

As some of the specific surface area measured by BET analysis may not be suitable for dye adsorption it is important to measure the surface area of the titania samples which is effective for dye adsorption to be able to suitably compare the different samples for use in dye-sensitized solar cells. All effective surface areas of titania samples measured in this work are relative to the N719 dye.

N719 dye adsorption studies were carried out on all of the samples by immersing the same mass of each dry powder sample in a 0.5 mM solution of N719 in ethanol for 24 hours to fully adsorb the dye, centrifuging the sample (4000 rpm, 10 minutes), removing the supernatant and then washing off all unbound dye with ethanol. The titania sample with bound dye was then immersed in a 1 M aqueous solution of potassium hydroxide to strip off the dye. UV/Vis transmittance spectroscopy was carried out on the base solution containing the stripped dye and the concentration calculated using $c = A/\varepsilon l$, using the value of $\varepsilon$ obtained from a Beer-Lambert plot of N719 in KOH. The number of moles ($n$) of N719 was calculated using $n = cV$, where $V$ is the volume of solution (L). The number of moles present was divided by the mass of the sample to show the moles of dye adsorbed per gram of titania, which was then
converted to molecules per gram by multiplying by the Avogadro constant \((6.022 \times 10^{23})\) and then converted to the area taken up by N719 dye molecules per gram of titania \((\text{m}^2\text{g}^{-1})\) by multiplying by the area estimated to be taken up by a single N719 molecule \((1.6 \times 10^{-18} \text{m}^2)\).\cite{16}

### 2.8 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a very useful technique to study the surface morphology of samples at very high magnification and resolution.\cite{17} Images are produced by scanning the sample with a focused beam of electrons which interact with the atoms in the sample and produce a signal (Figure 2.8.).

![Schematic diagram of Scanning Electron Microscope (SEM) using secondary electron imaging.](image)

**Figure 2.8.** Schematic diagram of Scanning Electron Microscope (SEM) using secondary electron imaging.
Electrons are produced by applying an accelerating voltage of 10 kV to a tungsten filament which heats it leading to thermionic emission of electrons over a wide area. The electrons are passed through a positively charged anode cylinder which focuses the electrons into a narrow beam. The focused beam is then passed through an electromagnetic condenser lens which controls the number of electrons in the beam relative to the aperture size. The electron beam is then passed between scanning coils which can manipulate the focus of the electron beam by creating a magnetic field which is controlled by changing the applied current. This allows the sample surface to be scanned in a raster scan pattern. The electron beam then passes through an electromagnetic objective lens which controls the point where the electron beam is focussed on the sample. The electron beam ionizes atoms at the sample surface which then emit secondary electrons. The amount of secondary electrons emitted depends on the topography of the sample. The emitted secondary electrons are then detected by a positively charged secondary electron detector. The signal is then converted by computer to an image of the sample surface where brighter spots indicate more secondary electrons were emitted relative to other areas of the sample. The technique is carried out in a high vacuum environment to avoid interference to the electron beam from air molecules. The sample is mounted on a motorized stage so the sample position can be adjusted.[18][19]

All Scanning Electron Microscopy was carried out on a Carl Zeiss SIGMA HD VP Field Emission SEM with an electron beam accelerating voltage of 10 kV using secondary electron imaging. Powder samples were mounted directly onto a sticky carbon pad on a sample holder. Films were prepared on FTO glass as previously described and placed face up on a carbon pad on a sample holder to view film morphology. Cross-sectional views of the films were obtained by scoring the back of the substrate and snapping the film in half using pliers. An alternative method of obtaining cross-sectional images is attempted in Chapter 6 by freezing the film and substrate in liquid N₂. The frozen substrate was then cracked apart using a hammer. A suitable piece of the substrate which has fractured through the film leaving a straight edge was selected. The suitable films were then mounted edge up on a sample holder to view film thickness. All samples were gold-coated prior to imaging to avoid charge build up at sample surface when scanning.
2.9 Mott-Schottky Analysis

Mott-Schottky analysis is an electrochemical technique which allows for the extraction of such parameters as charge carrier density and certain inbuilt potentials of the semiconductor film when forming a junction. This is done by investigating the capacitance of the space charge region ($C_{sc}$) at the interface of the sample film and an aqueous electrolyte over a range of applied potentials.

When an n-type semiconductor such as TiO$_2$ and electrolyte come together, an equilibrium is formed by electrons flowing from the semiconductor to the oxidised electrolyte so the Fermi level of both semiconductor and electrolyte are at the same energy level, leading to bending of the band edges (Figure 2.9.). This leaves a region at the semiconductor surface with positive charge carriers known as the space charge region. This is balanced by a very thin concentrated layer of negative charges which build up at the opposite side of the interface. The width of the space charge region ($d$) is inversely proportional to its capacitance when in a Schottky junction, as is shown by Equation 2.13.$^{[20]}

$$d = \frac{\varepsilon \varepsilon_0}{C_{sc}}$$  \hspace{1cm} \text{Equation 2.13.}

where $\varepsilon_0$ = permittivity of free space =8.854x10$^{-12}$ Fm$^{-1}$ and $\varepsilon$ is the dielectric constant of material whose values for TiO$_2$ vary from 31 to 117 due to crystallinity, phase, morphology etc. so an intermediate value of 60 is used throughout this work.$^{[21][22]}$

Altering the externally applied potential changes the size of the space charge region at the TiO$_2$ – electrolyte interface until the potential becomes so negative that no band bending occurs and the space charge region disappears, which is known as the flatband potential ($E_{FB}$). By investigating the capacitance of the space charge region at different applied voltages various properties of the sample can be extrapolated.
An external AC sine-wave of 0.01V amplitude and frequency of 100 Hz was applied and the current response recorded over a range of potentials. Frequency response analysis (FRA) software was used which then calculated the impedance (Z) using $Z = \frac{V}{I}$, where V and I are the sin wave voltage and current response. The software then modelled the impedance to extract the space charge capacitance at each applied voltage using a Randles circuit which is a simple equivalent circuit consisting of a resistor to represent the electrolyte resistance in series with a capacitor and resistor in parallel to represent the film. No capacitor is needed to represent the electrolyte as due to the infinitely high charge carrier density compared to the solid film the space charge region in the electrolyte can be considered infinitely thin and therefore no capacitive contribution is expected. The inverse of the square of the capacitance of the space charge region of the film was then plotted as a function of applied potential and the data examined using the Mott-Schottky relationship (Equation 2.14):
\[
\frac{1}{C_{Sc}^2} = \left( \frac{2}{\varepsilon_\epsilon_0 \epsilon N_D} \right) \left( E - E_{FB} - \frac{(k_B T)}{e} \right)
\]

Equation \ref{eq:2.14}.

Where the capacitance is measured in F per unit area (1 cm\(^2\) for all films), \(N_D\) = charge carrier density (cm\(^{-3}\)), \(E\) = applied potential (V), \(E_{FB}\) = flatband potential (V), \(\epsilon\) = electronic charge = \(-1.603 \times 10^{-19}\) C, \(k_B\) is the Boltzmann constant and \(T\) is the absolute temperature. The linear region of the plot proves the formation of a Schottky junction (\textit{Figure 2,10}). Using the Mott-Schottky relationship the charge carrier density (\(N_D\)) (electron concentration per unit area for n-type material) was calculated from the slope of the linear part of the graph (\textit{Equation 2,15.}) and the flatband potential of the sample in a sodium sulphate electrolyte solution calculated from the x-axis intercept of the extrapolated linear line.\textsuperscript{[24]}

\[
N_D = \frac{(2/\varepsilon_\epsilon_0 \epsilon)}{\text{slope}}
\]

\textit{Equation 2,15.}

As various assumptions are made such as the dielectric constant of the material and the ability of the Randles circuit to suitably model the porous films the exact accuracy of the results may be limited.

The sample films were prepared on conducting FTO-glass as previously described and used as working electrodes in a 3-electrode electrochemical cell containing aqueous 0.1 M Na\(_2\)SO\(_4\) solution at pH 7 along with a Platinum counter electrode and an Ag/AgCl reference electrode which were connected to an Autolab instrument using frequency response analysis (FRA) software. The capacitance of the space charge region of the films were measured over a potential range of -1.5 V to +1.0 V.
Figure 2.10. Example Mott-Schottky plot showing a linear region and how the flatband potential and charge carrier density of the sample are extrapolated from it.

2.10 Solar Cell Fabrication

Multiple DSSC devices were fabricated using the following method for each sample at each varying TiO$_2$ layer thickness to ensure reproducibility and reliability of results. The substrate used in this work is typically 2.2 mm thick glass coated with a TCO consisting of fluorine doped tin oxide (SnO$_2$:F) or FTO with a surface resistivity of 7 Ω/sq purchased from Solaronix. Pieces of FTO coated glass (2.5 x 1.5 cm$^2$) were scored and cut on the non-conducting side. The FTO glass was cleaned by sonicating in decon and water solution, in water, in deionised water and finally in ethanol for 15 minutes each. The FTO glass was then treated in UV-O$_3$ cleaner for 20 minutes. An optional thin compact TiO$_2$ layer was applied in certain devices by immersing the clean FTO-glass substrate conducting side up in a 40 mM solution of TiCl$_4$ in deionised
water which was heated to 70°C in a covered glass Petri dish. The substrate was left in the solution for 30 minutes, washed with deionised water and ethanol and left to air dry. The film was then heated at 450°C for 30 mins on a programmable hotplate and cooled to room temperature.

The mesoporous TiO₂ layer was applied using the doctor blading or screen printing method as described in the Film deposition section. Individual layers were levelled on a hotplate at 125°C for 10 minutes before addition of subsequent layers. After addition of the final layer the films were sintered. For standard devices the films were sintered on a programmable hotplate where the heating programme initially heats to 325°C over 35 minutes and stays at temperature for 5 mins, the temperature then increases over 5 mins to 375°C and holds for 5 mins, increases over 5 min to 425°C and holds for 5 mins, increases over 5 mins to 475°C and holds for 10 mins, then increases over 10 mins to 510°C and holds for 10 mins. The hotplate then switches off the heat and the samples are slowly allowed to cool on the hotplate to around 80°C. For devices which require low temperature sintering of the mesoporous layer the films were heated on a hotplate at 125°C for 30 minutes and allowed to cool to around 80°C.

The films were then placed in a 20 ml dye bath consisting of a 0.5 mM solution of N719 in 1:1 acetonitrile/t-butanol, with 2 electrodes to each dye bath, the titania layers facing apart, and left for a minimum of 24 hours in the dark. The working electrode was removed from the dye bath, rinsed with acetonitrile and ethanol and left to air dry. The edges of the doctor bladed films were scratched off using a glass slide and wiped with ethanol cloth to leave a 1 cm² active area. The screen printed films provide an active area of 0.36 cm². To produce the counter electrodes FTO coated glass (2.5 x 1.5 cm²) was scored and cut on the non-conducting side. Two holes were drilled through the non-conducting side of the glass using a diamond drill in positions to cover opposite corners of the working electrode active area. The drilled substrates were sonicated in deionised water for 15 minutes, in 0.1 M HCl in ethanol solution for 15 minutes and then in acetone for 15 minutes. The glass was placed in the furnace at 400°C for 10 minutes, removed and allowed to cool. A drop of platisol was smeared on the FTO side of the glass, covering the surface and the glass placed back in the furnace at 400°C for 15 minutes resulting in a thin Platinum coating on the FTO.
counter electrode was then allowed to cool to room temperature. A hole of the size of the active area was punched out of a sheet of 60 µm thick Surlyn plastic sealant slightly larger than the substrate size. The sealant was placed with the hole over the active area. The counter electrode was placed on top of the sealant, the platisol layer facing the working electrode so the drilled holes are at opposite corners of the active area and both electrodes have an exposed FTO contact area at opposite ends of the cell. The cell was placed on a hotplate at 125°C to melt the sealant and pressure evenly applied, sealing the electrodes together. A liquid electrolyte solution with an Iodide/triiodide redox couple, consisting of 0.6 M 1-butyl-3-methylimidazolium iodide, 0.03 M I₂, 0.5 M 4-tert-butylpyridine, 0.01 M guanidine thiocyanate in an 85:15 mixture of acetonitrile and valeronitrile was injected into the drilled holes, a vacuum applied, then slowly released, back flushing the electrolyte onto the active area of the cell. The top of the cell was gently wiped clean with an acetone cloth. The drilled holes were then sealed with plastic sealant and a glass coverslip. A layer of silver conducting paint was painted on the conducting side of the exposed contacts of each electrode.

Figure 2.11. General procedure for fabricating DSSC devices from doctor bladed titania film.
2.11 Solar Cell Testing

All Solar Cells were tested using Autolab potentiostat and analysed using General Purpose Electrochemical System (GPES) software. Solar illumination was provided by a Sciencetech 550-200 solar simulator with an AM 1.5 filter. The power output of 1000 W m\(^{-2}\) was calibrated using a silicon diode reference cell. The devices were all illuminated from the working electrode side. The cells were masked around the edge of the active area and connected to the potentiostat. A potential was applied and the current response measured across the applied voltage range (-1 V to +1 V), both under illumination and in the dark to ensure any current produced is due to illumination. The measured current (I) is divided by the cell area to provide the current density (J) and J-V curves were produced. The operating parameters \(J_{SC}\), \(V_{OC}\), Fill Factor and device efficiency were calculated by extracting data from the J-V curve as previously discussed.
2.12 References


Chapter 3. Initial Characterization of Huntsman TiO\textsubscript{2} Samples

3.1 Introduction

The aim of this chapter is to investigate some of the properties of the different titania samples produced and supplied by Huntsman Pigments & Additives as previously described and to identify which samples are most promising to be developed into Dye-Sensitized Solar Cells (DSSCs) for further study. The crystal phase, nanoparticle size, morphology and effective surface area for N719 dye adsorption was examined both as the powdered TiO\textsubscript{2} sample and as a 510°C sintered film as is used in a standard DSSC. Optical and electrochemical properties of the sintered films was also be assessed. All samples were compared to an Anatase Control Sample (purchased from Acros Organics, Titanium (IV) oxide, 98+% anatase powder) and a P25 Control Sample (purchased from Sigma Aldrich, Titanium (IV) oxide nanopowder, ~21nm particle size) which is commonly used as a standard TiO\textsubscript{2} in DSSCs. Electrochemical measurements on films are also compared to a commercially available TiO\textsubscript{2} Paste (Dyesol's 18NR-T Transparent Titania Paste, Average Nanoparticle Size 20nm).
3.2 Results & Discussion

3.2.1 BET & Effective Surface Area of Powder Samples

The specific surface area of the titania samples has previously been investigated at Huntsman using BET analysis. The BET method of measuring surface area uses small gas molecules such as N\(_2\) to saturate all the pores in the sample. Due to the pre-formed porous structure of nanoparticles in the Huntsman samples many of the pores may be too small or inaccessible to provide suitable adsorption sites for the larger dye molecules used in DSSCs. Dye adsorption studies were carried out to determine how much of the specific surface area of each sample is initially available for effective dye adsorption.

N719 dye adsorption studies were carried out on all of the samples by immersing the same mass of each dry powder sample in a 0.5 mM solution of N719 in ethanol and then washing off all unbound dye. The titania with bound dye was then immersed in a 1 M aqueous solution of potassium hydroxide to strip off the dye. UV/Vis spectroscopy was carried out on the base solution containing the stripped dye and the concentration calculated using \(c = A/\varepsilon \ell\), using the value of \(\varepsilon\) obtained from a Beer-Lambert plot of N719 in KOH. The number of moles (n) of N719 was calculated using \(n = cV\), where V is the volume of solution. The number of moles present was divided by the mass of the sample to show the moles of dye adsorbed per gram of titania, which was then converted to molecules per gram by multiplying by the Avogadro constant (6.022 x 10\(^{23}\)) and then converted to the area taken up by N719 dye molecules per gram of titania (m\(^2\) g\(^{-1}\)) by multiplying by the area estimated to be taken up by a single N719 molecule (1.6 x 10\(^{-18}\) m\(^2\)).\(^1\) The experiment was repeated 4 times to ensure reliability of results. The mean effective surface area is displayed along with the standard deviations from the mean for each sample and are compared to the BET results (Figure 3.1.).

It is much easier for the N\(_2\) molecules to penetrate the pre-formed porous network and also to occupy smaller pores without restricting access to other N\(_2\)
molecules when compared to the larger dye molecules, hence the measurement of effective surface area using molecules of dye, or molecules of comparable size and is a much more useful guide to the suitability of the titania for high dye adsorption. This is confirmed by the much lower effective surface area results in each of the Huntsman samples when compared to the BET specific surface area measurements.

All the Huntsman titania samples show very large specific surface areas when compared with the anatase and P25 control samples. A number of the samples show especially large specific surface areas, with the bead sample M712/21 showing the highest surface area of 276 m² g⁻¹. Porous titania has been produced in the literature with BET surface areas in excess of 400 m² g⁻¹ though time consuming or complicated synthetic routes are required for such high surface areas.[2] Commonly reported specific surface areas of mesoporous TiO₂ beads or spheres for use in DSSCs generally range between 100-250 m² g⁻¹ therefore the specific surface areas of a number of the Huntsman titania samples are particularly large in comparison.[3]

All the Huntsman titania samples have a higher dye adsorption, hence a higher effective surface area than the anatase control sample but not all are higher than the P25 standard. The M712 bead samples showed a significantly larger effective surface area with sample M712/12/1 repeatedly much higher than the others. It is interesting that the nanoparticle cluster samples which showed the highest effective surface area were samples 50-33-VP1 and 50-33-VP3 which were the only samples to undergo high temperature calcination treatment during synthesis to increase interparticle connectivity which usually decreases surface area.

The specific surface area results which were measured using the BET method show good agreement with the effective surface area results for the anatase control and P25 samples indicating all adsorption sites on the nanoparticles which are accessible by the small N₂ molecules are also accessible by the dye. Specific surface area results for P25 are consistent with findings from other groups.[4] The Huntsman samples do not show agreement or even a similar trend of results when comparing BET and effective surface area results, indicating that many adsorption sites in the pre-formed porous network of the Huntsman samples are not available to the dye due to either the
small size of the pores within the pre-formed structure or pores deep in the network made inaccessible due to steric hindrance of other dye molecules.

![Figure 3.1. Specific surface area of each TiO₂ sample (BET measurements) and the average effective surface areas and standard deviations (Dye adsorption measurements).](image)

### 3.2.2 XRD of Powder Samples

Powder XRD scans of the initial Huntsman samples and control samples were carried out to confirm crystal phase (Figure 3.2.). The anatase control sample exhibits diffraction peaks at 2θ angles of 25.3°, 37.9°, 48.0°, 54.0°, 55.1°, 62.7° and 69.7° which were assigned to diffraction from the 101, 004, 200, 105, 211, 204 and 116 planes of anatase TiO₂ (JCPDS card No. 21-1272). The peak around 25.3° is the major characteristic peak of the anatase phase. The M712/15 sample showed diffraction peaks at 2θ angles of 27.7°, 36.6°, 39.4°, 41.7°, 44.2°, 54.6°, 56.9°, 63.2°, 64.4° and 69.2° which were assigned to diffraction from the 110, 101, 200, 111, 210, 211, 220,
200, 310 and 301 planes of rutile TiO₂ (JCPDS card No. 21-1276).[5] The peak around 27.7° is the major characteristic peak of the rutile phase. Some slight peak shifting is observed between samples of the same phase mainly due to strain, stress and crystallite size differences in the powder layer.⁶ Factors such as stoichiometry, chemical composition, temperature and packing differences can also affect results. All Huntsman samples and the anatase control sample show as pure anatase phase except sample M712/15 which is pure rutile phase. The P25 control sample is around 93% anatase and 7% rutile phase which can be estimated from the XRD pattern by comparing the ratio of integrals of the distinctive anatase and rutile peaks at 2θ angles of around 25.3° (101 plane) and 27.4° (110 plane) respectively.⁷ Literature values of P25 phase composition generally describe a ratio of 85% anatase to 15% rutile however these values often vary depending on the sample preparation and the exact method used. There is also often a minor amorphous phase present which is not detected by XRD.⁷

---

**Figure 3.2. XRD pattern of all titania samples.**
XRD peaks for Huntsman samples are much broader than that of P25 and the control sample indicating the Huntsman samples have a smaller crystallite size (Figure 3,3). Crystallite size is a measure of the size of coherently diffracting domains in the particle and is not always the same as the particle size due to the formation of polycrystalline aggregates. The Scherrer equation was applied to the characteristic anatase and rutile peaks at 2θ angles of around 25° and 27° respectively to estimate the average crystallite domain size of the samples. As P25 has both crystal phases present the crystallite size was estimated using both characteristic peaks to find the size of each crystallite (Table 3,1.). As the unity value in the Scherrer equation is taken as 0.9 for all samples there may be some error present as the unity value may differ between samples due to packing differences and shape of particles in the sample.
All the Huntsman samples show crystallite sizes in the 8 – 13 nm range. It is worth noting that the 50-33-VP1 and 50-33-VP3 samples do not show noticeably higher crystallite size than the other Huntsman samples despite exposure to higher drying temperatures of 700°C and 300°C respectively during sample production, compared to the 110°C drying temperature of the other samples. This is most likely due to a short exposure time to the higher temperatures. The P25 and anatase control samples both have larger crystallite sizes than the Huntsman samples with the anatase control sample having a much larger crystallite size than the P25.

BET-specific surface area measurements which were carried out by Huntsman Pigments & Additives can also be used to estimate particle size (assuming spherical particle shape and uniform size) using Equation 3.1.

\[
D = \frac{6000}{(S_{\text{BET}} \times \rho)} \quad \text{Equation 3.1.}
\]

Where \( D \) is the particle size (nm), \( S_{\text{BET}} \) is the BET-specific surface area (m\(^2\) g\(^{-1}\)) and \( \rho = \) true density (4.2 g ml\(^{-1}\) for TiO\(_2\)).\(^8\)\(^9\) The particle sizes estimated here are for the individual nanoparticles which make up the bead or cluster formations of the Huntsman samples and do not relate to the size of the actual bead or cluster. The BET particle sizes are generally similar to the crystallite sizes estimated from XRD apart from the anatase control sample which is shown here to have a very large particle size of 163 nm which consists of multiple crystallite domains. The largest particle size of the Huntsman samples is the 50-33-VP1 sample (17 nm) indicating the high drying temperature may have caused more particle growth when compared to the other samples (Table 3.1). The small particles may be the same size as the crystallite domain however it is not possible that the size of the coherently diffracting domain extends beyond the size of the particle. The results which suggest this are most likely due to the number of assumptions which are made in both crystallite and particle size estimation methods and so it is not surprising to see a few disagreements in the results. The crystallite size and particle size results of the XRD and BET analysis on the P25 control sample show good agreement with literature values.\(^8\) Both sets of results do show a relatively low particle size of all Huntsman samples when compared to P25 which may partially explain the higher specific surface area observed by all Huntsman
samples as the smaller particles increase the surface area while also decreasing the pore size. The smaller pore size also partially explains the lower effective surface area observed by the mesoporous Huntsman samples when compared to the P25 as the small pores between connected nanoparticles may not be large enough to accommodate the dye. Small anatase nanoparticles of around 3 nm in size have been shown to provide high specific surface areas but will also provide smaller pores between nanoparticles.\(^\text{[2]}\) Very large particles such as those of the anatase control sample (163 nm) provide a very low surface area (8 m\(^2\) g\(^{-1}\)) as previously shown as there are fewer adsorption sites in a specific sample mass when compared to an equal mass of sample containing smaller particles.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diffraction_peaks.png}
\caption{Diffraction peaks from anatase planes 105 and 211 and rutile plane 211.}
\end{figure}

The diffraction peaks for planes 105 and 211 which are clearly defined in the anatase control and P25 samples merge into one broad peak in the anatase Huntsman
samples suggesting a slightly amorphous nature in the samples (Figure 3, 4). The integrated intensity was calculated from the area under the characteristic anatase and rutile peaks on the XRD patterns. This is a better guide when comparing sample crystallinity than maximum peak intensity as a sample with a large sharp peak may contain an equal proportion of crystalline material in the sample but more long range ordering of diffracting planes when compared to a sample which produces a smaller broader peak. This is particularly true when comparing samples of differing particle sizes as larger particles will contain more coherently ordered diffracting planes and increase the peak intensity as is seen with the anatase control sample. Smaller particles cause more varied orientation in the sample resulting in a broader peak. Peak intensities of different samples should not be compared quantitatively as no internal standard was used and any differences may be due to layer thickness and packing of the samples being measured.
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Table 3.1. Integrated peak intensity of characteristic anatase peak (rutile peaks in bold italic) of titania samples from XRD patterns and crystallite domain size estimation using Scherrer equation. Also shown are the particle size estimations from the BET measurements carried out by Huntsman Pigments & Additives.
3.2.3 SEM of Powder Samples

The P25 TiO$_2$ nanoparticle powder when viewed under SEM shows around 20-25 nm size individual particles which agrees with the results from XRD (Figure 3,5.). Some particle aggregation is obvious with the P25 but no larger structural morphology is present. The M712 samples when viewed under SEM show bead sizes in the 1-20 µm range which is considerably larger than beads normally used in solar cells.[10] The M712 bead samples are not perfect spheres as seen at lower magnification but on closer inspection more resemble donut shapes as part of the bead looks to collapse toward the centre, potentially due to the pressurised spray drying technique employed in the final step of fabricating the beads (Figure 3,6.). At higher magnification it can be seen that the bead is made up of a mesoporous network of small nanoparticles. The rest of the initial Huntsman samples are mesoporous nanoparticle clusters of varying cluster sizes up to ~8 µm with a distorted shape (Figure 3,7.). Bead sizes of 400-800 nm are better suited to scattering the light which is one of the goals of using the multi-functional bead morphology. The larger size could be an advantage as the nanoparticles are pre-fused over a larger bead, potentially improving electron transport.

Figure 3.5. SEM images P25 TiO$_2$ powder.
Figure 3.6. SEM images Huntsman sample M712/21.

Figure 3.7. SEM images Huntsman samples 50-33-VP1 (left) & ST2663/1 (right).
3.2.4 XRD of High Temperature Sintered Films

The samples were individually formulated into a printable terpineol based paste, applied to substrate, sintered at 510°C and characterized by powder X-ray diffraction to confirm the crystal phase (Figure 3,8.). The diffraction data were compared to the JCPDS data (card No. 21-1272 and 21-1276), confirming sintered paste samples are 100% anatase crystal phase for all samples except sample M712/15 which is produced from rutile TiO₂ nanoparticles and showed as 100% rutile and the P25 sample which shows as a mix of anatase and rutile phases in a similar ratio to that previously described. No phase conversion was observed for any of the samples during the processing or sintering of the paste.

![Figure 3,8. XRD pattern of 510°C sintered films of all titania samples.](image-url)
The high temperature sintered films of the Huntsman samples show a similar peak width and intensity to the P25 control sample film indicating a similar crystallinity and crystallite size (Figure 3,9.). The anatase control sample film shows a much higher intensity and narrower peak than all other samples indicating a higher degree of crystallinity in the film and larger crystallite size. The peak positions of all samples including P25 and anatase control samples show anatase or rutile peaks at 2θ angles of 25.35° and 27.44° after sintering indicating previous slight differences in peak position were primarily due to the amorphous nature of the unsintered samples.

![Figure 3,9. XRD pattern - Major Anatase & Rutile peaks of 510°C sintered films of all titania samples.](image)

The Scherrer equation was applied to the characteristic anatase and rutile XRD peaks to estimate the crystallite size in the sintered film (Table 3,2.). A substantial growth in crystallite size is observed for all Huntsman samples when compared to the unsintered powders with the lowest crystallite size raising from around 8 nm in powder
to 15 nm in the film, caused by the sintering at 510°C. As the heating of the films was conducted by gradually raising the temperature, the films are exposed to higher temperatures for a longer time period explaining why some of the M712 bead samples which were produced at 110°C then sintered in film at 510°C exhibit a similar crystallite size to the 50-33-VP1 sample which was initially produced using temperature of 700°C for a short time. The anatase control sample shows an increase in crystallite size during sintering of the film to around 43nm which is more than double the size of the P25 sample. No crystallite growth is seen in the anatase component of the P25 sample after sintering though the rutile crystallite size does increase. The lack of substantial increase in particle size when sintering P25 at 500°C is consistent with other reports from the literature.[8] As the crystallite domain size was roughly equal to the estimated particle size in the unsintered Huntsman samples and the crystallite size has increased after sintering in a film at 510°C it is necessary that the particle size must have also increased as the crystallite domain cannot extend beyond the particle. An increase in particle size will also provide a larger pore size within the sample and fewer grain boundaries in the film. After sintering at 510°C the diffraction peaks from the anatase Huntsman samples 105 and 211 planes show as distinct peaks rather than the single hump seen in the unsintered powder XRD pattern indicating an increase in crystallinity (Figure 3). The scale of the increase in crystallinity and size of the nanoparticles in the samples is controlled by the sintering conditions of the film. An optimum particle size can be obtained for use in a DSSC to maximize light harvesting through maximizing dye adsorption and reducing recombination though the exact size can differ depending on the system.[11] It has been shown that titania films with a nanoparticle size in excess of 20 nm increases the porosity of the film, thereby allowing easier access of dyes and leading to an increase in photocurrent in devices.[12]
Figure 3,10. Diffraction peaks from anatase planes 105 and 211 and rutile plane 211 of 510°C sintered films of all titania samples.
<table>
<thead>
<tr>
<th>TiO$_2$ sample</th>
<th>2θ angle at peak (deg)</th>
<th>Integrated Intensity</th>
<th>Peak width at 1/2 intensity (deg)</th>
<th>Crystallite size (nm)</th>
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<td>17</td>
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<td>876</td>
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</table>

Table 3.2. Crystallite domain size estimation of 510°C sintered film titania samples from XRD peaks.
3.2.5 Optical Microscopy of High Temperature Sintered Films

2 layers of each titania sample paste were screen printed onto a piece of FTO coated glass, sintered at 510°C, then soaked in a dye bath solution consisting of 0.5 mM N719 in ethanol, rinsed and left to dry. The films were examined under an optical microscope at up to 40x magnification. As the sintered TiO$_2$ film is mostly transparent to visible light very little can be seen of the undyed films. Once sensitized with N719 it can be seen that dye is definitely attached to the titania surface showing as red spheres indicating the bead morphology has possibly been retained as shown in sample M712/21 (*Figure 3,11.*). It is also clear that large cracks are present in the films which could prove problematic for the efficiency of devices. All other Huntsman M712 bead sample films looked similar to those displayed below. Of the non-bead samples, the 50-33-VP1 shows the least cracking in the film (*Figure 3,12.*). This is potentially due to the higher drying temperatures the samples were exposed to in the final stage of sample production providing a slightly larger particle size. As the samples have already crystallized more than the other samples it is possible less mechanical strain exists in the film while heating as less crystal growth is occurring so is more resistant to crack formation while heating and cooling.
Figure 3.11. Optical Microscope images of 510°C sintered M712/21 TiO₂ film: undyed - 10x zoom (top left), Dyed with N719 - 10x zoom (top right), Dyed with N719 - 40x zoom (bottom left & right).

Figure 3.12. Optical Microscope images 40x zoom - N719 dyed 510°C sintered films of sample 50-33-VP1 (top left), 50-33-VP3 (top right), ST2683/1 (bottom left) & ST2688/5 (bottom right).
3.2.6 SEM of High Temperature Sintered Films

A layer of each paste formulated from the control samples and all the Huntsman samples were each screen printed and sintered onto a piece of FTO coated glass, gold coated and viewed under SEM imaging to view the morphology of the sintered titania.

A uniform film is viewed on the control samples (Figure 3,13.) as there are very few or no preformed particle connections, leading to an even spread of available contacts.[13] Higher magnification reveals a porous network of nanoparticles with no higher structural ordering. The nanoparticles in the anatase control sample film when viewed under SEM are estimated to be around 160 nm in diameter which is similar to the BET particle size estimation carried out on the unsintered powder.

![Figure 3,13. SEM images of anatase control sample in screen printed 510°C sintered film.](image)

The M712 bead samples when viewed under SEM showed evidence that the bead morphology had been retained as shown in the film of sample M712/21 (Figure 3,14.). Similar images are seen for all M712 bead sample films. The film surface appears to be populated by large spherical lumps up to 20 µm in size which is consistent with the SEM images obtained for the powdered samples. The beads are surrounded in the film by more TiO₂ which is either other smaller beads or simply nanocrystals from the beads indicating that some of the beads had either collapsed
during sintering, or more likely had been crushed during formulation of the paste or screen printing. Small aggregates of nanoparticles are visible and are estimated to be around 60 nm in size but appear to be made up of nanoparticles around 20 nm in size which would agree with the XRD results for sintered films. The titania layers show lots of areas of aggregation and large cracks, unlike the control sample which appeared very uniform. This is potentially related to the presence of particles in the beads which have preformed linkages formed during the synthesis procedures of the beads, such as calcination.\textsuperscript{13} This leads to non-uniform film formation when sintering, as is seen on SEM imaging. As there is substantial crystal growth of the sample during heating as indicated by the XRD results it is also likely this has an effect on the film formation through additional mechanical strain imparted on the film. This strain is not present in the P25 film as no crystal growth is observed resulting in a crack free film. The final film quality and pore size distribution is heavily dependent on the initial environment of the sample particle aggregation. As pore coarsening is occurring during sintering where the small pores decrease in number and the large pores increase in size as the film dries until stabilized, the initial effects of large pores between beads are potentially magnified resulting in cracks in the film.\textsuperscript{14} It is also possible the ethyl cellulose used as a binder in the paste enhances the cracking in the bead sample films as it is creating more pores in an already large porous network.
Figure 3.14. SEM images of sample M712/21 in screen printed 510°C sintered film.

The films produced using the nanoparticle cluster sample 50-33-VP1 showed no sign of cracks in the film giving a very uniform layer (Figure 3.15.), while sample 50-33-VP3 films showed some cracking in the film but less than the other samples. These sample films as well as the four ST26 nanoparticle cluster sample films all showed micrometer sized particle clusters in a porous network with little order. The ST26 films all showed some cracking of the layers and some aggregation of nanoparticles but no sign of other morphological structure in the film (Figure 3.16.). Even though cracks in the film are seen in the non-bead samples there are much less than the M712 sample films, indicating the M712 beads did not fully crumble during paste formulation. This agrees with previous reasoning as there are more premade connections in the cluster samples than in the control sample powder, but much fewer than in the beads. Also a smaller crystal growth is observed during sintering for the non-bead samples. The individual nanoparticles are difficult to clearly define in the
film though the aggregates of the nanoparticles appear larger in the films using the non-bead cluster samples.

**Figure 3.15.** SEM images of sample 50-33-VP1 in screen printed 510°C sintered film.

**Figure 3.16.** SEM images 510°C sintered films of sample ST2683/1 (top left), ST2688/5 (top right), ST2683/9 (bottom left & bottom right).
3.2.7 Absorption Spectroscopy of N719 Sensitized Films

UV/Vis absorption spectroscopy was carried out on each of the dyed sample films to estimate the amount of dye adsorbed on the film. A blank piece of FTO glass was used as a standard baseline measurement. The absorption of each sample was then used to calculate the concentration as \( c = \frac{A}{\varepsilon l} \), where \( \varepsilon = 1.4 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \) which is the absorption coefficient of N719 on TiO\(_2\),\(^{[1]} \) \( l = \) path length of the light which is equal to the titania film thickness. Substrates were snapped in half through the film and the edge of the substrate viewed under SEM to estimate film thickness. The number of moles of N719 present on the dyed film was calculated using \( n = cV \), where \( V \) is the volume of the titania layer which is calculated using \( V = \pi r^2 h \), and then divided by 1000 to convert the volume into dm\(^3\), giving an estimated film volume of 3.85 x 10\(^{-7}\) dm\(^3\). The experiment was repeated 4 times to ensure reliability of results. The mean value of moles of N719 adsorbed on the sintered film along with standard deviations from the mean are shown (Figure 3.17.).

![Figure 3.17. Moles of N719 adsorbed on sintered film of each TiO\(_2\) sample, measured from UV/Vis absorption spectroscopy on dyed film. Mean value and standard deviations are shown.](image-url)
As each of the sample films show an absorbance peak in the visible region at 501 nm it confirms that dye was adsorbed onto each of the sample films. The tail of the absorbance peak across the visible region shown by the undyed TiO$_2$ is due to scattering effects of the film rather than visible light absorbance. This tail is also present in the dyed film which partially masks the absorbance peak of the sensitizer dye (Figure 3,18.). The large scattering effects in the visible region of the dyed films means the absorbance value obtained may be unreliable as higher scattering will reduce the amount of non-absorbed light transmitted through to the detector effectively showing as higher absorbance. The larger levels of cracking in the M712 bead films will add to this effect as the UV/Vis results depend on which part of the film the UV/Vis light beam is directed through, which is difficult to judge, as many of the films were not uniform, displaying high levels of cracking, meaning these areas have less dye to absorb light and the cracks themselves could scatter the light, further affecting results. This is shown in the results as the films with the least cracking when viewed under SEM were from the anatase control sample, which displays the most repeatable results as the film is more uniform. The anatase control sample film also shows a similar level of dye adsorption to all the Huntsman sample films which is unexpected when considering the difference in surface area observed in the powdered samples. It is likely the especially large particle size of the anatase control sample is scattering the incident light making the results unreliable.
3.2.8 Absorption Spectroscopy of Desorbed N719

To more accurately measure the dye adsorption of the sintered films the dyed films were placed into an aqueous 1 M solution of potassium hydroxide to desorb the dye. UV/Vis spectroscopy was then carried out on the base solution containing the desorbed dye and the number of moles of N719 calculated as previously (Figure 3.19). The molar absorption coefficient ($\varepsilon = 1.15 \times 10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$) for N719 in aqueous (1 M) KOH solution at the absorbance peak of 501nm was obtained from the relevant Beer-Lambert plot (Supp. Info). The experiment was repeated 4 times to ensure reliability of results. Only three results are generally required for statistical purposes but a practice run was carried out in the same manner and produced similar results to the following three runs and so the results were included. The mean value of moles of N719 desorbed from the sintered films along with standard deviations from the mean are shown.
All of the Huntsman titania samples show higher dye adsorption than the anatase control sample when measuring the dye desorbed from the film confirming the previous results from the UV/Vis directly on dyed films were not reliable.

The dye loading of the 510°C sintered films shows a slightly different pattern when compared to the dye loading of the unsintered powder samples. It is possible the sintering has removed any surface defects allowing an increase in dye loading in some samples. The effect appears more pronounced in certain samples such as M712/21 which showed the second highest effective surface area for dye loading as a powder but after sintering shows a significantly higher dye loading than all other films with a dye loading of $2.8 \pm 0.18 \times 10^{-7}$ mol cm$^{-2}$. The dye loading of the M712/21 film is statistically significantly higher than the other sample films as the second highest absorbing film is sample M712/12/1 and shows a 95% confidence interval of only $1.84 \pm 0.33 \times 10^{-7}$ mol cm$^{-2}$. The increase in dye loading of sample M712/21 after sintering is further investigated in Chapter 5 where the sample powder is sintered and shows an increase in effective surface area from around 38 m$^2$ g$^{-1}$ to 52 m$^2$ g$^{-1}$, leading to increased dye loading in the film and a higher photocurrent in the device.

The anatase M712 bead samples show the highest dye adsorption of the sintered films indicating the high surface area and porosity has been partially retained even though the bead morphology has been partially lost. Levels of dye loading for P25 films which have been optimized for use in DSSCs ranging from $8.2 \times 10^{-8}$ mol cm$^{-2}$ to $1.45 \times 10^{-7}$ mol cm$^{-2}$ are commonly found in the literature indicating most of the sintered Huntsman sample films adsorb a suitable amount of dye for potential use as films in devices. The effect of the sintering increasing dye loading is not as pronounced in other samples such as M712/15 which also showed the largest crystallite size of sintered film. The lower dye adsorption is most likely due to the larger particle growth as shown by XRD which decreases the surface area but can also increase the pore size increasing the number of accessible adsorption sites.

The results of stripping the dye from the film give a much more reliable view of the dye adsorption of the sintered titania than UV/Vis spectroscopy directly on the dyed film as factors such as cracking in the film are much less pronounced in the results as indicated by the lower error margins seen when repeating the experiment.
3.2.9 Diffuse Reflectance of High Temperature Sintered Films

2 layers of sample pastes were doctor bladed onto the FTO substrate and sintered at 510°C as previously done. Diffuse reflectance spectroscopy was carried out on each of the sample films using an integrating sphere and the reflectance spectra analysed (Figure 3.20.). The reflectance of the samples was standardised using the Kubelka-Munk function, the scattering and absorption coefficients of the TiO₂ films were obtained for all the wavelengths and the Kubelka-Munk function plotted as a function of wavelength which represents the normalised absorption of the sample taking into account the differing scattering effects of the samples (Figure 3.21.).[16]
A slight error may be associated with the diffuse reflectance measurements of the thin films as an infinite layer thickness is assumed which may not be present in the films. This may lead to some transmission of the light through the sample, lowering the measured diffuse reflectance. Also because the incident light does not penetrate as deeply into the film as it would a powdered sample the light scattering may be lowered but the specular reflection component increased. Even with the associated error the procedure was carried out to compare samples and ascertain the band gap of the materials. Each Huntsman sample and control samples were compared.

It can be seen that the Huntsman bead sample films display a lower diffuse reflectance than the other Huntsman non-bead sample films across the visible spectrum, potentially due to the larger size of nanoparticle aggregates in the non-bead sample films as observed under SEM. The rutile bead sample reflectance is higher than the anatase bead samples which is likely due to the superior light scattering and higher refractive index of the more tightly packed rutile phase, which is one of the reasons rutile is preferred over anatase as a white pigment in paints. The P25 film shows the lowest diffuse reflectance with the M712/12/1 and M712/13/1 films exhibiting similar reflectance values. The anatase control sample shows the highest diffuse reflectance of the films across the wavelength range potentially due to the large crystal size. A similar diffuse reflectance is shown by the 50-33-VP1 sample which was the sample exposed to the highest drying temperature during sample preparation.

All samples except P25 and M712/15 begin to absorb around 380 nm as the wavelengths are of energy greater than the band gap of the TiO₂ samples and so the absorption onset represents the size of the anatase TiO₂ band gap. The P25 and M712/15 samples containing rutile phase have a slightly red shifted normalized absorption onset beginning around 400 nm due to the slightly lower band gap of the rutile phase. Differences in the intensities of the normalised absorption are potentially due to slight differences in layer thickness or particle density in the film.
Figure 3.20. Diffuse Reflectance spectra of 510°C sintered TiO$_2$ films.

Figure 3.21. Diffuse Reflectance spectra with Kubelka-Munk conversion of 510°C sintered TiO$_2$ films.
The reflectance values were converted into a Tauc plot to further investigate the band gap of the samples (Figure 3,22.). It has been reported that drawing a line through the linear region of the plot and extrapolating to the x-axis shows the band gap energy for that sample.[18] The P25 and M712/15 samples show a lower band gap than the other samples as the x-intercept of the straight line of the slope is around 3.0 eV for these samples which is expected due to the rutile phase TiO₂. The P25 sample actually has 2 band gaps due to the rutile and anatase components however the slope of the lower band gap overshadows the other so only the lower band gap is indicated. All other samples show a band gap value around 3.2 eV which is as expected for nanocrystalline anatase samples.[19] Slight deviations in the band gap are potentially due to differences in particle size.

Figure 3,22. Tauc Plot of 510°C sintered TiO₂ films.
3.2.10 Diffuse Reflectance of N719 Sensitized Films

The sample films were sensitized with N719 as previously done and the diffuse reflectance measured (Supp. Info.). The Kubelka-Munk function was applied to the sensitized TiO$_2$ reflectance results to show the normalized absorbance of the films (Figure 3,23.). It can be seen the absorbance onset around 380 nm which is due to the TiO$_2$ is present as previously shown in the undyed film. A second larger peak with onset around 700 nm and peak around 520 nm which is not present in the undyed film is now seen confirming the N719 is bound to the TiO$_2$ film. The largest peaks are from the anatase M712 bead sample films indicating the dye absorption is greater on these films, especially films using samples M712/21 and M712/12/1, confirming previous results. The P25 film has a similar absorption peak to the lowest anatase bead sample peak which is M712/22. The rutile bead sample, all nanoparticle cluster samples and the anatase control sample all show a much lower normalized absorption peak than P25 indicating they do not have as much dye absorbed on their surface which is consistent with the previous effective surface area results.

Figure 3,23. Diffuse Reflectance spectra with Kubelka-Munk conversion of N719 sensitized 510°C sintered TiO$_2$ films.
The reflectance values were again converted into a Tauc plot to examine the band gap of the films (Figure 3.24). Two linear slopes are exhibited for the samples, one for the titania band gap as seen in the undyed films and one for the optical gap of the N719 sensitizer dye. The band gap of the TiO$_2$ shown by the linear slope at the higher energy is still exhibited by most samples but is much less obvious in the bead samples. The M712/15 sample still shows a lower band gap than the other samples of around 3.0 eV after sensitizing. The linear slope observed in the lower energy side of the Tauc plot which has an x-intercept around 1.5 eV for all samples would seem to indicate the optical gap of the sensitizer dye proving the films have indeed been successfully sensitized by N719.

![Figure 3.24. Tauc Plot of N719 sensitized 510°C sintered TiO$_2$ films.](image)

The above Tauc plot is calculated and plotted for an indirect band structure such as is found in TiO$_2$ so gives a good indication of the titania band gap. However, excitation of the sensitizer dye is an allowed optical gap transition of a molecule. Re-plotting the Tauc plot for a direct transition by changing the function of reflectance
equation from power of 0.5 to the square may give a better indication of the N719 optical gap though the model is not perfect as it is designed for inorganic solid state compounds.\textsuperscript{[20]} The re-plotted graph (\textbf{Figure 3,25.}) shows the N719 optical gap is actually above 1.95 eV rather than the 1.45 eV indicated by the indirect band gap plot which is in better agreement with literature values.\textsuperscript{[21]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_25.png}
\caption{Direct band gap Tauc Plot of N719 sensitized 510°C sintered TiO_2 films.}
\end{figure}
3.2.11 Mott-Schottky Analysis of Films

Sintered films of various sample pastes on conducting FTO substrate were used as the working electrode and placed in aqueous 0.1 M solution of sodium sulphate along with a reference electrode and platinum counter electrode. The capacitance of the films was measured across a range of applied voltages. A Mott-Schottky plot was produced showing the inverse of the square of the capacitance of the space charge region of the film as a function of potential (Figure 3.26). Though the Mott-Schottky relationship is generally used to describe planar interfaces rather than porous films, the procedure was carried out on selected samples to examine any broad trends which could potentially be used to interpret results. Using the Mott-Schottky relationship the charge carrier density \( N_D \) (electron donor concentration for n-type material) was calculated from the slope of the linear part of the graph and the flatband potential of the sample in a sodium sulphate electrolyte solution calculated from the x-axis intercept of the extrapolated linear line (Table 3.3).\(^{[22]}\)

All the films show a positive linear slope and a negative x-intercept. Therefore all the samples can be characterised as n-type and are suitable for electron transport in devices such as DSSCs.\(^{[22]}\) The charge carrier densities and flatband potentials of the sample films are comparable with various literature examples of TiO\(_2\) films, though the exact conditions such as pH, film morphology and fabrication methods can all affect results.\(^{[23]}\)\(^{[24]}\)\(^{[25]}\) The charge carrier density of the Huntsman samples appears to be roughly double that of both the P25 sample and the commercially available Dyesol paste which could increase the chances of recombination in a DSSC but is potentially beneficial as it means a lower resistance to charge transport.\(^{[26]}\) Sample ST2683/1 shows the highest charge carrier density potentially because of the addition of dopants during sample production. The flatband potential of the Huntsman bead samples and the P25 sample appears to be noticeably higher than the non-bead sample and the commercially available Dyesol paste. Lower and more positive flatband potentials can be a sign of a more protonated surface of the film which can aide dye adsorption and also lower the Fermi level of the titania which increases the driving force for electron injection from a sensitizer dye.\(^{[27]}\) A large negative flatband potential is however also
beneficial to photoelectrochemical cells as the higher Fermi level reduces the chances of recombination while also increasing the open circuit voltage in DSSCs.\[^{18}\][^{28}\][^{29}\]

![Figure 3.26. Mott-Schottky Plot of selection of 510°C sintered TiO$_2$ films.](image)

<table>
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<td>P25</td>
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</tbody>
</table>

*Table 3.3. Charge carrier density & flatband potential calculated from Mott-Schottky Plot of selection of 510°C sintered TiO$_2$ films.*
3.3 Conclusions

The initial differences in the sample properties cause differences in the final properties and quality of the sintered films. All the Huntsman titania samples are porous micrometer sized structures with large specific surface areas, possessing either an ordered spherical bead morphology or randomly clustered morphology formed from small nanoparticles. All of the titania samples were in the anatase phase except sample M712/15 which was in the rutile phase and the P25 control sample which is an anatase/rutile mix. The anatase samples all showed a higher band gap of 3.2 eV compared to the 3.0 eV of the rutile phase which is beneficial to the operation of DSSCs. The anatase control sample proved to show very low dye adsorption both as a powder and as a sintered film when compared to the other samples due to the low surface area caused by the relatively large particle size. All the Huntsman samples showed a much higher level of dye adsorption compared to the anatase control sample both as a powder and as a sintered film though only a few of the samples had comparable or greater dye adsorption than that of P25. The nanoparticle size of the Huntsman samples is generally much smaller than those of P25 resulting in a much larger specific surface area but many of the adsorption sites are unavailable to larger dye molecules due to small pore size and inaccessibility of the porous network so the effective surface area for dye adsorption is reduced. The pore size is potentially increased when sintering the film as some particle growth is indicated by XRD results. As a high level of dye adsorption is a critical factor in the successful operation of DSSCs the samples of particular interest are M712/21 which showed the highest dye adsorption of all sintered films while also having the highest specific surface area prior to sintering. Sample M712/12/1 is also of great interest as it not only showed the second largest dye adsorption of a sintered film but also showed the highest effective surface area for dye adsorption of all samples prior to sintering. This indicates its potential for use in flexible devices where a pre-formed mesoporous structure with a high surface area for dye adsorption may be of benefit due to the requirement of low temperature sintering methods used in the device fabrication. The samples of particular interest both possess the spherical bead morphology therefore sample ST2683/1 which showed the highest dye adsorption of a sintered film of all the non-bead samples will
also be fabricated into devices. This nanoparticle cluster sample is also of interest as it shows a much higher reflectance, higher charge carrier density and lower flatband potential than the other selected samples and will therefore be a useful comparison in device operation due to both its morphological and opto-electronic properties.
3.4 References


Chapter 4. Initial Device Performance, Low Temperature Application & Pre-Sensitized Titania for use in Flexible DSSCs

4.1 Introduction

In this chapter a selection of the previously identified Huntsman titania samples along with the control samples were formulated into the previously described terpineol paste, fabricated into standard DSSC devices and the performance properties compared. Different deposition methods of the titania are also compared for making reliable devices. Low temperature sintered TiO₂ devices are fabricated and different paste formulations attempted to assess the viability of the Huntsman titania for use in flexible devices. The devices are fabricated in a similar manner to the standard DSSCs except the mesoporous titania layer was only sintered at 125°C instead of the usual 510°C. The substrate used remains as FTO coated glass and the counter electrodes were still prepared at 400°C as previous however the performance of the low temperature prepared titania layer will be able to be examined and compared to P25. Literature studies of flexible DSSCs report efficiencies up to 8.6 % though high temperature sintering of metal substrates or compression methods are often used to achieve the higher efficiencies and are not always suitable for large scale commercial applications.[1][2][3] Flexible devices utilizing low temperature sintering methods of the titania film which are suitable for use on plastic substrates currently exhibit lower efficiencies up to around 5.5 %.[4][5][6][7] The lower efficiencies are mainly due to poor interparticle connections but the large pre-formed mesoporous structure of the Huntsman samples potentially offer a novel route to improving the performance. A large amount of time in the DSSC fabrication procedure is spent on sensitizing the working electrode therefore the possibility of pre-sensitizing the titania prior to paste formulation and application to the substrate is investigated in an effort to reduce device fabrication time. There are few examples of pre-sensitized TiO₂ in the literature.
Efficiencies up to 6.5 % have been reported though different methods of film formation such as compression were again used to achieve the higher efficiencies.\textsuperscript{[8]} Devices utilizing low temperature sintering of the pre-sensitized film currently report efficiencies below 1.5 % but the pre-connected structure of the Huntsman samples again offer a potential route to improving the performance.\textsuperscript{[9]} It is worth noting all devices fabricated in this chapter using the Huntsman titania are to assess the samples initial performance in devices and produce comparatively low efficiencies. The samples are modified and optimized for improved device performance in later chapters.
4.2 Results & Discussion

4.2.1 Screen Printed TiO₂ - DSSC Device Performance

Sets of dye-sensitized solar cells were produced utilizing the screen printing film deposition method of terpineol based titania pastes as described in Chapter 2. Devices were fabricated using the Huntsman samples M712/21 which showed the highest dye adsorption of a sintered film, M712/12/1 which showed the highest effective surface area for dye adsorption as a powder and second highest dye adsorption of a sintered film, and also sample ST2683/1 which showed the highest dye adsorption of a sintered film from the non-bead Huntsman samples as identified in Chapter 3. Devices were also fabricated using the anatase control sample and the commercially available Dyesol paste (Figure 4.1.). The Dyesol paste has a similar TiO₂ particle size to P25 and is specially formulated for screen printing deposition of the mesoporous titania layer in DSSCs, producing an optimum film thickness of ~12 µm with a 2-layer application and so should provide a good comparison for DSSC device performance.

Figure 4.1. Dyesol paste (left), terpineol based control sample paste (centre), screen printed Dye-Sensitized Solar Cell (DSSC) incorporating M712/21 TiO₂ sample (right).
The terpineol based pastes produced from the titania samples all appear as a white dispersion due to the TiO₂. Ageing of the paste changes its appearance to orange due to degradation of the organics in the paste. All cells were produced by screen printing two layers of the titania paste onto TiCl₄ pre-treated FTO glass substrates. The TiCl₄ pre-treatment of the substrate forms a very thin planar layer of TiO₂ ideally around 25 nm thickness on top of the FTO.¹⁰ This layer has been shown to block recombination at the FTO-electrolyte interface and also enhance photocurrent in the device. It has also been shown that increased thickness of this blocking layer can decrease the transmittance of incident light, decrease charge transport in the device and positively shift the conduction band energy of the mesoporous layer, potentially reducing the photocurrent and voltage.¹¹ The cells were then tested under standard AM 1.5 conditions using a solar simulator, the efficiencies calculated and the cell characteristics compared. Multiple devices were fabricated from all sample pastes to ensure reliability of the device fabrication process with only small deviations from the median shown in each set (Figure 4.2.). It is important the samples were all fabricated into devices using the exact same method so they could be reliably compared.

The Dyesol paste cells produced the highest efficiencies of all devices with the maximum efficiency approaching 3% (Table 4.1.). The higher efficiency is mainly due to the relatively high photocurrent of almost 8 mA cm⁻² resulting from the larger surface area caused by the small nanoparticle size (~20 nm). The 2.85% efficiency of the Dyesol paste device is lower than literature values of similar devices which is often around 7-8% with a record efficiency of 11.2% for devices using the N719 sensitizing dye and iodide electrolyte which demonstrate cell characteristics such as Vₘₚ of 0.84 V, Jₘₚ around 17 mA cm⁻² and fill factor of 74%.¹²¹³ The difference in efficiency when compared to literature values is most likely due to differences in the device fabrication procedure and lack of exact optimization of certain parts of the solar cell. The anatase control sample consistently showed the lowest cell efficiencies (~0.25 %) due to the very low observed photocurrent which is around 0.3 mA cm⁻². This is most likely due to poor dye adsorption caused by the low surface area resulting from the large particle size as observed in the previous chapter. The low efficiencies of the anatase control sample devices are similar to those observed by Grätzel in very early
DSSCs using smooth planar TiO$_2$ layers.$^{[12]}$ This would suggest it is not a good comparison for further devices incorporating mesoporous layers.

![Box plot showing DSSC efficiency ranges for each TiO$_2$ sample](image)

*Figure 4.2. Screen printed DSSC efficiency ranges for each TiO$_2$ sample showing maximum, minimum, median, first and third quartile values.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dyesol</td>
<td>638</td>
<td>7.84</td>
<td>0.57</td>
<td>2.85</td>
</tr>
<tr>
<td>Anatase control</td>
<td>987</td>
<td>0.32</td>
<td>0.79</td>
<td>0.25</td>
</tr>
<tr>
<td>M712/21</td>
<td>789</td>
<td>2.25</td>
<td>0.71</td>
<td>1.25</td>
</tr>
<tr>
<td>M712/12/1</td>
<td>787</td>
<td>3.29</td>
<td>0.67</td>
<td>1.74</td>
</tr>
<tr>
<td>ST2683/1</td>
<td>843</td>
<td>4.10</td>
<td>0.48</td>
<td>1.66</td>
</tr>
</tbody>
</table>

*Table 4.1. Characteristics of the best screen printed DSSC from each of the TiO$_2$ samples.*
Each of the three Huntsman titania samples were fabricated into working devices and consistently showed higher efficiencies than the devices incorporating the anatase control sample. This is mostly due to the higher photocurrent resulting from higher dye adsorption in the Huntsman samples compared to the anatase control sample, as shown in the previous chapter. The devices incorporating the non-optimized Huntsman sample pastes showed slightly lower, though comparable efficiencies to the devices incorporating the optimized Dyesol paste, indicating their potential for use in DSSCs. The nanoparticle cluster sample ST2683/1 devices showed slightly higher photocurrent and photovoltage than the devices using the bead samples M712/21 and M712/12/1. This is potentially due to the higher levels of cracking exhibited in the M712 bead sample films, as seen in SEM images in the previous chapter, highlighting the need for a uniform crack free mesoporous film. It is possible that the cracking of the films along with other differences such as particle size, film thickness, charge transport and recombination in the film stop the photocurrent from being as high as is seen in the Dyesol devices. All of the Huntsman devices showed a higher \( V_{OC} \) than the Dyesol devices which would generally agree with the Mott-Schottky results in the previous chapter where the Dyesol film showed the lowest flatband potential. The \( V_{OC} \) of the ST2683/1 device is higher than all devices except the anatase control sample. This would indicate that the sensitization and addition of electrolyte to the film has shifted the Fermi level of the ST2683/1 sample as it previously showed a comparatively low flatband potential as a sintered film.

The produced pastes are much less viscous than the Dyesol paste and layer optimization using the screen printing deposition method proved difficult and unreliable. The difference in cell efficiencies across and within batches of cells produced is potentially due in part to the screen printing procedure used. As the available screen printer was not a flatbed model and operated at an angle, the less viscous paste flowed on the substrate causing differences in film quality and thickness. This also causes problems when applying multiple layers as individual layers may not line up exactly to the previous layers, again causing differences in film quality. As the paste is forced through a wire mesh on the screen there is also the possibility of damaging the morphology of the bead samples and not achieving repeatable film quality. Applying two layers of a sample paste did not necessarily provide the same
layer thickness as with another sample due to differences in paste viscosity as well as different amounts of paste applied and pressure applied while screen printing, all of which lead to differences in the performance of the film in the device. With this in mind all following films produced in this work are fabricated using the doctor blading method which is more repeatable in a research laboratory environment, providing more uniform layers, whereas the screen printing method would be more suited to optimized large scale fabrication (Figure 4,3.).

*Figure 4,3. Two layers of screen printed (top) and doctor bladed (bottom) N719 sensitized 510°C sintered TiO₂ films using M712/12/1 sample paste (left) and M712/21 sample paste (right).*
4.2.2 Doctor Bladed TiO₂ - DSSC Device Performance

The doctor blading technique allows for a better control of layer thickness optimization than screen printing because the thickness and quality of each layer is repeatable as the less viscous paste could be applied to a flat surface while the use of Scotch tape can partially control the layer thickness. The TiCl₄ pre-treatment of the substrate was omitted in the following devices to allow for a more direct comparison of the samples’ performance. Devices with multiple layers were fabricated to find the optimum number of layers for each particular sample in each batch of paste due to differences such as viscosity which can affect layer thickness. Each layer was applied and levelled at 125°C before applying subsequent layers, turning the layer orange as the organics degrade (Figure 4, 4). The films were then all sintered by gradually raising the temperature to 510°C then allowing to cool slowly to minimise layer cracking, resulting in an opaque uniform film (Figure 4, 5). All films were added to N719 dye baths to sensitize the films, removed at the same time (Figure 4, 6) and then scraped to the desired active area size.

*Figure 4, 4. M712/12/1 sample films with increasing number of doctor bladed layers after levelling each layer at 125°C. Total number of layers in each film highlighted with 2 films each of 1-5 layers.*
Figure 4.5. M712/12/1 sample films with increasing number of doctor bladed layers after final 510°C sintering. Total number of layers in each film highlighted with 2 films each of 1-5 layers.

Figure 4.6. M712/12/1 sample films after 510°C sintering and N719 sensitization. Total number of TiO2 layers in each film highlighted with 2 films each of 2 & 3 layers.
The layer thickness was optimized by the number of layers applied as it was not feasible to measure the thickness of every film by SEM prior to cell fabrication. It has been shown the optimum TiO$_2$ film thickness for use in DSSCs using N719 dye is around 12-15 µm so it is assumed the optimum number of layers of paste applied in devices fabricated in this work achieves a similar film thickness to the literature values.$^{[14][15]}$ The layer thickness optimization for the P25 control sample devices and the effect of growing layer thickness on each of the DSSCs main operating parameters is shown in Figure 4,7, & Table 4,2. The highest efficiency for DSSC devices using P25 TiO$_2$ dispersed in the standard terpineol paste is found by applying 7 layers of the paste and levelling each layer individually before final high temperature sintering and dye-sensitization. With this layer optimization an efficiency close to 3% is achieved. This is similar to the highest efficiency achieved using the commercially available Dyesol paste during screen printing, indicating the fabricated P25 paste when doctor blading is a suitable reference sample. It can be seen the individual parameters have individually optimized values at different layer thicknesses, for example the highest $V_{OC}$ occurs with 3 layers of P25 but the highest $J_{SC}$ and FF values both occur with greater total layer thickness. The greatest overall efficiency is found with the layer thickness which provides the optimum balance between all contributing parameters.
Figure 4.7. DSSC parameters of example batch of devices for varying thicknesses of P25 TiO$_2$ layers.

<table>
<thead>
<tr>
<th>Layers TiO$_2$</th>
<th>Cell</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
<td>812</td>
<td>5.79</td>
<td>0.25</td>
<td>1.18</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>790</td>
<td>6.11</td>
<td>0.52</td>
<td>2.52</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>778</td>
<td>8.24</td>
<td>0.38</td>
<td>2.41</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>790</td>
<td>7.08</td>
<td>0.48</td>
<td>2.69</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>791</td>
<td>7.73</td>
<td>0.48</td>
<td>2.92</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>781</td>
<td>2.74</td>
<td>0.55</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 4.2. DSSC parameters of best performing cell for each varying thickness of P25 TiO$_2$ layer.

The selected Huntsman titania samples were formulated into optimized devices using the doctor blading method. The anatase control sample and the commercial
Dyesol paste were also used to fabricate similar devices for comparison. All samples used were fabricated into working DSSC devices. A number of devices were formulated and optimized using each sample paste and the best performing cell from each sample are compared in Figure 4,8. & Table 4,3. The cells produced using the doctor blade method show higher performance than the equivalent screen printed cells. This is potentially due to a more uniform layer application resulting in fewer defects in the films as well as each sample film having its layer thickness optimized.

The optimized cells using the Dyesol paste showed the highest efficiency of 4% with a higher photocurrent than the P25 and Huntsman devices, possibly due to better arrangement of nanoparticles and optimized charge transport in the film resulting from the commercially optimized paste formulation. The $V_{OC}$ of all optimized doctor bladed devices are very similar indicating all sensitized films have a similar Fermi level as the value of $V_{OC}$ is determined in the cell as the energy difference between the Fermi level of the sensitized TiO$_2$ and the redox potential of the electrolyte. As the redox potential of the electrolyte is the same in all devices any difference in the $V_{OC}$ is primarily due to differences of Fermi level energy. A slightly lower $V_{OC}$ is seen in the optimized Dyesol and ST2683/1 devices compared to the P25 and Huntsman bead sample devices which would agree with the Mott-Schottky results from the previous chapter.

The optimized P25 device showed a slightly higher efficiency (2.9%) than all Huntsman sample devices but some of the parameters are very similar, particularly when using the Huntsman bead samples which show efficiencies around 2%. The M712 bead sample devices both exhibit a higher photocurrent than the ST2683/1 device due to the higher dye absorption as shown in the previous chapter. The P25 and M712/12/1 devices exhibit similar $J_{SC}$ and $V_{OC}$ values. The difference in device efficiency is due to the lower fill factor of M712/12/1 device which is potentially due to the cracking of the film. A larger slope near the point of short circuit photocurrent can be seen in the J-V curves produced by devices using samples M712/12/1 and ST2683/1 when compared to the other samples indicating a smaller shunt resistance and hence a loss of current in the devices, most likely caused by defects in the film. These samples also exhibit lower fill factors in devices than sample M712/21 which is
the only sample to have undergone crossflow filtration during production to remove any remaining impurities. While any impurities are likely removed during sintering of the film, it may have an effect on final film quality and electron transport properties. The anatase control sample again shows very low efficiencies. A very low photocurrent is seen with this sample due to its low surface area caused by its large particle size. Due to these obvious inadequacies the anatase control sample will no longer be fabricated into devices in this work and all samples will be compared directly to the P25 standard.

Figure 4.8. J-V curves of optimized doctor bladed DSSCs incorporating selected Huntsman TiO₂ samples and control samples.
Table 4.3. Operating parameters of optimized doctor bladed DSSCs incorporating selected Huntsman TiO$_2$ samples along with optimized P25 and anatase control sample devices.

<table>
<thead>
<tr>
<th>TiO$_2$ Sample</th>
<th>layers</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dyesol</td>
<td>2</td>
<td>775</td>
<td>9.40</td>
<td>0.56</td>
<td>4.05</td>
</tr>
<tr>
<td>Control</td>
<td>1</td>
<td>798</td>
<td>0.19</td>
<td>0.64</td>
<td>0.10</td>
</tr>
<tr>
<td>P25</td>
<td>7</td>
<td>791</td>
<td>7.73</td>
<td>0.48</td>
<td>2.92</td>
</tr>
<tr>
<td>M712/21</td>
<td>3</td>
<td>791</td>
<td>5.37</td>
<td>0.48</td>
<td>2.05</td>
</tr>
<tr>
<td>M712/12/1</td>
<td>3</td>
<td>790</td>
<td>7.24</td>
<td>0.33</td>
<td>1.91</td>
</tr>
<tr>
<td>ST2683/1</td>
<td>1</td>
<td>771</td>
<td>3.98</td>
<td>0.29</td>
<td>0.90</td>
</tr>
</tbody>
</table>

With further optimization it may be possible to improve one or more parameters of the Huntsman samples which may allow them to outperform the P25 in DSSCs. For example, devices using M712/21 have an identical $V_{oc}$ and fill factor to P25 cells so an improvement in short circuit photocurrent may help to exceed the P25 cell performance which should be possible due to this sample having the highest effective surface area of a sintered film. If the problem of film cracking is addressed the fill factor and photocurrent could potentially increase in all devices therefore improving efficiencies. The fill factor is especially low in the best of the M712/12/1 sample devices most likely due to parasitic resistance of the cell caused by poor film formation and resistance to charge transfer through the film. The lower crystallite size observed in the sintered Huntsman sample films when compared to P25 adds more grain boundaries within the mesoporous layer which any photogenerated electrons must traverse, also potentially reducing charge transport in the film and lowering the photocurrent and fill factor in these devices. It should also be possible to further improve the overall device performance to achieve the higher efficiency values found in the literature by applying procedures such as the TiCl$_4$ pre-treatment of the substrate and post-treatment of the mesoporous layer which have been shown to improve device performance.$^{[16]}$
4.2.3 Low Temperature Paste Formulations

The paste used for low temperature sintering can only contain materials which will be removed from the film at sintering temperatures of 125°C therefore lower boiling point solvents are required as terpineol has too high a boiling point. Solvents with lower boiling points tend to be less viscous resulting in a thinner paste mix meaning the paste viscosity is mainly controlled by the ratio of TiO$_2$ to solvent. It is also not possible due to the lower sintering temperature to use the ethyl cellulose binder which is used to create porosity in the films. Two methods of fabricating low temperature pastes were attempted for comparison. The TiO$_2$ powder was dispersed in a 2:1 solution of tert-butyl alcohol and water, or alternatively in ethanol, both providing a 25% wt. TiO$_2$ solution which was stirred in the dark for 3 days, resulting in a runny white paste. The pastes were then doctor bladed onto the substrate, each layer levelled at 125°C for 10 mins, sintered at 125°C for 30 min on a hotplate then placed in a dye bath for 24 hrs before assembling the cell as shown in Figure 4.9.

Figure 4.9, 1 & 2 layer 125°C sintered M712/12/1 (left) and ST2683/1 (right) sample films doctor bladed from ethanol paste. Films undyed (top) and dyed with N719 (bottom).
4.2.4 XRD of Low Temperature Sintered Films

XRD was carried out on the low temperature sintered films to compare crystallinity and particle size to that of the powder samples and high temperature sintered films from the previous chapter (Figure 4.10). The integrated peak intensity of the high and low temperature sintered films is comparable as the samples will have similar thickness and packing. The integrated characteristic anatase peak intensity of the high temperature sintered film is more than double that of the low temperature sintered film indicating an amorphous phase is present in the Huntsman samples which is converted to the anatase phase during the high temperature sintering process. The 125°C heating of the sample films is not enough to further crystallize the samples and so the low temperature sintered films exhibit a similar crystallite size to the unsintered powders in the previous chapter (Table 4.4).

There is an obvious difference in the degree of crystallinity of the high and low temperature sintered films when using all Huntsman samples as demonstrated by the M712/21 sample films (Figure 4.11). It can be seen the 105 and 211 diffracting planes do not give two distinct peaks in the low temperature sintered film or in the unsintered powder but become defined peaks in the 510°C sintered film. This is due to the partially amorphous nature of the initial sample as shown in previous powder XRD measurements when compared to P25. The XRD technique cannot be used to assess the quantity of amorphous phase in the material as no coherently diffracting planes exist to cause a diffraction pattern and therefore there is no peak to compare to the anatase peak.\textsuperscript{18} The high temperature sintering of the film used in standard DSSC devices improves the crystallinity of the material and also causes increase in the crystallite size, however this heating is not available in low temperature sintered devices therefore the degree of crystallinity and particle size of the titania sample remains unchanged even after film formation.
Figure 4.10. XRD pattern of sample M712/21 as a powder and as 125°C and 510°C sintered films.

Figure 4.11. Major anatase XRD peaks (left) and XRD peaks from 105 & 211 diffraction planes (right) of sample M712/21 as a powder and as 125°C and 510°C sintered films.
Table 4.4. Integrated intensity, peak width at half maximum intensity and estimated crystallite size of sample M712/21 as powder, low temperature and high temperature sintered films.

<table>
<thead>
<tr>
<th>M712/21</th>
<th>2θ angle at peak (deg)</th>
<th>Integrated Intensity</th>
<th>Peak width at 1/2 intensity (deg)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>25.47</td>
<td>1706</td>
<td>0.87</td>
<td>9</td>
</tr>
<tr>
<td>125°C film</td>
<td>25.35</td>
<td>319</td>
<td>1.05</td>
<td>8</td>
</tr>
<tr>
<td>510°C film</td>
<td>25.35</td>
<td>720</td>
<td>0.53</td>
<td>15</td>
</tr>
</tbody>
</table>

4.2.5 Optical Microscopy of Low Temperature Sintered Films

All the low temperature sintered films were examined under an optical microscope. As with the high temperature sintered films the undyed films appear transparent or blue under the microscope and no morphology is visible. The N719 dyed films appear red for all samples. The P25 films appear very uniform at low magnifications but some cracks in the film are visible at higher magnification (Figure 4,12.). This cracking was not visible in the high temperature sintered P25 films and is potentially due to poor interparticle connections in the low temperature sintered film. The Huntsman samples exhibited poor film adhesion after multiple layer application with some peeling and cracking of the undyed film visible (Figure 4,13.). The dyed films of the M712 bead samples appear a darker red than the P25 and ST2683/1 films potentially indicating a higher dye adsorption. The M712 bead sample films also show cracking under magnification however the cracks are less random and are potentially boundaries between beads in the film indicating the morphology is at least partially retained during paste formulation and doctor blading.
Figure 4.12. Optical Microscopy images of 125°C sintered P25 film at 40x zoom (top left) & N719 sensitized 125°C sintered P25 films at 5x zoom (top right), 10x zoom (bottom left) & 40x zoom (bottom right) formed using H2O/TBA TiO2 pastes.

Figure 4.13. 125°C sintered M712/12/1 film (top left), Optical Microscopy image of N719 sensitized 125°C sintered M712/12/1 films at 10x zoom (top right & bottom left) & 40x zoom (bottom right) formed using H2O/TBA TiO2 pastes.
4.2.6 SEM of Low Temperature Sintered Films

The low temperature sintered films were imaged using SEM as shown in Figure 4.14. Large cracks are visible in the P25 film at lower magnifications which were not present in the high temperature sintered film. This cracking has likely developed due to poor particle adhesion to the substrate and poor interparticle connections indicating some instability in the film. No cracks are visible at higher magnification of the P25 film where a porous network of nanoparticles is revealed.

While cracking is observed in the low temperature sintered films using the Huntsman samples, it is much less pronounced than in the equivalent P25 film, as shown by the M712/21 sample film in Figure 4.14. There is no sign of any larger bead morphology at the surface of the films though some micrometer sized lumps may be remnants of beads that were broken during film formation. As the beads are in the size range 1-20 µm diameter, there is possibly a drying effect which takes all the large particles to bottom of the layer and the small particles to the top, resulting in a stratification or layering effect within the layer which is possibly why no large beads are visible at the surface. The doctor blading may simply remove any large beads from the substrate as the glass slide is swiped across the surface, leaving only the smaller beads within the film. It is also possible the doctor blading partially breaks apart the larger beads, especially with multiple layers due to the pressure applied by the glass slide used for blading the paste onto the substrate. At higher magnifications the individual nanoparticles still appear to be aggregated together in a densely porous network as was seen in the powder sample and high temperature sintered films indicating the pre-formed connections between nanoparticles in the bead or cluster samples still exist in the film after deposition even if the overall morphology is partially lost.
Figure 4.14. SEM images at varying magnifications of 125°C sintered films formed from ethanol paste using P25 (left) and M712/21 (right) TiO₂ samples.
The absorbance of the doctor bladed low temperature sintered films, both dyed and undyed, on FTO glass was examined using UV/Vis transmittance spectroscopy (Figure 4.15.). A blank piece of FTO glass was used as baseline therefore only absorbance of the films is measured. As with the high temperature sintered films in the previous chapter the light scattering effects from the TiO$_2$ layer cause a wide absorption peak across the visible spectrum making results unreliable. The undyed films actually show as opaque or white when viewed and so are less transparent than the equivalent high temperature sintered films which would add further error to results. A slight hump in the spectrum of the dyed films around 550 nm confirms the dye has been adsorbed on the film. Due to potential differences in the layer thickness of different sample films, scattering effects caused by the material and potential defects in the films, comparisons of different sample films are difficult due to potential errors. The potential differences in layer thickness also cause a potentially large source of error in dye uptake measurements on the films as the film volume cannot be calculated accurately.

Figure 4.15. Absorbance spectra from transmittance measurements of low temperature sintered P25 film (left) and M712/21 film (right) with and without N719 sensitization.
4.2.8 Diffuse Reflectance of Low Temperature Sintered Films

Diffuse reflectance measurements were carried out across the visible spectrum on low temperature sintered films of the selected Huntsman samples and P25, with and without N719 sensitization of the films. The absorbance was estimated using the Kubelka-Munk model and the band gaps estimated using a Tauc plot assuming an indirect band gap (Figure 4,16.). The band gap of the P25 is slightly lower than the anatase Huntsman samples due to the rutile component of the P25 as previously discussed. The N719 sensitized films show an absorbance peak around 520 nm which is not present in the undyed films. This is due to the absorbance of visible light by the N719 dye. Both M712 bead sample films show a significantly higher visible light absorbance when compared to the ST2683/1 nanoparticle cluster sample film. This is due to the higher surface area of these samples which allows a greater uptake of dye so more of the light can be absorbed. These results show a similar pattern to the effective surface area of the powder sample results in the previous chapter. The bead sample films also show a significantly higher absorbance and therefore greater dye uptake than the P25 film. As the films are formed from a binder free paste there is nothing to add extra porosity to the film such as the ethyl cellulose previously used. This may slightly reduce the dye uptake of the film as it is more difficult for the dye to penetrate the denser network. This is more likely to be an issue in the P25 film as the Huntsman samples already have a pre-formed mesoporous network which provides porosity in the film. This may explain why the bead samples show a significantly higher dye uptake as low temperature sintered films than the P25 even though the effective surface area of the samples as a powder was similar.
Figure 4.16. Diffuse reflectance measurements of low temperature sintered 2 layer TiO₂ films formed using ethanol paste, Kubelka-Munk conversion of TiO₂ films (top left) & N719 sensitized films (bottom left). Tauc plot of TiO₂ films (top right) & N719 sensitized films (bottom right).
4.2.9 Low Temperature DSSC Device Performance

DSSC devices were fabricated using low temperature sintering of the different TiO$_2$ samples in both the low temperature paste formulations. The devices are fabricated using the same procedure as the doctor bladed standard DSSC devices presented earlier except the titania layer was levelled for 10 minutes on a hotplate at 125$^\circ$C before subsequent addition of further layers and finally sintered on a hotplate at the lower sintering temperature of 125$^\circ$C for 30 minutes. The TiO$_2$ layer does not experience temperatures greater than 125$^\circ$C at any point during device fabrication and should therefore give a good indication of the potential of the samples for use in flexible DSSCs which require low temperature sintering due to the low thermal stability of the substrates generally used.

TiO$_2$ layer thickness optimization was carried out on devices for all selected samples using both low temperature paste formulations. It can be seen with the devices using P25 in the water based paste that the highest efficiency of 1.23% occurs with only 2 layers of paste (Figure 4,17.). Addition of further layers causes a decrease in efficiency due to decreases in both $V_{OC}$ and $J_{SC}$ (Table 4,5.). This is because the low sintering temperature of the films is not enough to create good connections between all the P25 nanoparticles. It is therefore more difficult for the photo-generated electrons to traverse the grain boundaries between P25 particles which increases the chance of recombination before reaching the FTO electrode. It is also likely the connections between the P25 and FTO may be weaker due to the low temperature sintering. This also partially explains why the optimized efficiency of 1.23% for the low temperature water based paste P25 device is significantly lower than the 2.92% efficiency of the equivalent high temperature sintered device shown previously. Other factors such as lack of a binder in the paste to create porosity in the film which may lower dye uptake and hinder diffusion of the electrolyte in the film and lack of TiCl$_4$ pre-treatment also effect the efficiency. Many of the literature reports of low temperature devices incorporate additives to the paste such as acetic acid which has been shown to improve the dispersion of TiO$_2$ in the paste, resulting in a more uniform film and also catalyses the formation of the TiO$_2$ network in the film which results in
improved device performance.\textsuperscript{[20][21]} It has also been shown in the literature that pre-treating the titania film with acid can affect interactions at the titania surface by adjusting the conduction band edge which has been shown to improve dye adsorption, electron injection and device efficiency.\textsuperscript{[22]} The acid was omitted from the paste in these devices to more accurately compare the performance of the initial titania samples without additional additives. The low temperature P25 device efficiency is slightly lower than some reported literature values. A similar device was reported with an efficiency of 3.6\% showing a similar J\textsubscript{SC} and V\textsubscript{OC} but a significantly higher FF.\textsuperscript{[6]} The lower efficiency is due to differences in the fabrication process and lack of exact paste and layer thickness optimization but the devices are made reliably and so the P25 devices can be used as a good indicator when comparing the performance of Huntsman sample devices to literature reports.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_17.png}
\caption{Layer thickness optimization of low temperature sintered P25 DSSCs using binder free H\textsubscript{2}O/TBA paste.}
\end{figure}
The same method was used to fabricate optimized low temperature devices from the Huntsman samples. However multiple layer application proved difficult as addition of a second layer caused some cracking and peeling of the final film while addition of a third layer caused the film to peel off the substrate. The effect was much more pronounced in the M712 bead sample films and is potentially due to poor adhesion of the large beads to the FTO. The large micrometer sized structures of the Huntsman samples have fewer points of initial contact with the FTO than the P25 nanoparticles which is not then aided by high temperature sintering, reducing the adhesion of the film to the substrate. The less ordered ST2683/1 sample showed slightly better adhesion than the bead samples, potentially due to a rougher surface creating more available contact points. The size, shape and surface chemistry of the beads could also cause particle aggregation on the substrate which is not hindered by the low viscosity solvents as it is in the terpineol paste, allowing additional layers to partially remove lower layers from the substrate. The adhesion of titania beads and P25 films to the substrate has been shown to be improved in the literature, increasing efficiency to around 4%, by chemical sintering or mechanical compression techniques which are suitable for the flexible substrates but may not be as suitable for large scale manufacturing.\(^\text{[23]}\)

All the best performing Huntsman devices were fabricated with 1 layer films as addition of multiple layers where possible reduced the cell efficiency by lowering

<table>
<thead>
<tr>
<th>Layers</th>
<th>Cell</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
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<td>794</td>
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<td>0.54</td>
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<tr>
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<td>708</td>
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<td>0.56</td>
<td>0.38</td>
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</tbody>
</table>

Table 4.5. DSSC parameters of best cells from layer thickness optimization of low temperature sintered P25 DSSCs using binder free H$_2$O/TBA paste.
photocurrent. The optimized cells made from P25 showed the highest efficiency of 1.23 %. The optimized cells made from sample ST263/1 gave the next best efficiency of only 0.13 %, while the devices fabricated from bead samples M712/21 and M712/12/1 gave the lowest efficiencies of 0.04 % & 0.08 % respectively (Figure 4, 18, & Table 4). The low efficiencies of the Huntsman sample devices result from very low V_{OC} and J_{SC} values when compared to the equivalent P25 device using the H_{2}O/tert-butanol paste. It is surprising the photocurrent is so low in all Huntsman sample devices as the high dye adsorption observed using diffuse reflectance of the low temperature sintered M712 bead sample films leads to the expectation of a higher photocurrent through greater absorption of photons in these devices. The low temperature sintering of the films may affect the interparticle connections as previously discussed for the P25 films. The nanoparticles have pre-formed interconnections in the Huntsman samples which make up the large bead or cluster samples but a high sintering temperature may still be required to improve these nanoparticle connections for effective charge transport through the film. The crystallinity of the Huntsman low temperature sintered films was lower when compared to the equivalent P25 film and high temperature films, as shown by XRD, which will also have an effect on charge transport through the film. Poor crystallinity can lower the photocurrent as excited electrons recombine before reaching the electrode as there is not a highly connected pathway through the full layer. As no crystal growth was observed during low temperature sintering of the Huntsman sample films there are also many more grain boundaries in the film which electrons must traverse to reach the electrode compared to both the P25 film which already had a larger crystallite size as a powder and the high temperature sintered films where crystal growth could occur. The nanoparticle size of the Huntsman samples is also initially small compared to the P25 nanoparticles, as shown by SEM, XRD and BET estimations, and as no particle growth is observed during the low temperature sintering of the films it is likely the pore size between the nanoparticles is also smaller in the Huntsman sample low temperature sintered films. This may inhibit electrolyte diffusion through the film potentially reducing charge transport which could also lower the performance of the device. Similar low temperature sintered devices have been reported elsewhere with improved photocurrent (~12 mA cm^{-2}) and efficiency (~5.5
% by increasing the particle size to around 60 nm to increase porosity in the film along with various other additions to the paste.\cite{17}

The lower $V_{OC}$ seen in all low temperature Huntsman sample devices when compared to those of P25 is most likely due to the lack of exposure of the samples to high temperatures during either sample production or during sintering of the film. This results in a lower crystallinity of the low temperature sintered Huntsman sample films compared to the equivalent high temperature film as shown by XRD. The reduced crystallinity indicates an amorphous content which will reduce charge transport and also contain any residual impurities present in the original material which are not burned out and are still present in the film. Any impurities can act as centres for recombination while adding defect energy levels into the TiO$_2$ band gap.\cite{24} This could lead to a lowering of the Fermi level in the titania sample when compared to high temperature devices which would result in a smaller difference in energy between the Fermi level of the TiO$_2$ and the redox potential of the electrolyte resulting in a lower overall $V_{OC}$ as is seen in the devices. Residual impurities present in the material may also have an effect on the charge transport through the film. A higher sintering temperature not only improves crystallinity but has also been shown to reduce the concentration of oxygen vacancies in the film which have been shown to increase recombination and reduce charge transfer near the interface.\cite{23,25} This highlights the need for highly crystalline titania for use in DSSCs to provide both a high $V_{OC}$ and also provide efficient charge transport for a high $J_{SC}$. The $V_{OC}$ of the P25 device is similar to the high temperature sintered device as most of the crystallinity is already present in the P25 sample prior to film formation and the P25 is relatively defect free therefore high sintering temperatures of the film are not required to improve this as is apparently required with the Huntsman samples. The Huntsman sample films do have the advantage of a pre-formed porous network which is not present in the P25 films due to lack of a binder in the paste.
Figure 4.18. J-V curves of best low temperature DSSCs using selected Huntsman TiO$_2$ samples and P25 control sample in H$_2$O/TBA paste.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layers</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>2</td>
<td>794</td>
<td>4.96</td>
<td>0.31</td>
<td>1.23</td>
</tr>
<tr>
<td>M712/21</td>
<td>1</td>
<td>565</td>
<td>0.13</td>
<td>0.49</td>
<td>0.04</td>
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<tr>
<td>M712/12/1</td>
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<td>603</td>
<td>0.25</td>
<td>0.49</td>
<td>0.08</td>
</tr>
<tr>
<td>ST2683/1</td>
<td>1</td>
<td>605</td>
<td>0.41</td>
<td>0.53</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 4.6. DSSC parameters of best low temperature cells using selected Huntsman TiO$_2$ samples and P25 control sample in H$_2$O/TBA paste.

It is possible the solvent used in the paste has an adverse effect on the samples or that any residual solvent left in the film may hinder charge transport or dye adsorption. The solvent used may affect the surface chemistry of the TiO$_2$ which may
affect dispersion in the paste and therefore film quality and also energy levels near the interface, altering photovoltage, dye adsorption and charge transfer. A paste formulation using only ethanol as a solvent was used to make low temperature sintered devices to investigate if the solvent interactions with the samples have any effect on device performance. Ethanol was chosen due to the lower boiling point so is less likely to remain in the film and is less likely than water to desorb dye if any residual solvent does remain. Other than the different paste formulation the following low temperature devices were made and optimized as previously. The J-V curve of the highest efficiency device for each TiO$_2$ sample is displayed along with the operating parameters in Figure 4,19. & Table 4,7.

A slightly more efficient low temperature sintered P25 device is fabricated with a maximum efficiency of 1.37% when using the ethanol paste. This is mainly due to the increased fill factor when compared to the equivalent device using the water based paste however the photocurrent is slightly reduced. This is potentially because the ethanol pastes have been shown to provide better film stability than water based pastes while also reducing the number of defect sites at the surface. The reduced number of defect sites potentially reduces the number of possible adsorption sites for the dye, resulting in a reduced photocurrent, though it is also possible the ethanol changes the surface charge resulting in less strongly bound dye.$^{[26]}$ The Huntsman sample devices again show very low cell efficiencies but the M712/21 sample does show a slightly increased $V_{OC}$ and $J_{SC}$ when compared to the equivalent device using water based paste. This is potentially due to the ethanol removing some of the defects in sample M712/21 leading to an increase in photovoltage and reduction in recombination. This effect is only seen in sample M712/21 which was the only sample to undergo crossflow filtration on sample production which removed the bulk of impurities from the material. It is possible the other Huntsman samples contain too many defects for the ethanol to have any significant effect. It is also possible the slight differences seen between devices using the same TiO$_2$ sample in different paste solvents is partly due to differences in film quality caused during cell production as well as solvent interaction during film formation. These differences between batches of cells is minimised through production of a number of cells of each type however the error is still present and should be taken into account when comparing solar cell parameters.
with similar values, especially those samples with lower efficiencies as effects of differences in substrate or counter electrode quality and other factors may be magnified.

The low efficiencies exhibited by the low temperature sintered Huntsman DSSCs when compared to the P25 devices is most likely due to residual impurities lowering dye uptake and impeding charge transport as well as the amorphous nature of the Huntsman samples as previously discussed. The ratio of amorphous material compared to anatase in the Huntsman samples cannot be quantified by XRD however the absence of defined peaks from 105 and 211 planes in low temperature sintered anatase Huntsman titania films would suggest an amorphous content is present. As this is the primary difference between all the Huntsman samples and P25 it would appear to be a common factor in the lower efficiency of the low temperature sintered Huntsman sample devices. The amorphous content is most likely due to the synthesis conditions of the initial samples as none were exposed to high temperatures for any significant amount of time. Literature procedures for producing highly crystalline titania generally expose the titania to high temperatures of around 300°C for a few hours and even this still leaves an amorphous component in the material.\[18\] It is likely the lower crystallinity of low temperature sintered Huntsman titania films when compared to P25 has an effect on charge transport through the layer and increases the defect concentration in the film. The other main differences between all Huntsman samples and P25 in low temperature sintered films are the small particle and crystallite size as previously discussed which potentially hinder charge transport and electrolyte diffusion through the film resulting in lower device efficiency. This is demonstrated in the J-V curves as the slope of the curve around V_{OC} is much greater for the P25 device when compared to the Huntsman sample devices indicating a much higher series resistance in the low temperature devices using the Huntsman samples due to poor charge transport in the devices resulting from the low crystallinity of the samples.
Figure 4.19. J-V curves of best low temperature DSSCs using selected Huntsman TiO₂ samples and P25 control sample in ethanol paste.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layers</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; (mV)</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>FF</th>
<th>Efficiency (%)</th>
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</thead>
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<tr>
<td>P25</td>
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<td>588</td>
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Table 4.7. DSSC parameters of best low temperature cells using selected Huntsman TiO₂ samples and P25 control sample in ethanol paste.
**4.2.10 Pre-Sensitizing Titania Methodology & Paste Formulation**

In an attempt to reduce device fabrication time, the possibility of pre-sensitizing the titania with N719 prior to paste formulation was attempted. This allows the paste to be applied to the substrate and immediately fabricated into a device without having to leave the TiO$_2$ film in a dye bath for 24 hours. The powder TiO$_2$ sample was added to a solution of 0.5 mM N719 in ethanol and left for 24 hours to adsorb the dye. The solution was centrifuged and the supernatant removed. The dyed TiO$_2$ was then washed with ethanol to remove any unbound dye. The dyed samples were then dried under vacuum and formulated into binder free pastes by dispersing in the same solvents as were used in the low temperature sintered devices. The films (Figure 4.20.) and devices were fabricated in the same manner as the low temperature devices without the 24-hour dye bath film sensitization step. Low temperature sintering of the pre-sensitized TiO$_2$ is essential as higher temperature sintering will degrade the N719 dye.

*Figure 4.20. N719 pre-sensitized M712/21 (top) and ST2683/1 (bottom) low temperature sintered films. Number of layers in each film highlighted with 2 films of 1 layer (left) & 2 layers (right) shown for each sample.*
4.2.11 Optical Microscopy of Pre-Sensitized Titania Films

Optical microscopy was carried out on the N719 pre-sensitized films to examine film quality as shown in Figure 4.21. A uniform film is viewed for all samples with some slight cracks or grain boundaries visible at higher magnifications. The red coloured N719 dye is obviously visible confirming dye is present across the whole film. The M712 bead sample films appear a darker red when compared to the P25 and ST2683/1 pre-sensitized films which appear more pink. This is due to the higher dye adsorption of the M712 bead samples as shown in previous dye adsorption and diffuse reflectance measurements.

![Figure 4.21. Optical microscopy images of 2 layer films formed using ethanol paste of N719 pre-sensitized P25 (top) and M712/12/1 (bottom) at 10x zoom (left) and 40x zoom (right).](image-url)
4.2.12 UV/Vis Spectroscopic Pre-Sensitized Film Characterization

Absorption spectroscopy of the pre-sensitized TiO\textsubscript{2} films showed similar results to the post-dyed high and low temperature sintered films where scattering effects of the film cause the tail of the TiO\textsubscript{2} absorbance peak to mostly mask the absorbance peak of the dye. It is difficult to observe the dye peak from the transmittance data though the larger absorbance peak of the TiO\textsubscript{2} from the films fabricated using the water based paste would indicate either a thicker film or greater levels of aggregation in the film compared to those fabricated from the ethanol paste as shown by the P25 films in Figure 4.22. This is further indicated in the reflectance data as a higher diffuse reflectance across the spectrum is observed as well as a higher normalized absorbance at wavelengths below 350 nm, corresponding to greater absorption by the titania, indicating more P25 is present in the film using the water based paste. Both P25 films were prepared using a one-layer application of each paste therefore it is likely the pre-dyed P25 is more dispersed in the ethanol paste resulting in a thinner, less aggregated uniform layer as was observed using optical microscopy. A potentially thicker layer should absorb more dye though this is not indicated by the reflectance data when applying the Kubelka-Munk model. Both pre-dyed P25 films show an absorbance peak around 520 nm indicating the dye is present in both films but a similar or slightly lower normalized absorbance peak is observed for the films formed using the water based paste. This suggests the potentially thicker film has less dye present than the thinner film formed from the ethanol paste. This is potentially due to a higher concentration of hydroxide ions in the water based paste which may partially desorb the bound dye from the surface of the TiO\textsubscript{2} prior to film deposition. Dye desorption is the result of competition between the dye and the solvent for binding to the Ti\textsuperscript{4+} sites and the weakening of dye-TiO\textsubscript{2} interactions due to dye solvation.\textsuperscript{[27]} As water has a higher binding energy to Ti\textsuperscript{4+} sites than ethanol it is more likely to desorb dye from the titania surface during paste formulation.\textsuperscript{[28]} The ethanol is unlikely to desorb any dye as the pre-dyed titania has already been subjected to several ethanol washes to remove any unbound dye during the pre-sensitization procedure. The TiO\textsubscript{2} particles which lose dye molecules may then begin to aggregate in the paste potentially
resulting in a slightly thicker, more aggregated film. The diffuse reflectance data appears generally similar to the previous post-sensitized low temperature sintered films. This confirms the dye is adsorbed on the TiO$_2$ and is successfully formulated from the dyed TiO$_2$ powder into a paste and applied to the substrate. The band gap of the titania and the optical gap of the N719 dye which can both be estimated from the Tauc plot show the same results as the post-sensitized low temperature sintered films indicating the pre-sensitized films are potentially suitable to function as light harvesting photoanodes in flexible DSSCs.

Figure 4.22. Absorbance spectra from transmittance data (top left), diffuse reflectance spectra (top right) with normalized absorbance from Kubelka-Munk conversion (bottom left) and Tauc plot (bottom right) of pre-sensitized P25 low temperature sintered films formed from 1-layer application of different paste formulations.
4.2.13 Pre-Sensitized DSSC Device Performance

The pre-sensitized samples were all formulated into working devices using the H$_2$O/tert-butanol paste formulation and the layer thickness optimized as previously done. The dye covering the surface of the TiO$_2$ creates a dispersing effect on the TiO$_2$ noticeably decreasing the viscosity of the paste and lowering the layer thickness of the film slightly when compared to the post-sensitized low temperature devices. This is shown by the increased number of layers required for optimum device performance when compared to the post-sensitized low temperature devices. This dispersing effect may also slightly reduce particle aggregation of the larger bead structures on film formation, or the dye increases the adhesion of the film to the substrate slightly, allowing for multiple layer application of the Huntsman samples which proved difficult in the post-sensitized low temperature sintered devices.

The pre-sensitized P25 devices gave a maximum efficiency with a 4-layer application of the paste resulting in an efficiency of only 0.29% as shown in Figure 4,23. & Table 4,8. This is much lower than the equivalent optimized post-sensitized low temperature sintered P25 device which gave an efficiency of 1.23%. This is potentially because the dye fully covers the TiO$_2$ surface and so partially hinders bonding between the TiO$_2$ and FTO substrate therefore reducing charge transfer at the interface. There may also be an issue of poor connections between the P25 nanoparticles for the same reason, potentially restricting transport of electrons through the film which explains why the photocurrent is lower than the equivalent post-sensitized device. The photovoltage is also lower than the post-sensitized devices potentially due to the restricted charge transfer while it is also possible the pre-sensitization procedure has lowered the Fermi level of the material. Pre-dye coated nanoparticles for use in DSSCs have been reported elsewhere, though the film sintering step is generally omitted due to the potential for dye degradation and replaced with a mechanical pressing method to improve nanoparticle interconnections and adhesion to the substrate. Using these methods efficiencies around 4.9%, with J$_{SC}$ and V$_{OC}$ values of 8.9 mA cm$^{-2}$ and 0.81 V, are reported for N719 pre-sensitized P25 devices.$^{[29]}$ Slightly higher efficiencies (~6.5 %) of devices incorporating pre-
sensitized, submicrometer size, highly crystalline anatase beads have also been reported by utilizing the light scattering effects of the beads and using different combinations of sensitizers to increase light absorption.\(^8\) It is worth noting many of the literature examples of DSSCs use very small active areas generally below 0.25 cm\(^2\) compared to the 1 cm\(^2\) areas used in this work. The smaller active area allows better selection of a more uniform, defect free area of the initial film to test while also having slight effects on overall device resistances.

![Figure 4.23. Layer thickness optimization of pre-sensitized P25 devices using H\(_2\)O/TBA paste.](image)

<table>
<thead>
<tr>
<th>Layers</th>
<th>Cell</th>
<th>(V_{oc}) (mV)</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>FF</th>
<th>Efficiency (%)</th>
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</tbody>
</table>

\(Table 4.8. DSSC parameters of pre-sensitized P25 devices of varying layer thickness using H\(_2\)O/TBA paste.\)
The optimized pre-sensitized M712/12/1 sample device also required multiple layer application with a maximum efficiency of around 0.03% seen with a 4-layer application as shown in Figure 4,24. & Table 4,9. This is much lower than the P25 device most likely for the same reasons as the low efficiency of the post-sensitized low temperature sintered Huntsman devices when compared with P25. As with the P25 devices all the operating parameters of the pre-sensitized M712/12/1 devices are lower than in the equivalent post-sensitized low temperature sintered device. As the beads already contain pre-formed linkages between nanoparticles it may be expected the charge transport in the film would be greater than the P25 film but as previously discussed regarding the post-sensitized low temperature sintered devices, the pre-formed linkages may not be strong enough to allow efficient charge transport.

![Figure 4,24. Layer thickness optimization of pre-sensitized M712/12/1 devices using H2O/TBA paste.](image-url)
When using the pre-dyed M712/21 and ST2683/1 samples in devices the addition of further layers resulted in lower efficiencies mainly due to a decreased photocurrent possibly caused by poor charge transport through the layers. Multiple layer applications with the Huntsman samples proved more difficult than with the P25 due to cracking and peeling of the films at greater layer thicknesses as was seen with the post-sensitized low temperature sintered devices. This effect was reduced as indicated by the greater number of possible layers as shown by the pre-sensitized M712/12/1 devices, though the reproducibility was still poor in the pre-sensitized devices.

It is possible the water in the paste is desorbing the dye from the TiO$_2$ surface, potentially lowering photocurrent as suggested by the diffuse reflectance measurements. Pre-sensitized devices using the ethanol paste formulation were therefore fabricated using the pre-sensitized P25 to examine solvent effects in the paste on pre-sensitized titania device performance. The J-V curves and operating parameters of the best performing cell of each pre-sensitized sample are shown in Figure 4.25. & Table 4.10.

A substantial increase in photocurrent is observed in the pre-sensitized P25 device when using the ethanol paste, indicating the water in the paste was indeed having an effect on the dye adsorption. The free OH$^-$ ions in the water based paste attack the TiO$_2$ surface, desorbing the dye and occupying the position on the surface.

<table>
<thead>
<tr>
<th>Layers</th>
<th>Cell</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>457</td>
<td>0.08</td>
<td>0.43</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>513</td>
<td>0.05</td>
<td>0.48</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>515</td>
<td>0.05</td>
<td>0.48</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>571</td>
<td>0.10</td>
<td>0.47</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>486</td>
<td>0.07</td>
<td>0.45</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Table 4.9. DSSC parameters of pre-sensitized M712/12/1 devices of varying layer thickness.*
The ethanol paste has less free OH ions and so does not replace the strongly bound dye at the TiO\textsubscript{2} surface allowing for higher photocurrent in the device. A slightly higher \textit{V}\textsubscript{OC} and FF is also observed when using the ethanol paste which would indicate the removal of some defect states from the titania by the ethanol as previously discussed, leading to an increase in the Fermi level and lower recombination. As the pre-sensitized P25 was treated with several ethanol washes during pre-sensitization prior to paste formulation it is likely any positive effects by the solvent would occur at this stage so it may be the H\textsubscript{2}O/tert-butanol solvent actually introduces defect states into the titania while positively shifting the Fermi level at the surface of the titania leading to a reduction of the operating parameters. The efficiency of 0.91\% achieved with the pre-sensitized P25 device using the ethanol paste is 3 times greater than the device fabricated using the water based paste and is close to the 1.37\% efficiency achieved with the equivalent post-sensitized low temperature sintered device. A similar increase in efficiency with the pre-sensitized Huntsman sample devices would be expected by simply changing the paste solvent to ethanol but due to the low efficiencies in the post-sensitized low temperature sintered devices further pre-sensitized Huntsman sample devices were not fabricated until the samples could be modified to improve low temperature sintered device performance. As the pre-sensitized Huntsman samples in the water based paste do indeed provide working devices it shows the fabrication procedure does work and with further modifications the samples are potentially suitable for such devices.
Figure 4.25. J-V curves of best pre-sensitized TiO$_2$ DSSCs using selected Huntsman TiO$_2$ samples and P25 control sample in H$_2$O/TBA paste. Also shown is optimized pre-sensitized P25 device using the ethanol paste.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Layers</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>Ethanol</td>
<td>2</td>
<td>735</td>
<td>2.14</td>
<td>0.58</td>
<td>0.91</td>
</tr>
<tr>
<td>P25</td>
<td>H$_2$O/TBA</td>
<td>4</td>
<td>659</td>
<td>0.95</td>
<td>0.46</td>
<td>0.29</td>
</tr>
<tr>
<td>M712/21</td>
<td>H$_2$O/TBA</td>
<td>1</td>
<td>279</td>
<td>0.05</td>
<td>0.41</td>
<td>0.03</td>
</tr>
<tr>
<td>M712/12/1</td>
<td>H$_2$O/TBA</td>
<td>4</td>
<td>571</td>
<td>0.10</td>
<td>0.47</td>
<td>0.02</td>
</tr>
<tr>
<td>ST2683/1</td>
<td>H$_2$O/TBA</td>
<td>1</td>
<td>482</td>
<td>0.09</td>
<td>0.42</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 4.10. DSSC parameters of best pre-sensitized TiO$_2$ DSSCs using selected Huntsman TiO$_2$ samples and P25 control sample in H$_2$O/TBA paste. Also shown is optimized pre-sensitized P25 device using the ethanol paste.
4.3 Conclusions

All the selected samples can be used in the fabrication of standard working DSSCs. The doctor blading technique of film deposition allows for a more uniform film with better control of layer thickness and greater reproducibility than the screen printed films. The standard high temperature devices fabricated using the Huntsman samples all showed much higher efficiencies than the anatase control sample (0.25 %) and comparable efficiencies with the P25 device (2.92 %) which all used the same paste formulation indicating their potential for use in DSSCs. The Huntsman bead samples M712/21 and M712/12/1 both showed higher efficiencies (2.05 % and 1.91 %) in the optimized devices than the ST2683/1 cluster sample (1.66 %) due to a larger photocurrent generated by greater dye uptake caused by the larger surface area of the bead samples. The device using the pre-optimized commercially available Dyesol paste showed the greatest efficiency (4.05 %) of all the standard DSSCs as the pre-optimized paste provided a uniform film with additives to tune the titania properties, though the device performance was lower than those reported in the literature due to differences in the fabrication procedures. The P25 and Dyesol paste both contain larger nanoparticles than the Huntsman samples and so may provide greater porosity and crystallite size in the sintered film, allowing for greater dye adsorption, electrolyte diffusion and charge transport leading to increased device performance. As the less crystalline Huntsman samples exhibit crystallite growth during sintering of the film this potentially leads to defects in the films lowering device performance.

The low temperature sintered and pre-sensitized P25 devices produced efficiencies which were slightly lower but comparable to various literature examples. While all the Huntsman titania samples were formulated into working devices, they were shown to be initially unsuitable for use in flexible and pre-sensitized DSSCs when compared to equivalent devices using P25 TiO$_2$. The films fabricated using the Huntsman bead samples showed a higher dye adsorption than the P25 films due to a larger surface area though the devices showed a considerably lower photocurrent, photovoltage and higher series resistance indicating poor charge transport and the presence of impurities in the Huntsman titania layers. This is due to
the lack of exposure of the Huntsman titania to high sintering temperatures during either the initial sample production or during device fabrication, explaining the difference in performance when compared to the standard DSSC devices. The higher sintering temperature both eliminates defect energy levels from the TiO$_2$ resulting in larger $V_{OC}$ and improves crystallinity and interparticle connections leading to increased charge transport of the photogenerated electrons resulting in a higher $J_{SC}$. Different paste formulations were investigated to examine the solvent effects on both the pre-sensitized titania and device performance. The ethanol paste was shown to provide a better film quality and have a beneficial effect on both low temperature and pre-sensitized device performance compared to the water based paste which appeared to add defect states into the titania and partially desorb dye from the pre-sensitized titania during paste formulation. The Huntsman titania samples are modified in the following chapters to improve performance in DSSCs, particularly for use in devices incorporating the low temperature sintering procedure where the device efficiency was substantially lower than the P25 standard.
4.4 References

27. De Angelis, F.; Fantacci, S.; Gebauer, R., Simulating dye-sensitized TiO$_2$ heterointerfaces in explicit solvent: Absorption spectra, energy levels, and


Chapter 5. **Huntsman TiO$_2$ Sample Modification for Low Temperature Application in Flexible DSSCs**

### 5.1 Introduction

The focus of this chapter regards modifying and optimizing Huntsman titania bead sample M712/21 to improve its performance in low temperature sintered and pre-sensitized DSSCs. The use of the Huntsman TiO$_2$ samples in low temperature sintered devices resulted in particularly low efficiencies in the previous chapter when compared to devices using the P25 control sample. Huntsman sample M712/21 previously showed the highest efficiency (0.21%) of the low temperature sintered Huntsman TiO$_2$ devices when using the ethanol paste formulation and therefore the focus of this chapter is to modify this sample to increase the device efficiency so it is at least comparable to the corresponding P25 device efficiency (1.37%). The low degree of crystallinity of the Huntsman samples in the low temperature sintered devices when compared to the P25 or high temperature sintered devices was shown to reduce photocurrent by inhibiting charge transport or reducing dye loading while residual impurities may also be present, lowering the V$_{OC}$ in devices. As the substrates generally used for flexible devices cannot survive high sintering temperatures it would be of benefit to improve the crystallinity of the M712/21 sample by pre-sintering at high temperature prior to paste formulation and device fabrication. A further reason for higher efficiency in the high temperature sintered devices is the improved interparticle connection. This could also potentially be improved by pre-sintering the Huntsman samples due to the pre-formed mesoporous structure. The effect of various pre-sintering temperatures on the sample and device performance are investigated to find the optimum pre-sintering temperature which provides the optimized low temperature post-sintered M712/21 DSSC efficiency. Pre-sensitized devices are also fabricated with the modified M712/21 sample to investigate if improvements in the low temperature sintered devices translate to improvements in pre-sensitized devices.
5.2 Results & Discussion

5.2.1 Pre-Sintering Sample M712/21 Powder

A small amount (~1 g) of sample M712/21 was placed into Pyrex bowls and individually heated in a furnace for 1 hour at 150°C, 200°C, 300°C, 400°C, 500°C, 600°C, 625°C and 650°C respectively. The samples were allowed to cool to room temperature and stored in sample vials (Figure 5,1.). It can be seen that pre-sintering the sample at temperatures of 200°C and above causes a discolouration of the sample, turning it from white to orange after pre-sintering at 200°C. This is likely due to initial degradation of residual organics still present in the material after the manufacturing process. Heating at higher temperatures further degrades the organics with the sample turning brown after pre-sintering at 300°C and an off-white cream colour observed after pre-sintering at 400°C. After pre-sintering for 1 hour at temperatures above 500°C it can be seen the sample again appears white indicating all residual organics have been fully degraded and burned out of the material.[1]

As the residual organics in the material are only fully removed after pre-sintering at temperatures above 500°C it is likely these impurities are at least partially removed in the high temperature sintered devices in the previous chapter. As the low
temperature sintered devices in the previous chapter did not expose the sample to higher temperatures it is probable that all the residual impurities were present in the final optimized devices which may partially explain the low performance as any impurities may affect charge transport and recombination in the film while lowering the Fermi level, resulting in reduced $J_{SC}$ and $V_{OC}$ in devices.[2]

It is worth highlighting that the 500°C pre-sintered sample only appears white after allowing to cool as when first removed from the furnace even the 650°C pre-sintered sample appears to glow yellow. This yellow colour only appears immediately after pre-sintering as the high temperatures cause the loss of some oxygen from the TiO$_2$, forming non-stoichiometric TiO$_{2-x}$. The oxygen vacancies create a defect energy level around 2 eV above the valence band and therefore some visible light absorption can occur, causing the observed colour to appear yellow immediately after heating. Upon cooling in air the sample is re-oxidized, eliminating the defect energy levels, returning to near stoichiometric TiO$_2$ and providing a white appearance as the band gap is again too large for visible light absorption. It is important the sample is cooled in air to reduce the final concentration of oxygen vacancies in the sample as they have been shown to cause defect states in the titania films in DSSCs resulting in lower dye adsorption, reduced charge transport and higher recombination. It is possible the concentration of oxygen vacancies could be further decreased by cooling the sample in a more oxygen rich atmosphere.[3][4][5]

### 5.2.2 XRD of Pre-Sintered Powder

Powder XRD patterns were obtained for sample M712/21 after 1-hour pre-sintering at various temperatures and compared along with the unsintered sample and the P25 control sample in Figure 5.2. Sample M712/21 shows no phase conversion after pre-sintering at temperatures up to and including 650°C as only the anatase peak is observed and no rutile peak is present. There is also a noticeable narrowing of the peak width in samples pre-sintered at temperatures above 400°C (Figure 5.3.). The peak width decreases with increasing pre-sintering temperature meaning the crystallite
domain size and potentially the actual nanoparticle size are growing with increasing temperature. The crystallite size when estimated using the Scherrer equation becomes similar to that of P25 with 1-hour pre-sintering treatment at temperatures above 600°C (Table 5.1.). The high temperature sintered M712/21 sample film in Chapter 3 provided a crystallite size of 15 nm after gradual heating up to 510°C. This is similar to the results of pre-sintering the sample at 500°C presented here and so presents a simple route to achieving optimized crystallite size prior to film deposition. At temperatures above 400°C the characteristic anatase peak intensity also increases with increasing temperature indicating an increase in the crystallinity of the material. This is also shown in the peaks corresponding to the 105 & 211 crystal planes which only become defined as two separate peaks at temperatures above 400°C and continue to narrow and increase in intensity with increasing temperature, again indicating an increase in crystallite size and crystallinity (Figure 5.4.). An increase in crystallinity should lead to increased charge transport and increase the number of available sites for dye adsorption, potentially improving the photocurrent and efficiency of devices.\(^{[6]}\)

![Figure 5.2. XRD patterns of sample M712/21 powder before and after heating in furnace for 1 hour at varying temperatures (°C). P25 powder XRD pattern shown for comparison.](image-url)
Figure 5.3. XRD patterns - Major Anatase & Rutile peaks of sample M712/21 powder before and after heating in furnace for 1 hour at varying temperatures (°C). P25 powder also shown.

Figure 5.4. XRD patterns - Diffraction peaks from 105 and 211 planes of P25 and sample M712/21 powder before and after heating in furnace for 1 hour at varying temperatures (°C).
Table 5.1. Integrated intensity, peak width at half maximum intensity and estimated crystallite size from XRD pattern of sample M712/21 powder after 1-hour pre-sintering treatment at various temperatures. P25 powder also shown for comparison using anatase and rutile (bold+italic) peaks.

<table>
<thead>
<tr>
<th>TiO$_2$ sample</th>
<th>1 hour heating temperature ($^\circ$C)</th>
<th>2θ angle at peak (deg)</th>
<th>Integrated Intensity</th>
<th>Peak width at 1/2 intensity (deg)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>N/A</td>
<td>25.57</td>
<td>2113</td>
<td>0.42</td>
<td>19</td>
</tr>
<tr>
<td><strong>P25</strong></td>
<td>N/A</td>
<td>27.70</td>
<td><strong>149</strong></td>
<td><strong>0.29</strong></td>
<td><strong>28</strong></td>
</tr>
<tr>
<td>M712/21</td>
<td>N/A</td>
<td>25.47</td>
<td>1706</td>
<td>0.87</td>
<td>9</td>
</tr>
<tr>
<td>M712/21</td>
<td>150</td>
<td>25.47</td>
<td>1975</td>
<td>1.07</td>
<td>8</td>
</tr>
<tr>
<td>M712/21</td>
<td>200</td>
<td>25.52</td>
<td>2208</td>
<td>1.10</td>
<td>8</td>
</tr>
<tr>
<td>M712/21</td>
<td>300</td>
<td>25.52</td>
<td>1650</td>
<td>0.91</td>
<td>9</td>
</tr>
<tr>
<td>M712/21</td>
<td>400</td>
<td>25.62</td>
<td>1866</td>
<td>0.68</td>
<td>12</td>
</tr>
<tr>
<td>M712/21</td>
<td>500</td>
<td>25.62</td>
<td>1956</td>
<td>0.53</td>
<td>15</td>
</tr>
<tr>
<td>M712/21</td>
<td>600</td>
<td>25.67</td>
<td>2124</td>
<td>0.45</td>
<td>18</td>
</tr>
<tr>
<td>M712/21</td>
<td>625</td>
<td>25.62</td>
<td>2347</td>
<td>0.36</td>
<td>23</td>
</tr>
<tr>
<td>M712/21</td>
<td>650</td>
<td>25.52</td>
<td>2656</td>
<td>0.31</td>
<td>26</td>
</tr>
</tbody>
</table>

The M712/21 sample was also sintered at 600$^\circ$C for 15, 30, 45 and 60 minutes and the XRD patterns compared to investigate the effect of heating time on the pre-sintering method. A much narrower anatase peak is seen after just 15 minutes of heating at 600$^\circ$C when compared to the unsintered sample (Figure 5,5.). Longer heating times further narrow the peak slightly and increase intensity but no significant difference is seen between heating times of 45 and 60 minutes. A similar pattern of
results is seen in the peaks from the 105 & 211 planes with the first 15 minutes of heating causing significant increase in the peak definition when compared to the unsintered sample and longer heating times slightly affecting the peak width and intensity. This allows a different variation on the method of increasing crystallinity by pre-sintering at a certain temperature and changing the heating time to fine tune the crystallite size.\cite{7}

Figure 5.5. XRD pattern - Major anatase peak (top) & diffraction peaks from 105 & 211 planes of sample M712/21 before and after sintering at 600°C for varying times in furnace. P25 powder also shown for comparison.
5.2.3 SEM of Pre-Sintered Powder

The various temperature pre-sintered M712/21 powder samples were examined using SEM. The bead morphology is retained after 1 hour heating in furnace at a range of temperatures up to 650°C (Figure 5.6, & Figure 5.7.). There is no sign of any beads breaking apart or fusing together as a result of the pre-sintering treatment. There is also no obvious sign of a change in the distribution of bead sizes when compared to the unsintered sample seen in Chapter 3. The wide distribution of bead sizes makes it difficult to estimate any specific individual change in bead size due to the pre-sintering treatment. Literature reports of solvothermally calcining fully amorphous TiO$_2$ beads of 1000 nm diameter at 160°C for 16 hours to provide highly crystalline anatase TiO$_2$ beads only reduces their size to around 850 nm.$^8$ A lower decrease in bead size, if any, would therefore be expected for the already partially crystallized Huntsman sample. The nanoparticles which make up the porous bead are visible under higher magnification and clearly show a particle size of around 30 nm diameter after pre-sintering at 650°C which is in agreement with the estimation from the XRD results.
Figure 5.6. SEM images of sample M712/21 after 1-hour sintering in furnace at 200°C (top left), 300°C (top right), 400°C (bottom left) and 500°C (bottom right).

Figure 5.7. SEM images of sample M712/21 after 1-hour sintering in furnace at 625°C (top left) and 650°C at varying magnifications (top right, bottom left and bottom right).
5.2.4 Effective Surface Area of Pre-Sintered Powder

The pre-sintered samples were soaked in an N719 dye bath for 48 hours to fully adsorb dye to the powder samples surface. Any excess dye was washed away and the bound dye was then stripped from the sample using KOH solution. The absorbance of the stripped dye in the KOH solution was then measured using UV/Vis transmittance spectroscopy and the effective surface area of each pre-sintered M712/21 sample was calculated as in Chapter 3 (Figure 5, 8). An increase in effective surface area is observed after pre-sintering the sample at increasing temperatures up to 400°C for 1 hour. This is potentially due to degrading and burning off residual organics in the sample which also accounts for the colour change seen in the samples below 500°C. As the organics are burned out of the sample and the crystallinity increases more surface area becomes available for dye adsorption which is consistent with what is seen in the literature.[6] After pre-sintering at 500°C the effective surface area reduces below that of the unsintered sample. The reduction in effective surface area indicates particle growth is occurring as larger particles have a lower surface to volume ratio, hence the same mass of TiO₂ will hold less dye if the particles are larger. Further reductions in effective surface area are observed as the pre-sintering temperature is increased, falling to around half the value of the unsintered sample after 1-hour pre-sintering at 650°C which is consistent with the increase in particle size indicated by the XRD results. It is possible the particle growth occurs with pre-sintering temperatures below 500°C but still results in an increase in effective surface area. As the nanocrystals grow during sintering so does the pore size, therefore some pores which were previously too small to accommodate the N719 molecules are now available resulting in an increase in effective surface area.[9] Some of the smaller pores may disappear while some larger pores may shrink slightly at higher temperatures to accommodate the larger particle size.[6] The effective surface area of P25, as measured in Chapter 3 to be around 55 m² g⁻¹, is higher than sample M712/21 but a similar effective surface area is observed after pre-sintering M712/21 at 400°C. The pre-sintering does appear to increase crystallinity of the sample at temperatures above 400°C as shown by XRD. A more crystalline TiO₂ should provide better electron transport giving a better performing DSSC, but heating the sample at higher
temperatures does increase the particle size which lowers the effective surface area of the sample, lowering the amount of dye which it can adsorb which will affect the photocurrent of the device. As previously shown, a sample with low crystallinity is not desirable and a high surface area is essential so a balance between the crystallinity and surface area must be found for an optimized device.

![Bar chart showing effective surface area of sample M712/21 after pre-sintering at varying temperatures. Mean value and standard deviations of repeated experiments are shown.](image)

**Figure 5.8. Effective surface area of sample M712/21 after pre-sintering at varying temperatures. Mean value and standard deviations of repeated experiments are shown.**

BET surface area measurements of the M712/21 sample were carried out after pre-sintering the sample at 500°C for 1 hour which resulted in a drop in specific surface area to around 1/3 of the value of the unsintered sample. Heating for further amounts of time at the same temperature did not result in any further drop in specific surface area (Supp. Info.). As the decrease in BET surface area is probably due to the smaller pores disappearing as the nanocrystals grow in size it is likely that heating the sample
for longer than 1 hour would not result in further crystal growth as no further change in BET surface area is observed, even after 5 hours of heating.

5.2.5 UV/Vis Spectroscopic Pre-Sintered Low Temperature Film Characterization

The pre-sintered samples were dispersed in a 25% wt. solution of ethanol which was doctor bladed onto FTO glass substrates and the film sintered at 125°C for 30 minutes as in the previous chapter (Figure 5,9.). More than a 2-layer application of paste induced large cracking and peeling of the film from the substrate as previously observed. Absorbance measurements using UV/Vis transmittance spectroscopy were carried out on the pre-sintered M712/21 sample films and showed similar results to previous films with the scattering effects of the films and slight differences in film thickness meaning it is difficult to gain any reliable comparative information using transmittance measurements of the films. (Supp. Info.). The sensitized films again show an absorption peak around 520 nm confirming dye is successfully adsorbed onto the TiO₂.

*Figure 5.9. Pre-sintered M712/21 low temperature sintered films.*
The optical properties of the undyed and N719 sensitized pre-sintered low temperature post-sintered films were also examined using diffuse reflectance spectroscopy. The reflectance data was converted using the Kubelka-Munk model to compare the estimated normalised absorbance of the films and the data are also represented as a Tauc plot to compare the band gaps of the films (Figure 5,10.).

![Figure 5,10.](image)

*Figure 5,10. Diffuse reflectance of various temp. (°C) pre-sintered M712/21 low temperature sintered TiO₂ films. Kubelka-Munk conversion of TiO₂ films (top left) & N719 sensitized films (bottom left). Indirect band gap Tauc plot of TiO₂ films (top right) & N719 sensitized films (bottom right).*

The slight differences in normalised absorbance of the undyed films at energies higher than the TiO₂ band gap are mostly likely due to differences in film quality and layer thickness of the films, potentially indicating a thicker titania layer in the unsintered, 600°C and 625°C pre-sintered M712/21 films caused by slight differences in paste viscosity and pressure applied during doctor blading. Differences in
absorbance of the undyed films at energies lower than the band gap are likely due to slight differences in the films used for the reflectance measurements and also the assumptions made when using the Kubelka-Munk model. As the films are not infinitely thick as is assumed in the model, the transmission of some light with longer wavelengths through the film is wrongly assumed to be absorbed as it does not reach the detector during the measurement. The Kubelka-Munk plot of the N719 sensitized pre-sintered films shows a peak around 520 nm for all films indicating successful dye adsorption. Though the comparative absorbance of the thicker films using the unsintered, 600°C and 625°C pre-sintered M712/21 samples is slightly exaggerated, a general trend of lower visible light absorbance with increasing pre-sintering temperature by the sensitized films can be clearly observed. This indicates a lower dye adsorption and hence a lower effective surface area in the film with increasing pre-sintering temperature as was indicated by the effective surface area results for M712/21 samples which were pre-sintered at temperatures of 400°C or greater. It could be expected the sample film with no pre-sintering treatment should have a similar or lower absorption than the 400°C pre-sintered film due to the lower effective surface. This is not directly indicated by the normalised absorption spectra but the discrepancy is likely due to a slight difference in film thickness.

The measured band gap of the pre-sintered M712/21 titania films remains constant at 3.2 eV for all pre-sintering temperatures further indicating no phase change has occurred during the pre-sintering of the sample. The optical gap of the N719 dye which can be estimated from the Tauc plot of the sensitized films appears to increase slightly with films incorporating the sample pre-sintered at temperatures of 600°C or greater. The Tauc plot for a direct band gap is shown to better highlight this phenomenon which indicates the optical gap increases from 1.8 eV with the unsintered sample to 2.0 eV with samples pre-sintered at temperatures of 600°C or greater (Figure 5,11.). This is potentially due to different surface interactions of the dye with the sample film due to the higher pre-sintering temperature but is also potentially due to differences in scattering effects as these films incorporate larger nanoparticles than the other films as a result of the higher pre-sintering temperature which may affect the results.
5.2.6 SEM of Pre-Sintered Powder after Paste Formulation

The 600°C pre-sintered M712/21 powder was added to ethanol and stirred for 3 days with a magnetic stirrer bar to formulate the paste used for low temperature film sintering. The solvent was then removed by vacuum and a portion of the remaining TiO₂ was placed on a sample holder and examined with SEM to establish if any morphological changes of the sample occur during paste formulation.

It can be seen many of the larger beads are not present but smaller beads with diameters up to 4 µm are still seen intact (Figure 5.12). Other pieces of aggregate structures of varying sizes and shapes are also visible which are presumably formed from the larger beads which have been broken during mixing of the paste due to the
shear forces and mechanical stresses exerted on the beads during mixing (Figure 5,13.). This shows that while the paste formulation process does not destroy all of the beads, the larger beads up to 20 µm in diameter are particularly unstable. This occurs because mixing the paste with a magnetic stirrer is equivalent to a low energy grinding process which breaks up larger agglomerates. Once the agglomerates are broken down to a certain size the grinding becomes inefficient and the smaller agglomerates remain.[10] As the larger beads are broken apart into smaller micro-structures rather than individual nanoparticles it can be assumed the pre-formed interconnected mesoporous structure is still present in these micro-structures as they are in the bead. The breaking apart of the larger beads during paste formulation partially explains why the films shown in previous chapters do not appear to contain larger beads, while also showing lots of non-bead structures which are not initially present in the sample. It is possible the screen printing and doctor blading film application methods also contribute to further breaking of beads during film deposition.

Figure 5,12. SEM images at varying magnifications of 600°C pre-sintered M712/21 powder sample after paste formulation with solvent removed under vacuum exhibiting bead structure.
5.2.7 SEM of Pre-Sintered Low Temperature Film

One layer films of the 650°C pre-sintered M712/21 sample dispersed in ethanol were doctor bladed onto FTO glass and post-sintered for 30 minutes at 125°C. The films were examined using SEM for both topographical and cross-sectional images of the films (Figure 5.14.). Films using the 650°C pre-sintered M712/21 sample give very uniform films when compared to the film quality of the low temperature sintered films fabricated from the unsintered M712/21 sample and P25 control sample in the previous chapter. None of the large cracking which was evident in both the unsintered sample and P25 sample films in the previous chapter is observed. It is possible the pre-sintering treatment may alter the surface chemistry of the sample, both aiding adhesion to the FTO substrate and reducing aggregation or repulsion effects between beads in the film. Also no particle growth occurs during film formation when using the pre-
sintered beads, which was a potential cause of film cracking in the previous chapter, resulting in lower stresses on the film while drying. Some micrometer sized structures are visible at the surface, most likely from the smaller pre-formed beads or micro-structures from the broken beads, indicating the doctor blading does not completely destroy the morphology and some pre-formed particle interconnections still exist in the film. At higher magnification a well-connected, highly porous network of nanoparticles is seen.

The sectional view of the film was obtained by scoring the back of the FTO glass and snapping the film through the middle. The sample was gold coated and mounted edge up on a sample holder for imaging. This method caused difficulty in acquiring useful images as much of the film and glass were damaged during snapping meaning it was often difficult to see where the glass ended and the layer began. It can however be seen in the image provided that a 1-layer application of the paste gives a layer thickness of around 5 µm.

![Figure 5.14. SEM images of low temperature post-sintered 650°C pre-sintered M712/21 sample film using 1-layer doctor blading application. Sectional view of film shown (bottom right).](image-url)
5.2.8 Pre-Sintered Low Temperature DSSC Device Performance

The various temperature pre-sintered M712/21 samples were formulated into ethanol paste, fabricated into low temperature sintered DSSC devices and tested as in the previous chapter to find the pre-sintering temperature which provides the optimum performance in devices. Layer thickness optimization was carried out as before and the J-V curves of the best cells using sample M712/21 pre-sintered at different temperatures are shown and the performance parameters compared (Figure 5.15. & Table 5.2.).

![Figure 5.15. J-V curves of best performing low temperature sintered DSSC devices using various temperature (°C) pre-sintered sample M712/21 titania.](image)

Figure 5.15. J-V curves of best performing low temperature sintered DSSC devices using various temperature (°C) pre-sintered sample M712/21 titania.
Table 5.2. Operating parameters of best performing low temperature DSSC devices using various temperature (°C) pre-sintered sample M712/21 titania.

<table>
<thead>
<tr>
<th>Pre-Sintering temp. (°C)</th>
<th>Layers</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1</td>
<td>703</td>
<td>0.48</td>
<td>0.61</td>
<td>0.21</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>728</td>
<td>1.40</td>
<td>0.65</td>
<td>0.66</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>769</td>
<td>3.31</td>
<td>0.51</td>
<td>1.30</td>
</tr>
<tr>
<td>600</td>
<td>2</td>
<td>764</td>
<td>5.89</td>
<td>0.49</td>
<td>2.20</td>
</tr>
<tr>
<td>625</td>
<td>2</td>
<td>784</td>
<td>5.76</td>
<td>0.53</td>
<td>2.41</td>
</tr>
<tr>
<td>650</td>
<td>2</td>
<td>794</td>
<td>4.08</td>
<td>0.58</td>
<td>1.89</td>
</tr>
</tbody>
</table>

The pre-sintering treatment of sample M712/21 has a highly positive effect on the performance of the low temperature sintered DSSCs. It can be seen the $V_{oc}$ of the devices is increased as the pre-sintering temperature of the sample increases. An increase of up to 91 mV is observed by pre-sintering the sample at 650°C. This is similar to the highest $V_{oc}$ achieved among all the high temperature sintered standard DSSCs in the previous chapter. The increased $V_{oc}$ is likely due to the pre-sintering treatment removing impurities from the sample meaning there are fewer defect states to occupy in the band gap of the material, raising the Fermi level of the titania and so causing a greater difference between Fermi level and redox potential of the electrolyte. Higher pre-sintering temperatures remove more defect energy levels resulting in a greater $V_{oc}$ in the low temperature sintered devices. The high temperature sintered M712/21 devices in the previous chapter all exhibited a $V_{oc}$ of around 790 mV after post-sintering at 510°C which is only achieved in the low temperature post-sintered M712/21 devices after pre-sintering at 650°C. The 500°C pre-sintered M712/21 device exhibited a slightly lower $V_{oc}$ of 769 mV than the equivalent post-sintered temperature device most likely due to differences in the terpineol based paste and the ethanol paste formulations which can affect the conduction band edge of the titania film. The $V_{oc}$
may also be affected by poorer connections to the substrate resulting from the low-temperature post-sintering of the film.

The $J_{SC}$ is also observed to substantially increase with increasing pre-sintering temperature to a maximum value of 5.89 mA cm$^{-2}$ in the 600°C pre-sintered device, while a similar photocurrent (5.76 mA cm$^{-2}$) is obtained in the 625°C pre-sintered device. The effective surface area and dye adsorption of these films was shown to be lower than both the unsintered sample and the 400°C pre-sintered films but the degree of crystallinity and crystallite size were both shown to increase with increasing pre-sintering temperature. Any residual organics still present in the lower temperature pre-sintered devices greatly inhibits charge transport. Higher pre-sintering temperatures remove more residual organics and convert more of the amorphous phase to anatase leading to increased charge transport in the film with increasing pre-sintering temperature, resulting in a substantially increased photocurrent in the devices using the higher temperature pre-sintered M712/21 sample. The improved charge transport in devices with higher pre-sintering temperatures is confirmed by the reduction in series resistance in these devices, shown by the increased slope of the tangent to the $J$-$V$ curve near the point of open circuit voltage. A similarly high shunt resistance is observed for all devices indicating they are all reliably fabricated and comparable. At pre-sintering temperatures above 600°C the photocurrent in the devices begins to decrease. This can be attributed to the reduction in effective surface area in the higher temperature pre-sintered samples indicating there is an optimum balance between high surface area for increased charge generation and high crystallinity for increased charge transport in the film. The size of the individual nanoparticles in the unsintered M712/21 sample was estimated by XRD and BET analysis in Chapter 3 to be no bigger than 9 nm in size and XRD analysis of the pre-sintered samples show crystallite sizes up to 26 nm. It is therefore indicated particle growth has occurred during the pre-sintering treatment. This may increase porosity in the film with increasing pre-sintering temperature, allowing better diffusion of the electrolyte through the film leading to better regeneration the dye and lower recombination.

The optimum balance between properties is found in the device fabricated using the 625°C pre-sintered M712/21 sample, resulting in an optimum efficiency of
2.41%. This is a substantial increase on the 0.21% efficiency achieved with the unmodified M712/21 sample and far exceeds the 1.37% efficiency of the equivalent P25 device fabricated in the previous chapter, indicating once modified the Huntsman M712/21 sample is very suitable for use in low temperature sintered DSSCs (Figure 5,16. & Table 5,3.). The pre-formed mesoporous structure of the 625°C pre-sintered M712/21 sample offers significant advantages over the individual P25 nanoparticles for use in low temperature sintered devices. Most binders cannot be added to the paste to improve the porosity of the P25 film as it cannot then be removed. This leads to lower dye adsorption and electrolyte diffusion. No binder is required with the mesoporous beads as the porosity already exists in the pre-formed structure. The major limiting factor on charge transport in the low temperature sintered P25 device is the poor interparticle connections in the film caused by the lack of high sintering temperatures. As the crystallinity of the individual nanoparticles in sample M712/21 is increased with increasing pre-sintering temperature, so is the strength of the interparticle connections within the pre-formed bead structure. This greatly improves the charge transport in the resulting low temperature post-sintered 625°C pre-sintered M712/21 film compared to the P25 film as the pre-formed structure was shown to be at least partially intact in the film when using SEM. It is also worth noting that multiple layer devices become optimum in devices using the sample pre-sintered at temperatures above 600°C, highlighting the increased charge transport in the sample film as multiple layers in devices with lower sample pre-sintering temperatures caused a lowering of photocurrent and overall performance due to the poorer interparticle connections. The results compare well with literature reports of pre-sintering porous micrometer size TiO₂ ‘micro-balls’ for use in similar devices which show slightly lower efficiencies of 2.06% and slightly lower V_{OC} and J_{SC} values than found in the optimized 625°C pre-sintered M712/21 sample device, while the comparative P25 device reported alongside this showed a similar efficiency of 1.43% to the P25 device presented here (1.37%).[11] The improved performance compared to P25 was mainly attributed to the pre-formed connections and improved light scattering of the ‘micro-ball’ structure which is also the case with the 625°C pre-sintered M712/21 sample device. The higher performance of the Huntsman sample compared to the ‘micro-balls’ is due to the optimization of the pre-sintering conditions. Similar devices using
electrospray deposition to produce hierarchically structured spheres with strong pre-connected particles are also reported where an additional compression treatment is applied to increase connectivity between the particles, the hierarchical structures and the substrate, increasing the efficiency from around 2% to 5%.\textsuperscript{12} These pre-formed interparticle connections are obviously of great benefit as they reduce the need for high temperature sintering on the substrate and so expand the range of suitable substrates for DSSCs. This is highlighted by the optimized 2.41% efficiency of the 625°C pre-sintered M712/21 low temperature post-sintered device which actually exceeds the optimized efficiency of 2.05% achieved with the standard M712/21 in the optimized high temperature sintered DSSC device in Chapter 3.

\textbf{Figure 5.16.} J-V curves of the highest efficiency low temperature fabricated DSSCs using P25, sample M712/21 and 625°C pre-sintered M712/21 TiO$_2$ in ethanol paste.
Table 5.3. Operating parameters of the highest efficiency low temperature fabricated DSSCs using P25, sample M712/21 and 625°C pre-sintered M712/21 TiO$_2$ in ethanol paste.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layers</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>1</td>
<td>781</td>
<td>2.79</td>
<td>0.63</td>
<td>1.37</td>
</tr>
<tr>
<td>M712/21</td>
<td>1</td>
<td>703</td>
<td>0.48</td>
<td>0.61</td>
<td>0.21</td>
</tr>
<tr>
<td>625°C - M712/21</td>
<td>2</td>
<td>784</td>
<td>5.76</td>
<td>0.53</td>
<td>2.41</td>
</tr>
</tbody>
</table>

5.2.9 Pre-Sintered Pre-Sensitized DSSC Device Performance

As the 625°C pre-sintered M712/21 Huntsman titania sample displayed increased performance in the low temperature sintered post-sensitized DSSCs when compared to both the unsintered sample and P25 it was also examined for suitability in pre-sensitized titania devices. The pre-sensitized devices were fabricated as in Chapter 4 using the ethanol paste formulation. The paste again appeared much less viscous than the low temperature paste. Layer thickness optimization of the pre-sensitized film was carried out as previously done (Figure 5.17. & Table 5.4.).

The highest efficiency device incorporating N719 pre-sensitized 625°C pre-sintered M712/21 titania used a 1-layer application of the paste and provides an efficiency of 0.46%. It can be seen that the addition of multiple layers results in a decrease in $V_{OC}$, $J_{SC}$ and efficiency. The addition of the dye to the titania prior to film deposition causes a partially insulating monolayer to be formed on the beads surface. When the dyed beads are fabricated into a film the monolayer of dye likely inhibits the formation of connections between the beads. This lack of a well-connected network is expected to inhibit charge transport of photogenerated electrons within the film, meaning the electrons cannot reach the conducting substrate before recombination.
occurs. A similar insulating layer of dye will be formed at the FTO-TiO₂ interface which also potentially reduces charge transport in the device. Thicker layers of pre-sensitized titania create a longer path length with more grain boundaries and therefore more dye-inhibited interfaces for the electrons to cross, leading to a decrease in performance with increasing layer thickness. The V_{OC} and J_{SC} values of the optimized N719 pre-sensitized 625°C pre-sintered M712/21 device are lower when compared to the equivalent low temperature post-sensitized device. This further illustrates the insulating effect the dye molecules between beads and between beads and the substrate have on charge transport in the device.

![Graph showing efficiency vs. number of layers](image)

*Figure 5.17. Device efficiencies of N719 pre-sensitized TiO₂ DSSCs using 625°C pre-sintered M712/21 TiO₂ in ethanol paste with varying number of layer depositions.*
Table 5.4. Operating parameters of best cell at each layer thickness for N719 pre-sensitized TiO₂ DSSCs using 625°C pre-sintered M712/21 TiO₂ in ethanol paste.

<table>
<thead>
<tr>
<th>layers</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm⁻²)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>679</td>
<td>1.32</td>
<td>0.51</td>
<td>0.46</td>
</tr>
<tr>
<td>2</td>
<td>664</td>
<td>1.24</td>
<td>0.44</td>
<td>0.37</td>
</tr>
<tr>
<td>3</td>
<td>652</td>
<td>1.14</td>
<td>0.48</td>
<td>0.36</td>
</tr>
<tr>
<td>4</td>
<td>581</td>
<td>0.45</td>
<td>0.42</td>
<td>0.11</td>
</tr>
<tr>
<td>5</td>
<td>596</td>
<td>0.76</td>
<td>0.46</td>
<td>0.21</td>
</tr>
</tbody>
</table>

The 0.46% efficiency achieved with the N719 pre-sensitized 625°C pre-sintered M712/21 is a substantial improvement on the 0.01% efficiency achieved with the pre-sensitized unsintered sample but not as high as the 0.91% achieved when using the P25 control sample (Figure 5.18, & Table 5.5). Pre-sintering the M712/21 sample prior to pre-sensitization shows a dramatic improvement in both the photocurrent and open circuit voltage when compared to the unsintered sample due to the elimination of impurities from the initial material, improved charge transport within the bead due to the strong interparticle connections formed during pre-sintering as well as increased porosity in the film resulting from increased nanoparticle size as previously discussed regarding the post-sensitized devices.

It is surprising the N719 pre-sensitized 625°C pre-sintered M712/21 device did not outperform the equivalent P25 device as was the case with the post-sensitized low temperature devices. A large series resistance of around 130 Ω cm² is estimated from the J-V curve of the pre-sensitized 625°C pre-sintered M712/21 device which is much higher than the 64 Ω cm² estimated for the pre-sensitized P25 device, potentially leading to poorer charge transport and higher recombination in the film resulting in lower photocurrent and voltage. The series resistance estimated from the post-sensitized 625°C pre-sintered M712/21 devices of around 35 Ω cm² are lower than all
the pre-sensitized devices potentially indicating the pre-sensitization lowers charge transport in devices. Literature reports show the adhesion of particles larger than the surface features is greatly affected by the size of the particle and the number of possible contact points.\cite{13} It is possible the pre-sensitized large bead provides a smooth surface with few contact points and so has a lower adhesion to the substrate than the pre-sensitized P25 or undyed sample, potentially further decreasing charge transport at the interface.

There are a small number of literature examples of DSSCs incorporating pre-sensitized TiO$_2$ but it has been shown to be possible using a variety of methods. TiO$_2$ has been synthesised with natural dye mixed in the TiO$_2$ precursor solution then precipitated into individual pre-sensitized nanoparticles and fabricated into DSSCs with higher temperature sintering of 250°C. Such devices have been shown to outperform equivalent post-sensitized devices due to an increased photocurrent resulting from more effective dye adsorption though efficiencies are low at 1.47\%.\cite{14,15} The pre-sensitized film could also be post-sensitized which has been shown to further increase dye adsorption and could potentially increase performance.\cite{16} Alternative methods of film formation such as compression with a hydraulic press have also been shown to provide N719 pre-sensitized devices with efficiencies approaching 4.9 % due to improved connection to the substrate.\cite{17} Addition of a thin initial TiO$_2$ layer to the substrate immediately prior to the pre-sensitized layer to aid in film adhesion may also potentially improve the $V_{OC}$, $J_{SC}$ and efficiency of the device.
Figure 5.18. J-V curves of N719 pre-sensitized P25, M712/21 & 625°C pre-sintered M712/21 TiO₂ DSSC devices.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Paste</th>
<th>Layers</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (mV)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>Ethanol</td>
<td>2</td>
<td>735</td>
<td>2.14</td>
<td>0.58</td>
<td>0.91</td>
</tr>
<tr>
<td>M712/21</td>
<td>H₂O/TBA</td>
<td>1</td>
<td>279</td>
<td>0.05</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td>625°C - M712/21</td>
<td>Ethanol</td>
<td>1</td>
<td>679</td>
<td>1.32</td>
<td>0.51</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 5.5. Operating parameters of N719 pre-sensitized P25, M712/21 & 625°C pre-sintered M712/21 TiO₂ DSSC devices.
5.3 Conclusions

These results indicate the 625°C pre-sintered M712/21 titania bead is potentially a promising candidate for use in devices which require low temperature application to substrates such as flexible DSSCs. The pre-formed mesoporous bead structure of the M712/21 sample allows for pre-sintering treatment of the sample which not only increases particle size, improves crystallinity, removes defect levels and optimizes porosity but also provides pre-formed strong interparticle connections which are not available in the low temperature sintered P25 films. A substantial increase in low temperature DSSC device efficiency is observed by pre-sintering sample M712/21 prior to paste formulation. The optimum 1-hour pre-sintering temperature for the sample was found to be 625°C for use in N719 sensitized, iodide/triiodide devices. This modification to the sample produced low temperature sintered DSSCs with an optimized efficiency of 2.41%. This greatly improves upon the 0.21% achieved with the unsintered M712/21 sample and the 1.37% achieved with P25 in the same low temperature sintered devices and is also comparable to all the optimized high temperature sintered devices fabricated in the previous chapter.

The optimized 625°C pre-sintered M712/21 sample showed a lower dye loading than the unsintered M712/21 and P25 sample but this is balanced against the removal of organic impurities in the sample. It is worth highlighting the dye loading of the M712/21 sample actually increased when pre-sintered at temperatures up to 400°C. This is thought to be due to the degradation and removal of organic impurities on the sample surface which are still present from the production process. Such impurities potentially include sulphates, citrate, carbon, chloride and MIPA as well as any of their degradation products. The discolouration of the sample when sintered at temperatures up to 400°C confirms the presence of such impurities. The exact nature of the impurities could be further examined using thermal analysis (TGA/DSC). I.R spectroscopy could also be employed to characterise the samples surface states and to investigate which, if any organics remain after pre-sintering. Any such impurities at the sample surface will occupy adsorption sites, lowering dye loading in the film and reducing photocurrent in the device. It is likely these impurities are removed during
film sintering in the high temperature fabricated devices but when using low temperature fabrication techniques, it is essential these impurities are removed prior to film fabrication.

The 625°C pre-sintering also results in an increase in crystallite size from ~9 nm to ~23nm, an increase in crystallinity and the strengthening of the pre-formed nanoparticle connections within the bead structure, all of which leads to greatly improved $V_{OC}$ and $J_{SC}$ parameters in the device and a large improvement in device efficiency, indicating the need for a well-connected network of highly crystalline anatase phase TiO$_2$ nanoparticles as well as a high surface area for dye loading. The pre-sintered M712/21 films also appear more uniform with no cracking when compared to the standard M712/21 & P25 low temperature sintered films. It is interesting that the nanoparticle size within the bead structure and the material properties can be easily controlled by varying the pre-sintering temperature and time without affecting the overall bead morphology. This allows simple control of surface area, crystallinity, pore size and porosity and therefore the sample could potentially be adapted for different materials and devices. The 625°C pre-sintering treatment of sample M712/21 has also been shown to greatly improve the performance of the N719 pre-sensitized devices compared to the unsintered sample, though the efficiency is still lower than the pre-sensitized P25 device. It is thought the formation of multiple strong bonds at the TiO$_2$-FTO interface is restricted by the large smooth ordered structure of the dye-coated bead providing fewer contact points with the substrate compared to the pre-sensitized P25 nanoparticles or undyed sample. The pre-sintering treatment of the Huntsman samples is further investigated in the following chapter using sample M712/12/1, which showed the highest effective surface area for dye adsorption of all samples, in an attempt to achieve greater performance in low temperature fabricated DSSCs.
5.4 References


Chapter 6. 625°C Pre-Sintered M712/12/1 Sample Properties and DSSCs

6.1 Introduction

This chapter follows up on the studies conducted in the previous chapter which modified sample M712/21 with a pre-sintering treatment to increase crystallinity and improve interparticle connections within the bead structure. The pre-sintering treatment also resulted in a decrease in surface area and so the conditions were optimized to provide the balance of properties which gave the highest efficiency low temperature DSSC. In this chapter the optimized pre-sintering treatment is used to modify sample M712/12/1 which showed the highest initial effective surface area of all samples with the goal of further improving the performance of low temperature DSSCs incorporating Huntsman bead samples. An alternative sensitizer dye (D102) which has a higher molar absorption coefficient than N719 was also used in the optimized low temperature device to compare performance. The 625°C pre-sintered M712/12/1 sample was also fabricated into standard high temperature sintered DSSCs to investigate the effects of sample modification on standard DSSC device performance compared to devices incorporating the unsintered Huntsman titania samples, P25 control sample and commercial Dyesol paste. Electrochemical studies were also carried out in an attempt to further investigate the effects of pre and post sintering on the sample films.
6.2 Results & Discussion

6.2.1 625°C Pre-Sintered M712/12/1 Sample Characterization

The M712/12/1 titania sample which previously displayed the highest effective surface area of all samples was pre-sintered in a furnace for 1 hour at 625°C. The effective surface area of the 625°C pre-sintered M712/12/1 powder sample for N719 dye adsorption was measured as in previous chapters and XRD patterns of the 625°C pre-sintered M712/12/1 sample were obtained and compared to the unsintered M712/12/1 sample and P25 control sample (Figure 6.1.).

The effective surface area of sample M712/12/1 drops to around half the value of the unsintered sample after the 625°C pre-sintering treatment. This is similar to the surface area decrease observed in sample M712/21 after pre-sintering in the previous chapter. The 625°C pre-sintered M712/12/1 sample effective surface area of 40 m² g⁻¹ is almost double that of the 22 m² g⁻¹ observed in sample M712/21 after pre-sintering but is still slightly lower than that of P25. The higher effective surface area of sample M712/12/1 compared to sample M712/21 after pre-sintering at 625°C is consistent with the higher effective surface area displayed before the pre-sintering treatment. This shows a comparatively higher effective surface area in the initial samples is beneficial is at translates to a higher effective surface area in the pre-sintered samples. The initially higher surface area for dye adsorption is potentially caused by the higher levels of citric acid used in the M712/12/1 sample production compared to M712/21 which leads to slightly larger pores in the sample, increasing the number of accessible sites for dye adsorption.
Figure 6.1. Effective surface area of sample M712/12/1 before and after 625°C pre-sintering with mean value and standard deviations of repeated experiments shown (top left). XRD patterns of sample M712/12/1 powder before and after 625°C pre-sintering; full pattern (top right), major anatase & rutile peaks (bottom left) and diffraction peaks from anatase 105 and 211 planes (bottom right). P25 powder XRD pattern also shown for comparison.

<table>
<thead>
<tr>
<th>TiO₂ sample</th>
<th>1 hour heating temperature (°C)</th>
<th>2θ angle at peak (deg)</th>
<th>Integrated Intensity</th>
<th>Peak width at 1/2 intensity (deg)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>N/A</td>
<td>25.57</td>
<td>2113</td>
<td>0.42</td>
<td>19</td>
</tr>
<tr>
<td><strong>P25</strong></td>
<td>N/A</td>
<td><strong>27.70</strong></td>
<td><strong>149</strong></td>
<td>0.29</td>
<td><strong>28</strong></td>
</tr>
<tr>
<td>M712/12/1</td>
<td>N/A</td>
<td>25.62</td>
<td>973</td>
<td>0.67</td>
<td>12</td>
</tr>
<tr>
<td>M712/12/1</td>
<td>625</td>
<td>25.72</td>
<td>1425</td>
<td>0.39</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 6.1. Crystallite size and anatase peak intensity comparison of sample M712/12/1 before and after 625°C pre-sintering treatment as estimated from XRD patterns. P25 anatase and rutile (bold) phase sizes and intensities also shown.
Pure anatase phase TiO$_2$ is exhibited by sample M712/12/1 before and after the 625°C pre-sintering treatment. A narrowing of the XRD peak width is again observed after pre-sintering and applying the Scherrer equation gives an estimated crystallite size which is similar to that of the P25 anatase component and the 625°C pre-sintered M712/21 sample in the previous chapter (Table 6.1.). An increase in integrated peak intensity of the characteristic anatase peak is also seen after the 625°C pre-sintering treatment when compared to the unsintered sample. The peaks caused by diffraction from the 105 and 211 planes also convert from a wide hump to two definable peaks after the pre-sintering treatment. This further indicates the pre-sintering treatment is converting an unquantified amorphous component present in the initial Huntsman sample to anatase phase therefore increasing the percentage of anatase phase present in the sample. This is due to both insufficient heating of the initial sample needed to cause full conversion to anatase phase and the possible presence of impurities within the initial sample due to the sample production procedure as discussed in previous chapters.

### 6.2.2 Diffuse Reflectance of 625°C Pre-Sintered M712/12/1 film

Low temperature sintered films using the 625°C pre-sintered M712/12/1 sample in ethanol paste were prepared on FTO glass substrates by doctor blading two layers and sintering at 125°C as previously done. As with all previous films UV/Vis transmittance spectroscopy proved unreliable due to the scattering effects of the films. Diffuse reflectance spectroscopy was therefore carried out on the 625°C pre-sintered M712/12/1 low temperature post-sintered films. The results were compared to the those of the low temperature post-sintered films using the unsintered M712/12/1 sample and the P25 control sample. The diffuse reflectance data for the dyed and undyed films are represented as Kubelka-Munk plots to better compare absorption of the sample films and as indirect band gap Tauc plots to examine the band gap of the pre-sintered sample (Figure 6.2.).
No obvious difference is seen in the normalized absorption or band gaps of the undyed M712/12/1 sample films, regardless of pre-sintering treatment, indicating no phase transition occurs during pre-sintering and all films are of similar thickness. The normalized absorbance of the N719 sensitized 625°C pre-sintered M712/12/1 film shows a decrease in the peak around 520 nm when compared to the unsintered sample film. This confirms the pre-sintering treatment reduces the surface area of the samples as shown by the previous effective surface area results.

Figure 6.2. Diffuse reflectance of low temperature post-sintered 2 layer TiO₂ films using sample M712/12/1 before and after 625°C pre-sintering treatment. P25 films also shown for comparison. Kubelka-Munk conversion of TiO₂ films (top left) & N719 sensitized films (bottom left). Indirect band gap Tauc plots of TiO₂ films (top right) & N719 sensitized films (bottom right).

As was the case with the M712/21 sample in the previous chapter, the lower energy band gap indicated in the Tauc plot of the sensitized films which is representative of the N719 optical gap appears to raise in energy in the 625°C pre-
sintered M712/12/1 film when compared to the equivalent film using the unsintered sample. The Tauc plot for the N719 sensitized films was re-plotted for a direct band gap to better compare differences in the estimated optical gap provided by the dye on the different sample films (Figure 6.3.). The direct band gap Tauc plot also indicates a lower optical gap for the sensitized films using unsintered samples when compared to the sensitized films using the pre-sintered samples and the P25 sample. This may be due to different surface interactions of the unsintered sample with the N719 dye due to the presence of impurities and/or defects in the sample. It is also likely the measurements are affected by the different scattering effects of the films. All the unsintered sample films have a smaller particle size than the P25 and 625°C pre-sintered Huntsman samples and this may cause the optical gap in films using smaller nanoparticles to be underestimated when measuring with this method.

![Tauc plot](image)

*Figure 6.3. Direct band gap Tauc plot of N719 sensitized low temperature post-sintered 2 layer films of samples M712/21 and M712/12/1 with and without 625°C pre-sintering. P25 film also shown for comparison.*
6.2.3 SEM Sectional View

Low temperature sintered films using one layer of the 625°C pre-sintered M712/12/1 sample in ethanol paste on FTO glass substrate were examined using SEM to estimate layer thickness. Unlike in previous chapters the films were first frozen by dipping the substrate in liquid N\textsubscript{2} then cracking through the film. The cracked films were mounted edge up on an SEM sample holder, gold coated and examined using SEM (Figure 6.4.). The technique of freezing the films in liquid N\textsubscript{2} and cracking the substrate provides a much improved sample for sectional views of the film using SEM compared to the previously used method of scoring the substrate and snapping the film. Freezing the substrate to such low temperatures makes it substantially more brittle and a small amount of force causes rapid crack propagation throughout the substrate and film.\textsuperscript{[1]} Previous attempts conducted at room temperature resulted in a rounded edge to the glass and deformation of the film due to the slow crack propagation and increased force required to break the film making layer thickness estimation difficult.

The sectional views of the films show a uniform film thickness across the whole layer. At higher magnification it can be seen there is a porous network within the film. While no distinct bead structures can be observed there are obvious areas of nanoparticle aggregation attributed to the pre-formed mesoporous network and any gaps are filled by the smaller microstructures resulting from the breakdown of larger beads as observed during paste formulation in the previous chapter. A film thickness of 7 µm is observed from a one-layer doctor blading application of the sample paste. This is similar to the thickness of the M712/21 film observed in the previous chapter and means no beads of diameter greater than 7 µm can be present in the film. As the sample bead sizes ranged from 1-20 µm it is likely the larger beads were crushed or broken during paste formulation and doctor blading. The broken parts of these beads would still contain the strong pre-formed connections developed during the pre-sintering and therefore would retain the benefit of increased charge transport in the film even though the overall morphology has changed.
6.2.4 Mott-Schottky Studies of Modified Huntsman Sample

High (510°C) and low (125°C) temperature post-sintered films were prepared by doctor blading two layers of ethanol based titania paste on FTO-glass substrates using sample M712/12/1, with and without the 625°C pre-sintering treatment. The films were used as working electrodes and placed in aqueous 0.1 M solution of sodium sulphate along with a reference electrode and platinum counter electrode. The capacitance of the films was measured across a range of applied voltages using a frequency of 100 Hz without illumination and a Mott-Schottky plot was produced to investigate the effect of pre and post-sintering on the flatband potentials and charge carrier densities of the sample films. (*Figure 6.5, & Table 6.2.*).
The differences between the Mott-Schottky plots of the various M712/12/1 films highlight the effect the different pre and post-sintering conditions have on the electrode. The results initially indicate the 625°C pre-sintering treatment lowers the flatband potential of the M712/12/1 sample in both low and high temperature post-sintered films. This indicates fewer defect sites at the titania surface resulting from the increased crystallinity and removal of impurities by the pre-sintering treatment, improving charge transport within the beads and allowing the remaining interface states to be filled at less negative potentials, eliminating the space charge region at less negative potentials and therefore lowering the observed flatband potential. A similar effect is observed with the high temperature post-sintering lowering the flatband potential compared to the low temperature post-sintered films. The 510°C high temperature post-sintering removes many of the interfacial defects between beads in the film and at the substrate, eliminating any defect contribution to the capacitance. The pre-sintering treatment appears to have little effect on charge carrier density in the film but the high temperature post-sintering causes a slight reduction in charge carrier density compared to the low temperature post-sintered films.

The Mott-Schottky plots of the high temperature post sintered films both exhibit one obvious linear region in the plots as the square of the capacitance increases linearly with increasingly negative voltages while the width of the space charge region decreases until it is eliminated when the flatband potential is reached. The Mott-Schottky plots of porous films are not always linear, as is observed in the plots resulting from the low temperature post-sintered films. This is due to various factors such as the film packing, surface morphology, surface chemistry, the back contact capacitance at the FTO and other small resistance effects which are typically neglected in Mott-Schottky capacitance modelling and can lead to slight unreliability in the flatband potentials estimated from the plots as the paste formulation and sintering conditions will alter these factors. This results in a slight hump in the plots of the low-temperature post-sintered films at more negative voltages signifying the space charge region of the electrode has not been fully eliminated, indicating the presence of multiple contributing interfaces and is likely due to capacitance effects at the FTO-TiO₂ interface or between beads in the film as the interfaces are not as well formed due to the low post-sintering temperature.
Figure 6.5. Mott-Schottky Plots of high (510°C) and low (125°C) temperature post-sintered films formed using sample M712/12/1 with and without 625°C pre-sintering treatment in ethanol paste.

Table 6.2. Flatband potentials (vs. Ag/AgCl) and charge carrier densities estimated from linear regions of Mott-Schottky plots of high (510°C) and low (125°C) temperature post-sintered films formed using sample M712/12/1 with and without 625°C pre-sintering treatment in ethanol paste.
Capacitance measurements of the films using a range of frequencies between 50-1500 Hz were carried out confirming there is a slight frequency dependence on results though the general trend across samples was obvious at all the applied frequencies used (Supp. Info.). The 100 Hz frequency was selected for analysing the films as this is within the frequency range commonly used in the literature to measure capacitance of TiO\textsubscript{2} films and shows the presence and elimination of the space charge region in the applied voltage range.\textsuperscript{[3][4]} This frequency also consistently produced the most linear plots, clearly highlighting the differences between the films. Frequency dispersion in Mott-Schottky results is common and is due to inhomogeneous current flow caused by surface roughness, doping inhomogeneity, changing resistivity through the film, film thickness and deep donor levels among other effects.\textsuperscript{[5]} Replacing the capacitor in the equivalent circuit with a constant phase element, modelling the data of the various frequency Mott-Schottky plots and calculating the capacitance at each frequency has been shown to reduce the frequency dispersion in results.\textsuperscript{[5]} The dielectric constant of the material may also differ in different regions of the film and between samples as a result of differences in particle size and morphology, further adding error to results. The influence of differing surface states and the choice of equivalent circuit model have also been shown to effect the evaluated flatband potential and charge carrier densities.\textsuperscript{[6]} This would indicate the calculated capacitance, charge carrier density and flatband values do have an error associated when using this simplified modelling of the capacitance. Despite the associated error, the Mott-Schottky plots are significant as they emphasise the differences between the films by highlighting the different resistances encountered in the various films when observed at the same frequency. While the flatband and charge carrier density values of a film may differ slightly depending on the frequency used, the differences between different films measured at the same frequency are consistently observed at various applied frequencies. As the flatband potentials and charge carrier densities are highly dependent on pH and film packing of nanoparticles among other factors, a range of values are reported in the literature. Flatband potentials ranging from -0.2 to -0.9 V (vs. Ag/AgCl) and charge carrier densities of the order 10\textsuperscript{17} to 10\textsuperscript{21} are common for porous TiO\textsubscript{2} films used in DSSCs and are heavily dependent on the experimental conditions.\textsuperscript{[7][8]}
6.2.5 Low temperature DSSC Device Performance with Modified M712/12/1 sample

The 625°C pre-sintered M712/12/1 sample was fabricated into multiple low temperature post-sintered DSSC devices and the layer thickness optimized as previously done. An optimized efficiency of 2.83% was achieved with a simple one-layer application which is more than double the efficiency achieved with the equivalent optimized P25 device (Figure 6,8 & Table 6,3.). The optimized device using the unsintered M712/12/1 sample is also shown to further illustrate the benefit of presintering the sample prior to device fabrication.

The low temperature post-sintered 625°C pre-sintered M712/12/1 device shows a substantially greater performance than the equivalent P25 device for similar reasons as the optimized M712/21 sample in the previous chapter with regards to improved charge transport in the film due to the well-connected pre-formed structure of the pre-sintered large mesoporous bead. This is demonstrated by the lower series resistance in devices using the 625°C pre-sintered M712/12/1 sample compared to the P25 device as estimated from the J-V curves. The 625°C pre-sintered M712/12/1 sample also provides a higher V_{OC}, J_{SC} and efficiency than the optimized 625°C pre-sintered M712/21 low temperature sintered device in the previous chapter. The increased photocurrent is due to the increased effective surface area for dye adsorption as shown in the 625°C pre-sintered powder samples. The correlation between higher effective surface area and higher photocurrent in devices using similar pre-sintered mesoporous bead samples would indicate a higher dye adsorption in the film or potentially an improved charge injection.

The higher V_{OC} observed in the M712/12/1 device is likely due to slight differences of dye interactions at the interface. This may be due to lower concentration of defect levels at the surface caused by slight differences in pre-sintering temperature or cooling environment. The M712/12/1 sample did not undergo crossflow filtration during initial sample production, unlike sample M712/21, so it could be expected there would be a higher concentration of impurities, leading to more defect levels and a lower V_{OC}, though it is likely the impurities are removed during the pre-sintering
treatment. Any impurities not removed during crossflow filtration which remain in the sample and survive the pre-sintering treatment could potentially cause a slight shift of the Fermi level of sample M712/12/1 compared to M712/21 and lead to an increased $V_{OC}$ though this effect is not seen in the previous high temperature devices. The 625°C pre-sintering of sample M712/12/1 provides a low-temperature post-sintered device with $J_{SC}$ (6.41 mA cm$^{-2}$), $V_{OC}$ (806 mV) and efficiency (2.83%) values which are higher than all other low temperature devices fabricated in this work and also many of the standard high temperature post-sintered devices. This indicates that once pre-sintered at the optimum temperature, sample M712/12/1 is highly suitable for use in flexible DSSCs. These results support the theory put forward in the previous chapter that the pre-formed mesoporous network formed in the initial sample synthesis and the strong interparticle connections developed during the pre-sintering treatment, which are not present in the low temperature sintered P25 film, provide increased porosity and charge transport in the film. This theory agrees with literature reports of pre-sintered TiO$_2$ ‘micro-balls’ as discussed in the previous chapter, while the increased efficiency shown by the 625°C pre-sintered M712/12/1 sample device further improves on the reported low temperature sintered device efficiency using pre-sintered porous beads.$^{[9]}$ The 625°C pre-sintered M712/12/1 sample device also exhibits comparable efficiencies and superior $J_{SC}$ and $V_{OC}$ values when compared to many of the similarly prepared low temperature sintered DSSCs reported in the literature.$^{[10]}[11][12]$ With further improvements in the fill factor and photocurrent the device could potentially exceed the highest reported efficiency of 5.5 % of any similar device.$^{[13]}$

The film thickness of the optimized 1-layer application of the 625°C pre-sintered M712/12/1 sample in ethanol paste post-sintered at 125°C was measured as 7 µm by SEM imaging. This is thinner than the 12 µm thickness generally found to be optimum in high temperature post-sintered N719 devices. Increasing the layer thickness to increase dye uptake proved to actually lower photocurrent and device performance. This is thought to be due to the weaker bead-bead connections in the low temperature post-sintered films compared to the strong inter-bead connections developed during high temperature post-sintering of the films. This leads to higher series resistance and lower fill factor being observed in devices with increasing layer
thickness when using the low temperature post-sintered films which indicates a reduction in charge transport. The ideal thickness of the TiO$_2$ layer is essentially a balance between increased dye loading providing greater light absorption in thicker films and increased charge transport resulting from lower series resistance in thinner films. Rather than increase layer thickness to improve light absorption a sensitizer dye with a higher molar absorption coefficient was used on the 7 µm thick film and fabricated into devices for comparison. The organic indoline D102 dye was selected due to the high molar absorption coefficient of around 5.58 x 10$^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$, suitably aligned energy levels and availability (Figure 6,6). The D102 sensitized films provide a much brighter red appearance in devices when compared to the N719 sensitized films (Figure 6,7). This highlights one of the main benefits of dye-sensitized solar cells compared to other solar cells as the colour and design of the device can be easily adapted for more widespread commercial use.

Figure 6,6. Molecule of D102 sensitizer dye.
The D102 sensitized 625°C pre-sintered M712/12/1 low temperature post-sintered films provided working devices indicating the pre-sintered sample can potentially be optimized for different materials. It can be seen from the J-V curves that a similar series resistance is observed by the low temperature sintered devices incorporating the 625°C pre-sintered M712/12/1 sample with both N719 and D102 sensitzers, indicating a similar charge mobility is present in both films. The D102 devices showed a lower photocurrent, open-circuit voltage and efficiency than the equivalent N719 device. It is possible the optimized layer thickness of 7 µm for the low temperature post-sintered N719 sensitized films is too thick for an optimized D102 sensitized film. Due to the increased molar absorption coefficient of the D102 dye compared to N719 it is likely a thinner titania layer with lower series resistance would provide a more efficient D102 sensitized device as has been shown in the literature with devices incorporating solid-state hole transport materials where thicknesses of around 2 µm were found to be optimum.\[14]\] While the D102 dye has a higher molar absorption coefficient it also has a slightly larger optical gap as a result of a lower HOMO level and higher LUMO level than the N719 dye.\[15]\] This means it absorbs a narrower range of wavelengths of light and that the energy levels are not as optimally aligned to the TiO$_2$-iodide/triiodide system as the N719 dye. D102 has been shown to

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**Figure 6.7. Low temperature post-sintered DSSCs using N719 (left) and D102 (right) sensitizer dyes.**
be more sensitive to environmental conditions than N719 and so additives in the liquid electrolyte could potentially further shift the energy levels.[15] D102 has also been shown to be prone to aggregation on the titania surface which could also lower device efficiency.[16] With further optimization of the titania layer thickness the 625°C pre-sintered M712/12/1 Huntsman titania sample could be employed in a more efficient D102 sensitized device with efficiencies approaching the 8% reported for standard D102 sensitized DSSCs, while selection of a suitable hole-transport material would potentially allow the sample to be used in flexible solid-state devices.[17][18]
Figure 6, 8. J-V curves of the best low temperature sintered DSSC devices incorporating P25 and sample M712/12/1 with and without 625°C pre-sintering treatment all sensitized with N719. Also shown is the best 625°C pre-sintered M712/12/1 low temperature device using D102 sensitizer dye.

Table 6.3. Low temperature DSSC operating parameters of best devices incorporating P25 and sample M712/12/1 with and without 625°C pre-sintering treatment sensitized with N719. Also shown is the best 625°C pre-sintered M712/12/1 low temperature device using D102 sensitizer dye.
6.2.6 DSSC Device Performance with Modified M712/12/1 sample

As the 625°C pre-sintered M712/12/1 sample showed the greatest efficiency of all the low temperature post-sintered devices with a simple 1-layer application it was fabricated into a high temperature post-sintered DSSC and compared to the previous low temperature device as well as the optimized high temperature devices incorporating the unsintered M712/12/1 sample, P25 control sample and the Dyesol paste from previous chapters (Figure 6.9. & Table 6.4.).

It is worth noting the device using the 625°C pre-sintered M712/12/1 sample was fabricated from the ethanol paste and not the optimized terpineol paste used in the other high temperature post-sintered devices. The 625°C pre-sintered M712/12/1 device has also not been optimized for layer thickness so only a 1-layer application is used. Even without this device optimization the 625°C pre-sintered M712/12/1 high temperature post-sintered device shows an efficiency of 3.15% which is higher than the 2.92% achieved with the optimized P25 device. The high efficiency is due to the superior $V_{OC}$ (811 mV) and $J_{SC}$ (10.32 mA cm$^{-2}$) values exhibited when compared to all other optimized devices fabricated in this work and further indicates the high potential of the optimally pre-sintered material for use in DSSCs. The high temperature post-sintering of the film improves inter-bead connections within the film, improves adhesion of the titania to the FTO substrate and reduces defect states at the TiO$_2$-FTO interface as indicated by the Mott-Schottky results. This leads to a greatly increased photocurrent in the high temperature post-sintered 625°C pre-sintered M712/12/1 device when compared to the equivalent low temperature device which has a similar layer thickness. The slight 5 mV increase in open-circuit voltage seen in the high temperature device compared to the equivalent low temperature device is likely due to better removal of residual impurities present on the substrate and slight improvements in film formation caused by the higher post-sintering temperature. This indicates no further impurities are removed from the 625°C pre-sintered M712/12/1 sample with further heating and subsequently the Fermi level of the material cannot be raised without different pre-treatments such as doping the crystal lattice of the material. As
only a slight increase in efficiency is observed with high temperature post-sintering of the 625°C pre-sintered M712/12/1 film compared to the low temperature device this further confirms the suitability of the material for low temperature fabricated flexible devices.

As only one layer of the paste is applied it is possible there are point defects present in the film which are not filled with additional layers of paste. The high temperature sintering of the film could potentially extend these defects as some film cracking was observed in previous high temperature post-sintered films without pre-sintering. This along with other factors such as lack of layer thickness optimization or incomplete dye adsorption could potentially explain the low fill factor observed in the 625°C pre-sintered M712/12/1 high temperature post-sintered device. The acetic acid used in the terpineol paste formulation which is used in all other high temperature devices has been shown to reduce aggregation in the paste leading to a more uniform film while also positively shifting the conduction band edge of the titania, potentially allowing stronger binding of the dye and more efficient charge transfer at the interface.

The use of a more optimized paste formulation could potentially improve the fill factor of the device. Only a slight improvement in the comparatively low fill factor of the non-optimized 625°C pre-sintered M712/12/1 high temperature post-sintered device would be required to improve the overall efficiency and exceed that of the device using the commercially optimized Dyesol paste. Similarly fabricated optimized devices in the literature that report a similar P25 device efficiency also report optimized efficiencies of 5.0 % when using 250 nm size porous TiO₂ spheres which could potentially be exceeded by the 625°C pre-sintered M712/12/1 device by slightly increasing the fill factor.[19] The 625°C pre-sintered M712/12/1 mesoporous Huntsman bead sample performs as a highly efficient semiconductor layer in standard DSSCs. The optimized M712/12/1 sample has been shown to provide superior performance when compared to the P25 nanoparticles which is the standard TiO₂ commonly used in the fabrication of solar devices. As the beads already possess a highly porous structure the need for a binder in the paste such as ethyl cellulose is also eradicated, allowing for a wider range of potential paste formulations and simpler production methods.
Figure 6.9. J-V curves of 510°C post-sintered TiO\textsubscript{2} DSSC devices incorporating the 625°C pre-sintered M712/12/1 in ethanol paste and also the optimized devices using the commercial Dyesol paste and the unsintered M712/12/1 and P25 control sample in terpineol paste.

<table>
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<tr>
<th>TiO\textsubscript{2} Sample</th>
<th>Paste</th>
<th>layers</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm\textsuperscript{-2})</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
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<td>Terpineol</td>
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<td>0.48</td>
<td>2.92</td>
</tr>
<tr>
<td>M712/12/1</td>
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<td>811</td>
<td>10.32</td>
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</table>

Table 6.4. Operating parameters of 510°C post-sintered TiO\textsubscript{2} DSSC devices incorporating the 625°C pre-sintered M712/12/1 in ethanol paste and also the optimized devices using the commercial Dyesol paste and the unsintered M712/12/1 and P25 control sample in terpineol paste.
The 625°C pre-sintering of sample M712/12/1 improves crystallinity, increases crystallite size, removes defect levels and improves the interparticle connections within the mesoporous bead as was shown in the previous chapter with sample M712/21. The higher initial effective surface area displayed by sample M712/12/1 was shown to translate to a higher effective surface area after the 625°C pre-sintering treatment when compared to sample M712/21 as a reduction in effective surface area of around 50% was observed for both samples as a result of the pre-sintering treatment.

Due to the higher effective surface area and optimized pre-sintering treatment the 625°C pre-sintered M712/12/1 sample was used to fabricate a low temperature DSSC with higher efficiencies than previous devices and more than double that of the low temperature P25 device. The device also showed comparable efficiencies and device parameters to those reported in the literature. Only slight increases in device performance were observed when fabricating similar devices with high temperature post-sintering of the 625°C pre-sintered M712/12/1 film, confirming the high surface area pre-sintered mesoporous beads are highly suitable candidates for use in low temperature fabricated flexible DSSCs.

The high temperature post-sintered 625°C pre-sintered M712/12/1 device displayed higher photocurrent, photovoltage and efficiency than the P25 device despite not using an optimized paste formulation. This confirms a further benefit of the pre-formed mesoporous bead structure as the need for binders in the paste to provide porosity in the film is removed, allowing for a wider range of paste formulations and film fabrication methods. It has also been shown that the sample can potentially be adapted to a wider range of materials as working devices were fabricated using the organic sensitizer dye D102.
Chapter 7. Overall Conclusions & Future Work

7.1 Overall Conclusions

The Huntsman titania used in this work has been shown to be a superior candidate for use in various types of DSSCs when produced under certain conditions. The peptization step during initial sample production induces greater dispersion of the TiO$_2$ nanocrystals and has been shown to lead to a higher effective surface area for dye adsorption in the initial samples. Spray drying these dispersed samples provides micrometer sized spherical beads formed in a mesoporous structure of connected nanoparticles. Sample M712/12/1 displays the highest initial effective surface area of all samples. This sample had a higher level of nuclei added during Mecklenburg precipitation which potentially results in slightly smaller nanoparticles. A higher level of acetic acid was added which increases dispersion leading to slightly larger pores in the sample. The impurities not removed during crossflow filtration are potentially eliminated during spray drying, resulting in increased porosity in the final sample. The combination of these effects lead to a higher effective surface area in the M712/12/1 Huntsman bead sample compared to all other samples.

The low degree of crystallinity and small crystallite size in the initial Huntsman samples has been shown to reduce charge transport in the film and limit device efficiency. Pre-sintering the initial samples prior to paste formulation has been shown to increase crystallinity, increase crystallite size, eliminate defects and improve interparticle connections within the bead structure. This leads to increased charge transport and open-circuit voltage in devices. The optimized pre-sintering treatment also reduces the initial effective surface area to around half the initial value and so a high initial effective surface area is essential. The pre-sintering conditions which provide the optimum balance between crystallinity and surface area for the samples has been shown to involve heating in a furnace at 625°C for one hour and cooling in air. The 625°C pre-sintered M712/12/1 Huntsman bead sample has been shown to provide substantially increased performance of DSSCs when compared to the standard
P25 TiO$_2$ nanoparticles commonly used in devices. Particularly, comparatively high efficiencies are seen with this sample in low temperature post-sintered devices. The highly connected pre-formed mesoporous network present in the pre-sintered bead structure offers significant advantages over the P25 nanoparticles, providing effective charge transport and porosity which cannot be developed with binders in the P25 film due to the low fabrication temperatures involved.$^{[9]}$ While some of the larger bead morphology is lost during paste formulation and film deposition, the pre-connected network remains in the film. Low temperature fabricated DSSCs incorporating the 625$^\circ$C pre-sintered M712/12/1 bead sample showed efficiencies more than double that of the equivalent P25 device. Similar devices incorporating the 625$^\circ$C pre-sintered M712/21 bead sample also displayed higher efficiencies than the P25 device. Working low temperature fabricated devices were also manufactured using the D102 sensitizer dye. While a lower efficiency was observed when compared to the N719 device it shows the 625$^\circ$C pre-sintered M712/12/1 bead sample can potentially be used successfully with a range of materials. The superior efficiencies and adaptability in low temperature fabricated devices show the pre-sintered Huntsman bead samples, particularly sample M712/12/1 pre-sintered at 625$^\circ$C, are highly desirable candidates for use in flexible DSSCs. The main advantages of the 625$^\circ$C pre-sintered M712/12/1 sample are the strong pre-formed interparticle connections within the large pre-formed mesoporous bead and the high degree of crystallinity while still providing a relatively high surface area for dye adsorption which provide comparable and often superior photocurrent, open circuit voltage and efficiencies in low temperature sintered DSSCs when compared to literature reports.$^{[10][11][12][13]}$

The 625$^\circ$C pre-sintered M712/12/1 sample has also shown superior efficiency and performance parameters in standard high temperature fabricated DSSCs when compared to the P25 TiO$_2$ and a commercially optimized titania paste. Further optimization of this device when using the 625$^\circ$C pre-sintered M712/12/1 sample could potentially further increase device efficiency closer to the literature values.$^{[20]}$ The highly connected pre-formed mesoporous structure again provides increased charge transport in the film but also eliminates the need for binders in the paste, allowing for simpler production methods. The pre-sintered bead samples can also be successfully pre-sensitized with N719 dye, eliminating the lengthy sensitization step.
which limits device production time. While the pre-sintering treatment substantially improves performance compared to the unsintered sample, the maximum efficiency displayed by N719 pre-sensitized 625°C pre-sintered M712/21 devices still requires further optimization to outperform the pre-sensitized P25 devices or be comparable to the post-sensitized device efficiencies. While efficiencies of the pre-sensitized devices are relatively low they are comparable to literature reports of similarly fabricated devices.[21]

7.2 Future Work

The substantially increased performance of the low temperature post-sintered devices observed when using the 625°C pre-sintered M712/12/1 sample leads to the conclusion this sample is much more suited for use in flexible devices than the commonly used P25. It would be interesting to fabricate similarly optimized devices using a flexible substrate to confirm the suitability and effectiveness of the sample for use in such devices. Other methods which could aid low temperature sintering could be investigated to further improve performance, such as optimum pH levels of the beads, as beads with a more basic pH will have a higher concentration of hydroxide groups at the surface, potentially increasing the chances of successful dehydration reactions between individual titania particles, between the titania and substrate and between the titania and dye.[22] It would also be of benefit to further investigate methods to improve the performance of the pre-sensitized devices such as applying an initial titania layer to mediate charge transfer between the pre-sensitized TiO₂ and the FTO substrate. Different film deposition methods such as mechanical compression could also be attempted to improve contact to the substrate, though such methods would need to be suitable for industrial scale fabrication processes. As the 625°C pre-sintered M712/12/1 sample displayed higher efficiencies in a standard DSSC without layer thickness optimization compared to the optimized P25 device it would be of great benefit to fabricate devices with optimized layer thickness to further investigate the
potential of the sample. It would also be of benefit to construct optimized devices using additional treatments such as TiCl₄ pre and post-treatment of the film which are commonly used in the literature and could potentially further increase device efficiency. Other factors in device fabrication such as a smaller active area, optimized counter electrodes, electrolyte and better sealing of the cell among others could all be implemented in future devices to increase efficiencies of the optimized Huntsman sample devices and the comparative P25 devices closer to the higher efficiencies reported in the literature. Investigation of the charge transfer and recombination processes in the optimized devices using electrochemical impedance spectroscopy would further increase the level of understanding of the performance of the titania layer as the multiple interfaces present in the device could be individually examined across a frequency range and the parameters for individual charge transfer processes extracted by using a suitable equivalent circuit model.[23]

It has been shown the pre-formed bead structures eliminate the need for binders in the paste as the porosity is already present in the samples. It would therefore be of great benefit to optimize paste formulations suitable for both the low and high temperature post-sintering methods using the 625°C pre-sintered M712/12/1 sample. Addition of acid to the ethanol paste formulation could potentially reduce aggregation in the paste, leading to faster dispersal times and more uniform films. Various solvents and additives such as tert-butanol and ammonia among others could potentially be employed in the paste to improve long term dispersion and stability of the paste and to fine tune the conduction band edge of the titania film.[24] Additives and solvents in the paste have been shown to affect the surface chemistry of the film and so alter dye adsorption and charge transfer properties and would therefore need to be optimized for the sample. Due to the high efficiencies of the 625°C pre-sintered M712/12/1 sample compared to the standard P25 TiO₂ which is commonly used, employing this sample in optimized paste formulations which provide long term dispersion of the sample in the paste and an easily applied uniform film with a suitable conduction band edge could potentially result in a high performance, low cost, commercially viable and patentable titania paste for use in various types of DSSCs. The application range of the sample could be easily extended by slight adjustment of sample production procedures.
to modify particle size and porosity or changing the paste formulation to alter TiO$_2$ concentration, viscosity and pH to tune layer thickness and energy levels of the film.

As all the initial Huntsman samples are pre-formed structures it would be of interest to break the samples into individual nanoparticles using bead milling or ultrasonic irradiation before and after the pre-sintering treatment to examine how the individual nanoparticles synthesised using the patented Huntsman method compare to both P25 and the pre-formed beads.[25] The size of the Huntsman beads is very large (up to 20 µm) compared to those reported in the literature which are normally in the 250-1000 nm range and therefore suited to scatter light in the visible range. The large size beads appear to induce aggregation, causing cracking of the film and poor adhesion to the substrate. It would be of benefit to try and reduce the bead size by altering the spray drying conditions or potentially by precipitating the beads directly from the sol using thermal treatment and eliminating the aerosol process. Other modifications to the initial sample production procedure could be investigated, such as employing higher levels of nuclei in the precipitation step to reduce nanoparticle size while adding more citric acid to create larger pores, potentially increasing the effective surface area. Solvothermal calcination of the dispersed nanocrystals could potentially improve the crystallinity of the sample during production without decreasing the effective surface area in the final sample as is the case with pre-sintering treatment. Further modifications to the pre-sintering treatment could also be attempted such as finer tuning of the optimum pre-sintering temperature and time. The cooling environment used during pre-sintering could also be adjusted to a more oxygen rich or reducing atmosphere to control the bulk and surface concentration of oxygen vacancies to optimize dye adsorption and charge transport properties in the film.

The production procedure of the pre-sintered Huntsman mesoporous beads offers various simple routes to controlling surface area, crystal phase, crystallite size, particle size, morphology and pH as well as the energy levels and charge transfer properties. This not only provides a simple route for optimizing the sample for different materials used in solar cells but also for other applications where a different balance of properties in the TiO$_2$ is required. It would therefore be highly beneficial to optimize samples and assess the performance in other solar devices such as solid-state
dye-sensitized solar cells and perovskite solar cells as well as in other systems such as photocatalysis, water splitting and energy storage which also currently employ high surface area TiO$_2$.[26][27][28][29]

### 7.3 References


