Optimisation of TiO2 and Zn2SnO4 Photoanode Materials for Efficient Dye-Sensitized Solar Cells

Kadhim Mustafa Kadhim Al-Attafi
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Optimisation of TiO$_2$ and Zn$_2$SnO$_4$ Photoanode Materials for Efficient Dye-Sensitized Solar Cells

Kadhim Mustafa Kadhim Al-Attafi

Supervisors
Prof. Jung Ho Kim
Dr. Andrew Nattestad
Prof. Shi Xue Dou

This thesis is presented as part of the requirements for the conferral of the Degree of Doctor of Philosophy

This research has been conducted with the support of the Higher Committee for Education Development in Iraq (HCED)

University of Wollongong
Institute for Superconducting and Electronic Materials
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School of Physics

May 2019
Abstract

Solar energy is a promising technology for energy generation and represents an important candidate with other clean energy technologies as an alternative to fossil energy resources. Research into Dye-sensitized Solar Cells (DSCs) continues in spite of the advent of new solar technologies (such as perovskite solar cells), and decreases in the costs of silicon photovoltaic cells. A number of significant developments have been made in recent times, leading to more diverse research (novel redox mediators, dyes, dye binding mechanisms, and electrolytes, and the development of more efficient photoanode structures). New record efficiencies of DSCs of over 14% and more targeted applications (such as indoor application and power windows for integrated buildings) make it one of the technologies with a broad general interest.

In spite of the enormous research that has been conducted to develop efficient photoanode for DSCs, some important drawbacks of photoanode materials have been overlooked and not deeply investigated, such as the effects on DSC performance of amorphous TiO$_2$, different sizes of aggregated mesoporous TiO$_2$ nanoparticles as scattering layers, dye packing density in terms of the isoelectric point, TiO$_2$ paste preparation methods in term of scattering and transparent TiO$_2$ photoanodes, and the different quantum efficiencies of DSCs based on Zn$_2$SnO$_4$ photoanode, used with either ruthenium dye or organic dye in terms of its dye binding mechanism, in comparison with devices based on TiO$_2$.

In this thesis, some barriers that could affect DSC performance based on either the commonly used anatase TiO$_2$ or mixed phase, anatase and rutile TiO$_2$ (P25), or other promising alternative photoanode materials such as Zn$_2$SnO$_4$, are addressed in terms of dye loading or binding capability, and the light scattering ability that affects in part the light harvesting efficiency and thus the photocurrent of DSCs. In this thesis, device performances have been enhanced compared to devices based on commercial photoanode materials. Efficient solvothermal synthesis approaches have been developed to design appropriate TiO$_2$ or Zn$_2$SnO$_4$ photoanode materials. This thesis involves five aspects: investigating the effects of amorphous TiO$_2$ on the DSC performance, using aggregated mesoporous nanoparticles for high-surface-area light scattering layers in TiO$_2$ photoanodes for DSCs, the synthesis of efficient anatase TiO$_2$ nanoparticles for efficient organometallic or organic DSCs, investigating the effects of using different paste preparation approaches on DSC performance, and finally, the synthesis of cubic...
aggregated zinc tin oxide (ZTO) nanoparticles and investigating their application in DSCs.

The performance of hydrothermally treated P25 (amorphous free, H-P25) was compared with that of the as-received material as a photoanode material for DSCs, realizing 5.3% and 3.2% power conversion efficiencies (PCEs) respectively. More importantly, the results reveal important information about the detrimental effects of amorphous TiO$_2$ on DSC performance.

Hierarchically structured aggregates consisting of TiO$_2$ nanoparticles were produced via one-step solvothermal synthesis. There were two promising resultant structures, one ~700 nm and the other ~300 nm in diameter. These particles were incorporated into DSCs as high-surface-area scattering layers, along with a layer of commercial transparent material (NR18-T). PCEs of 9.1% and 8.2% were achieved using these aggregated nanoparticles as compared to 7.4% for the commonly used large-particle scattering layer (WER2-O).

Solvothermally-synthesized anatase TiO$_2$ nanoparticles (SANP) were obtained by a new and simple approach and applied as a photoanode material in DSCs using organometallic N719 and organic D149 dyes. The light harvesting efficiency in terms of dye packing density, iso-electric point (IEP) and the light scattering capability of DSCs based on SANP have been investigated and compared to those based on commercial products. The SANP|D149 devices achieved a PCE of 6.9%, which is higher than those for commercial products either using transparent photoanodes (NR18-T, 5.6%) or bi-layers with large scattering particles (NR18-T/WER2-O, 5.9%). Furthermore, an efficiency of 7.7% was achieved using a photoanode film of SANP|N719 compared to 7.2% for NR18-T photoanode, although this value is slightly lower than that of devices based on NR18-T/WER2-O (7.9%). The higher iso-electric point (IEP) of SANP compared to NR18-T and WER2-O materials has mainly resulted from the solvothermal synthesis approach using a mixed solvent of acetic acid/ethanol. This led to higher dye loading/packing and thus higher performance (higher photocurrent).

The effects of using two approaches to paste production on DSC performance were studied, one including drying and calcining steps post-synthesis (before making the paste), and the other using a solvent exchange approach to incorporate the as prepared particles into a screen printing paste, with the two approaches labelled SANP-S and SANP-T, respectively. These pastes were sensitized with either N719 or D149 dyes. Since transparent Building Integrated Photovoltaics (BIPV) remain a field that silicon
cannot full address, most of DSC research has not consider this. Therefore, the effects of light scattering and the transparency of photoanodes using these two approaches on DSC performance were investigated. The drying approach resulted in a light scattering photoanode (SANP-S) due to the nanoparticles agglomeration, while the non-drying approach resulted in a highly transparent photoanode (SANP-T). SANP-T resulted in a uniform morphology, a uniform pore size distribution, a high surface area, and more mesoporous structure compared to SANP-S. The performance of devices based on dried SANP-S was higher, however, than for those based on SANP-T due to having higher light scattering. On the other hand, SANP-T is suitable for large area applications so that these photoanodes could potentially be used in power windows for BIPV applications. SANP-T sensitized with D149 as an organic dye with a high extinction coefficient showed comparable performance 6.4% to SANP-S device performance (6.9%) which could be considered for a low-cost BIPV with further future optimization. Zinc tin oxide (Zn$_2$SnO$_4$ or ZTO) has emerged as an alternative photoanode material for DSCs, as it offers some advantages as compared to titania (TiO$_2$). Crystalline ZTO nanoparticles, formed into cubic aggregate structures were synthesised by a solvothermal reaction and employed in photoanodes of DSCs, using either a high extinction coefficient organic (D149) or an organometallic (N719) dye. These were investigated in comparison with devices based on TiO$_2$ photoanodes, with DSCs based on ZTO|D149 showing a promising PCE of 4.9%, close to that of TiO$_2$|D149. In addition, experiments were performed using ZTO and TiO$_2$ in aqueous dispersions to degrade Rhodamine B, which suggested that ZTO based DSCs should cause less dye degradation (i.e. the dye on ZTO should last longer than on TiO$_2$). Furthermore, the low photocurrents seen in ZTO|N719 based devices were investigated, with the dye binding mechanism appearing to have a significant impact on the charge injection efficiency. While the reported PCEs using this material are not as high as for the best TiO$_2$ based devices, the device engineering strategies outlined here provide guidelines for future development of DSCs based on this material.

The overall aim of this thesis is to improve the synthesis of TiO$_2$ or ZTO materials for efficient DSCs, and to investigate and overcome the barriers that affect the light harvesting efficiency in terms of the dye loading, light scattering, dye packing density, and dye binding mechanism of DSCs based on the synthesised TiO$_2$ or ZTO in comparison to the commercial products.
Acknowledgments

This thesis work was carried out and completed in the Institute for Superconducting and Electronic Materials (ISEM), the Intelligent Polymer Research Institute (IPRI) and Australian National Fabrication Facility (ANFF) at the Australian Institute for Innovative Materials (AIIM), University of Wollongong (UOW, Australia). I gratefully acknowledge The Higher Committee for Education Development in Iraq (HCED) for financial support.

Firstly, I would like to deeply thank my supervisors, Dr. Andrew Nattestad (IPRI), Prof. Jung Ho Kim (ISEM), and Prof. Shi Xue Dou (ISEM), for their supervision and consistent support.

I would like to acknowledge, Prof Brian Jones for assistance on running and analyzing the X-ray measurements for quantifying the amount of amorphous content in the synthesized materials, Dr. Patricia Hayes for her assistance on running and analyzing Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy measurements, Dr. Klaudia Wagner for assistance on running cyclic voltammetry (CV) measurements, Dr. Pawel Wagner for training on using the rotary evaporator equipment, Dr. David Mitchell, Dr. Gilberto Garcia, and Mr. Tony Romeo for training on using the electron microscopes, Dr. Konstantin Konstantinov for training on using Brunauer-Emmett-Teller (BET) and thermogravimetric analysis (TGA) equipment. Mr. Alexander Morlando for assistance on running BET and TGA measurements, and Dr. Dongqi Shi for help in running the X-ray photoelectron spectroscopy (XPS) measurements.

Many thanks to my colleagues for their contributions to my publications and for their assistance on my experimental work.

I would like to thank my dear mother for her support, prayers, and love for me.

I would like to thank my dear wife and my dear children for their patience, support, and love for me.

Finally, but not least, I would like very much to thank my sister and brothers and all my friends for their support and encouragement.
Dedication

To the spirit of my dear father,

To my dear mother, brothers, sister, and

To my lovely wife and children, who love and support me all

the time.
Certification

I, Kadhim Mustafa Kadhim Al-Attafi, declare that this thesis submitted in fulfilment of the requirements for the conferral of the degree of Doctor of Philosophy, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Kadhim Mustafa Kadhim Al-Attafi
May 2019
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>One Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three Dimensional</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>AM</td>
<td>Air Mass</td>
</tr>
<tr>
<td>APCE</td>
<td>Absorbed Photon to Current Conversion Efficiency</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total FTIR Reflectance</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BIPV</td>
<td>Building Integrated Photovoltaic</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyn-Halenda</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance</td>
</tr>
<tr>
<td>c</td>
<td>Dye concentration</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant Phase Element</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>C&lt;sub&gt;µ&lt;/sub&gt;</td>
<td>Chemical Capacitance</td>
</tr>
<tr>
<td>D&lt;sub&gt;p&lt;/sub&gt;</td>
<td>Crystal Size</td>
</tr>
<tr>
<td>D149</td>
<td>Organic Indoline standard Dye [5-[(4-[4-(2,2-Diphenylethynyl)phenyl]-1,2,3-3a,4,8b-hexahydropyrenyl)ethynyl]-2-(3-ethyl-4-oxo-2-thioxo-5-thiazolidinylidene)-4-oxo-3-thiazolidineacetic acid]</td>
</tr>
<tr>
<td>d&lt;sub&gt;hkl&lt;/sub&gt;</td>
<td>Interplanar Distance of Crystalline Structure</td>
</tr>
<tr>
<td>DSCs</td>
<td>Dye-Sensitized Solar Cells</td>
</tr>
<tr>
<td>e</td>
<td>Electron Charge</td>
</tr>
<tr>
<td>E&lt;sub&gt;fb&lt;/sub&gt;</td>
<td>Flat Band Potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Energy band gap</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>E&lt;sub&gt;ox&lt;/sub&gt;</td>
<td>Oxidation Potential</td>
</tr>
<tr>
<td>f&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Frequency at the Local Impedance Maxima</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscope</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped Tin Oxide</td>
</tr>
<tr>
<td>hkl</td>
<td>Miller indices</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>H-P25</td>
<td>Hydrothermally treated P25</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>hν</td>
<td>Photon Energy</td>
</tr>
<tr>
<td>I/I&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Iodide/Triiodide Redox Couple</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric Point</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident Photon to current Conversion Efficiency</td>
</tr>
<tr>
<td>J&lt;sub&gt;sc&lt;/sub&gt;</td>
<td>Short-Circuit Photocurrent Density</td>
</tr>
<tr>
<td>J-V</td>
<td>Photocurrent-Photovoltage Characteristics</td>
</tr>
<tr>
<td>K&lt;sub&gt;B&lt;/sub&gt;</td>
<td>Boltzmann Constant</td>
</tr>
<tr>
<td>LHE</td>
<td>Light Harvesting Efficiency</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>M</td>
<td>Mass</td>
</tr>
<tr>
<td>N&lt;sub&gt;A&lt;/sub&gt;</td>
<td>Avogadro Number</td>
</tr>
<tr>
<td>N&lt;sub&gt;d&lt;/sub&gt;</td>
<td>Donor Charge Density</td>
</tr>
</tbody>
</table>
| N719         | Organometallic standard Dye [Di-tetrabutylammonium cis-
bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium (II)]

NR18-T Commercial TiO₂ nanoparticles (Dyesol)
P/P₀ Relative Pressure
P25 Commercial Mixed Phase (Anatase: Rutile) TiO₂ Nanoparticles
PCE, η Power Conversion Efficiency
Pᵢn Incident light intensity
Pₘₐₓ Maximum Power
R Roughness Factor
Rₙₜ Charge Transfer Resistance
RIR Reference Intensity Ratios
Rₛ Series Resistance
S Constant (the strength of interaction between gas and solid)
Sₐ Specific Surface Area
SAED Selected Area Electron Diffraction
SANP-S Dried Solvotheramally synthesised Anatase TiO₂ nanoparticles
SANP-T Not-Dried Solvotheramally synthesised Anatase TiO₂ nanoparticles
T Absolute Temperature
TCO Transparent Conducting Oxide
TEM Transmission Electron Microscopy
TiO₂-300 Aggregated mesoporous Anatase TiO₂ Nanoparticles (300 nm)
TiO₂-700 Aggregated mesoporous Anatase TiO₂ Nanoparticles (700 nm)
UV-Vis Ultraviolet-Visible Spectrophotometer
V Volume
Vₔ Adsorbed Gas Volume
Vₘᵣ Theoretical Monolayer amount of Adsorbed Gas
Vᵦ Open-Circuit Photovoltage
Vₚ Specific Cumulative Pore Volume
WER2-O Commercial TiO₂ scattering particles (Dyesol)
XPS X-ray Photoelectron Spectroscopy
XRD X-Ray Diffraction
-Z'' Imaginary Part of Electrochemical Impedance
Z' Real Part of Electrochemical Impedance
ZTO Zinc Tin Oxide (Zn₂SnO₄)
α Absorption Coefficient
β₁/₂ Full Width Half Maximum
γ Optical Constant
ε Dielectric Constant
ε₀ Vacuum Permittivity
εₘ Molar Extinction Coefficient
θ Bragg Diffraction Angle
λ Wavelength
ρ Density
P Porosity
τ₀ Electron Transit Lifetime
τᵦ Electron Recombination Lifetime
Φₑ Charge Collection Efficiency
Φᵢnj Charge Injection Efficiency
Φₑᵦᵦ Dye Re-generation Efficiency
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Conferences

I attended the *Dyenamo conference on dye-sensitised solar cells* in Uppsala, Sweden, 16-17 October 2017 and presented my scientific poster ‘‘Zinc Tin Oxide (Zn$_2$SnO$_4$) nanocubes as a photoanode for organic dye-sensitised solar cells’’ as a part of my PhD project and also represented the University of Wollongong in this conference.

Statement of Publications

I Kadhim Mustafa Kadhim Al-Attafi, declare that all the publications listed above are wholly my own work unless otherwise referenced or acknowledged. I am the main author of all publications and I have done the vast majority of the work on them using the contributions of all co-authors.
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Chapter 1

1. Introduction and Literature review

1.1 Background in Dye-sensitised Solar Cells (DSCs)

With the rapid increase in global energy consumption along with less easily accessible fossil fuel resources, in addition to the serious long-term effects of climate change, searching for alternative energy resources has become a major priority. Solar energy is the most abundant renewable energy resource. Nevertheless, the cost of solar cells needs to be able to compete with that of nonrenewable energy resources.[1, 2] Less than 0.4% of the world’s surface area covered by photovoltaic devices, with 15% conversion efficiency, could satisfy global energy demands. Thus, not surprisingly, there has been persistent research in the solar cells field.[3] Solar cells based on crystalline, inorganic semiconductors have achieved an outstanding conversion efficiency of over 28% in single-junction, and 37% in multi-junction architectures (under full-sun illumination).[4] although this type of solar cell suffers from high production and energy costs.[5] The high production cost must be reduced by adopting a cost-effective solar technology including low-cost materials, and low-cost and straightforward energy-efficient manufacturing methods.[6] The promising outdoor application of DSCs in the energy landscape of the future as power windows for integrated buildings, as well as their indoor application due to their good performance under low light intensity conditions make DSCs a favorable technology compared to other solar cell technologies.[7-10] Since a significant breakthrough in 1991, the DSCs attracted more research consideration over the following 20 years, and the majority of work has been done to design efficient photoanode materials by improving the light harvesting and charge transport in respect to the other components (typically, sensitizers or electrolytes), (Figure 1.1).[11, 12] The most attractive properties of DSCs are low-cost and simple manufacturing processes; light weight, flexibility, colorability, transparency, low toxicity, and functional performance under various light conditions.[8, 10, 13] In addition, the recent progress on the synthesis of organic dyes could reduce the cost compared to using ruthenium based sensitisers. This can make all DSC components abundant and lead to lower manufacturing costs compared with other solar cell technologies.[14, 15]

Although of the best DSCs have achieved over 14% efficiency [16], certain drawbacks in photoanode materials related to dye loading/binding, light scattering, and charge injection that affect the device performance, need to be overcome. This thesis examines
a number of aspects of DSC research that are related to photoanode materials, but less well explored. These include the role of amorphous TiO$_2$, the unique relationship between N719 dye and TiO$_2$ (but not ZTO), suggesting that certain materials could be re-evaluated as candidates, and the re-evaluation of the necessity of the photoanode being highly light-scattering if the dye extinction coefficient is high enough.

![Figure 1.1: The number and distribution of publications for DSCs components, taken with permission from Ye et al. [12]](image)

**1.1.1 Aims and objectives of thesis**

This thesis examines a number of issues related to the design of metal oxides and their incorporation into photoanodes for DSCs. Specifically the following topics are addressed:

- Investigating the effect of amorphous TiO$_2$ in commercial mixed phase anatase and rutile TiO$_2$ (P25) on DSC performance in term of improving the light harvesting efficiency by increasing the dye loading capability.
- Synthesizing aggregated mesoporous nanoparticles for a high-surface-area light scattering layer in TiO$_2$ photoanodes to improve the performance of devices based on bi-layer commercial TiO$_2$ photoanodes in DSCs.
- Synthesizing high-surface-area anatase TiO$_2$ nanoparticles by the solvothermal method and investigating the effects of the isoelectric point (IEP) on the dye loading and dye packing density; and optimizing the performance of DSCs based on efficient thin photoanodes sensitised with N719 or D149 dyes compared to the commercial TiO$_2$ nanoparticle (NR18-T) photoanode.
• Preparing non-scattering films using an alternative paste production method and comparing them side-by-side with those produced by a more conventional approach; and investigating the effects of using these two approaches on the performance of DSCs with N719 or D149 dyes.

• Synthesizing and optimizing the performance of DSCs based on aggregated nanoparticles of cubic Zn$_2$SnO$_4$ compared to the commercial TiO$_2$ using N719 and D149 as organometallic and organic dyes respectively; and investigating the possibility of replacing TiO$_2$ with another $n$-type metal oxide semiconductor (MOS), in this case ZTO. Also, investigating the reasons behind the comparatively low conversion efficiencies seen with ZTO to date.

1.2 Literature review of DSC

DSCs are generally based on a wide-gap semiconductor film that works as a photoanode coated on a conductive substrate such as transparent conducting oxide (TCO), a sensitizer (e.g. organometallic or organic dye capable of monolayer adsorption), a counter electrode, mostly a catalytic material, deposited on another TCO substrate, and an electrolyte to shuttle charge (redox couples) between the sensitizer and the counter electrode. [17]

The working principle of the DSC is based on the photosynthesis process. Light absorption and charge generation take place separately in specifically designed device components. In conventional $p$-$n$ junction-based photovoltaic devices, however, these tasks are carried out by the same material, an inorganic semiconductor. [18] The operating principle of the DSC is based on the photo-injection of electrons from the sensitizer into the conduction band of the metal oxide semiconductor upon irradiation by sunlight. Subsequently, the excited sensitizer is reduced back to the ground state by electron donation from (I/I$_3^-$) redox couples in the electrolyte. Regeneration of iodide ions, which are oxidized to triiodide in this reaction, is achieved by the transfer of electrons from the counter electrode. The circuit is completed through the external load. Recombination reactions may occur during the process. The injected electrons in the conduction band of the semiconductor can recombine with either the excited sensitizer or the oxidized form of the iodide electrolyte [19], as shown in (Figure 1.2). [20]
Figure 1.2: (a) DSC structure and working principles of DSC, taken with permission from Bai et al. [20]

The performance of a DSC depends on the energy levels of the components (photoanode, sensitizer, and electrolyte). The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the sensitizer along with the light harvesting, electron injection, and collection efficiencies determine the amount of photocurrent density \( J = LHE \times I_{ph-inj} \times I_{ph-cc} \) in the DSC, where, \( J \) = photocurrent current density, \( LHE \) = light harvesting efficiency, \( I_{ph-inj} \) = photo-injected current density and \( I_{ph-cc} \) = photocollected current density. The voltage (V) of the DSC depends on the energy difference between the quasi-Fermi energy level of the electrons in TiO\(_2\) and the electrolyte potential.\[21\] For efficient electron injection, the energy level of the LUMO must be well matched with the conduction band energy level of the photoanode.\[21\] The HOMO energy level of the sensitizer must be sufficiently lower in energy than the redox potential of the electrolyte for efficient dye regeneration (oxidized dye).\[22\] The power conversion efficiency of the solar cell (PCE) is determined by the current-voltage characteristics.\[23\]

The performance and cost of a DSC strongly depend on each of its components (i.e. research efforts would be well divided between the different components). Therefore, the majority of research has been focused on the modification of semiconductor photoanodes with effective nanostructure for high dye loading and efficient electron transport. This approach can miss the importance of the inter-relations between DSC components, however. For example, organometallic N719 dye has been widely used as the best dye for TiO\(_2\), but it is not necessarily the best dye for other photoanode materials.\[16\] Therefore, further investigation is required to address previously
unnoticed limitations that can affect the dye loading/binding or charge transport on photoanodes based on TiO₂ or other alternative materials. On the other hand, research on the synthesis of new sensitisers with high visible light harvesting capability and the development of efficient redox electrolytes for efficient hole charge transport, along with optimisation of the counter electrode, has also been conducted, taking into account the performance and processing costs.[24]

Although the maximum efficiency of a DSC has reached 14%[16], further optimisation is required to minimise the losses from the fill factor, the potential difference between the photon energy and the open-circuit potential, and the photocurrent.[25]

1.2.1 Operation of DSC

Photocurrent-voltage characterization is normally used to determine the PCE or (η) of a DSC under the standard illumination conditions, air mass 1.5 global spectrum (AM1.5G, 100 mA·cm⁻²) at room temperature. The parameters that can be obtained from the J-V characterization (Figure 1.3) are the open circuit potential (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), maximum voltage (V_{max}), maximum current (J_{max}), maximum power (P_{max}), power conversion efficiency (PCE), shunt resistance (R_{sh}), and series resistance (R_{s}).

The maximum voltage that can be supplied by a DSC when the device has no load on it is known as the open-circuit potential (V_{oc}). V_{oc} refers to by how much the quasi-Fermi level of the photoanode material is distinct from the redox couple’s electrochemical potential.[17, 26] The open-circuit condition is used to measure V_{oc}, where there is no flow of current. The J = 0 mA·cm⁻² intercept provides the value of V_{oc}, which does not depend on the cell area and is consistent with identical illumination conditions.

The highest current density that can be supplied by DSC when the device has no load on it, is known as the short-circuit current (J_{sc}), which is determined when there is a short-circuit while zero potential is applied across the DSC. The V = 0 V intercept from the J-V curve provides the value of J_{sc} when normal conditions apply. The J_{sc} depends on various factors, such as the extent of dye absorption on the photoanode, the dye’s molecular structure, and electrochemical qualities of the photoanode when electrolyte is present.[17, 26] J_{sc} also depends on the electron diffusion length.[27]

The performance of a DSC is affected by the fill factor (FF), which represents the ratio between the highest power yield (P_{max}) and the product of V_{oc} and J_{sc}. The FF values are in the range between 0 and 1, where a high value is indicative of the rectangular shape that is preferred. In an ideal situation, there is dissipation of the power created in the
DSC in the external circuit, and no power losses are encountered. In reality, however, dissipation of power in a solar cell takes place by means of contact resistance, leakage current, charge transport and other losses, as dictated by the laws of thermodynamics.[28] In combination, these effects electrically signify series and parallel (shunt) resistances, which bring about a decrease in the FF.

The FF can be computed as follows:

\[
FF = \frac{P_{\text{max}}}{V_{\text{oc}} J_{\text{sc}}} = \frac{V_{\text{max}} I_{\text{max}}}{V_{\text{oc}} J_{\text{sc}}} \quad \cdots \cdots (1-1)
\]

The ratio between the maximum power generated \((P_{\text{max}})\) and the incident power \((P_{\text{in}})\) signifies a solar cell’s power conversion efficiency \((\eta)\). The PCE represents the ratio between the output power created by the DSC and the input power (incident on a given cell area), under standard simulated sunlight. When the values of \(V_{\text{oc}}\), \(J_{\text{sc}}\), and FF are high, the value of PCE will also increase (Equation 1-2). These parameters are directly affected by the mesoporous structure of the photoanode, and therefore, it is important to decrease the loss in the mesoporous network so that the DSC can be built with a higher PCE.[26]

\[
PCE, \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{V_{\text{oc}} J_{\text{sc}} FF}{P_{\text{in}}} \quad \cdots \cdots (1-2)
\]

The onset of the \(J-V\) curve under dark conditions can also be used to estimate the charge recombination in DSC.

**Figure 1.3:** Typical \(J-V\) response of a DSC under 1 sun illumination and in the dark.
The incident photon-to-current efficiency (IPCE) is the external quantum efficiency of the DSC, which represents the efficiency of the DSC in converting the incident photons at a specific wavelength to generated electrons across the device circuit. It can be used to determine how efficient the cell is at transforming photons into electrons at a specific wavelength. It is also possible to express IPCE as being related to four efficiency parameters that are given below in Equation (1-3):

\[
\text{IPCE}(\lambda) = \text{LHE}(\lambda) \cdot \phi_{\text{inj}}(\lambda) \cdot \phi_{\text{reg}}(\lambda) \cdot \phi_{\text{cc}}(\lambda) \quad \ldots \ldots \quad (1-3)
\]

Where; LHE is light-harvesting efficiency \((1 - 10^{-\text{Absorbance}})\), \(\phi_{\text{inj}}\) is the charge injection efficiency, \(\phi_{\text{reg}}\) is the dye regeneration, and \(\phi_{\text{cc}}(\lambda)\) is the charge collection efficiency.

In a specific spectral region (the visible region) the IPCE can reach values of up to 80-90% in high-efficiency DSC devices based on TiO\(_2\) photoanode.[29] The sensitizer is a central component of the DSC because it is responsible for harvesting sunlight and the generation of photoelectric current at the semiconductor interface. Thus, developing dyes with requirements including groups that can be adsorbed by the semiconducting material, appropriate energy levels for effective charge injection efficiency into the semiconductor, high regeneration by the electrolyte oxidization state, high molar extinction coefficients in the visible and near-infrared region for light-harvesting, and high photostability and solubility is therefore essential.[14, 30] It is a challenge, however, to control the open-circuit voltage.[31]

Additionally, light harvesting can be enhanced significantly by the addition of scattering layers, one-dimensional or three-dimensional photonic crystals.[32] It should be noted that DSCs only achieve high performance with a monolayer of sensitizer. [33] It is also the case that the mesoporous photoanode needs to have a high surface area for efficient dye adsorption and be relatively thin to ensure charge transport, although this leads to recombination related losses.

Additional information regarding the properties of a device can be obtained by Absorbed Photon to Current conversion Efficiency (APCE) measurements. These can demonstrate the efficiency with which the amount of absorbed photons can be changed into current. The IPCE number is divided by the light-harvesting efficiency to obtain the value of APCE (LHE, 0-100%) as in Equation (1-4).

\[
\text{IPCE}(\lambda)/\text{LHE}(\lambda) = \phi_{\text{inj}}(\lambda) \cdot \phi_{\text{reg}}(\lambda) \cdot \phi_{\text{cc}}(\lambda) \quad \ldots \ldots \quad (1-4)
\]

The loss in FF is normally occurs due to the series resistance across the device.
components [17] and the recombination losses at the interface between the metal oxide and the electrolyte (dark current processes).[34, 35]

1.2.2 Photoanode materials in DSCs

The nanostructure of a photoanode has a significant impact on the DSC performance, since it is not only acting as a support for sensitizer loading, but also as a transporter of photogenerated charges from the sensitizer to the external circuit. [36] The requirements on a photoanode material (semiconductor metal oxide) are high surface area for sufficient dye adsorption, highly mesoporous structure for effective mass transport, and appropriate energy levels that match that of the sensitizer for effective electron injection and collection efficiencies.

Modification of the photoanode can effectively contribute to higher charge-collection efficiency.[37] Therefore, many wide-band-gap metal oxide semiconductors ($E_g > 3eV$) such as TiO$_2$, ZnO, Zn$_2$SnO$_4$, BaSnO$_3$, SnO$_2$, and Nb$_2$O$_5$ have been commonly used as photoanode materials due to their stability against photo-corrosion, resulting from the oxidation of holes generated through band-gap excitation by the redox electrolyte, which can affect the performance of the semiconductor, and their electronic properties.[38]

In DSCs, a three-dimensional network of dispersed TiO$_2$ nanoparticles is commonly used as the photoanode. [11] Although the high surface area of TiO$_2$ nanoparticles is sufficient to ensure high dye adsorption, the disorder in the mesoporous network along with the grain boundaries affects the electron mobility and electron transport, resulting in increased charge recombination of photogenerated electrons.[39] This eventually limits the overall efficiency of the DSC device.[40] Table 1.1 shows the efficiency of DSCs based on different photoanode materials. To date, TiO$_2$ nanoparticles have been used in the DSCs which exhibit the highest recorded efficiencies (12.3% and 14 %). [14, 16] Moreover, TiO$_2$ is a low-cost, environmentally friendly, and abundant material. There are three main crystalline structures of TiO$_2$, rutile, anatase, and brookite with energy gaps of 3.0 eV, 3.2 eV, and 3.3 eV, respectively. [41, 42]

The anatase phase nanoparticles exhibit higher surface area for dye loading and a higher electron diffusion coefficient than that of a rutile nanoparticle based photoanode, while brookite is not commonly used in DSC application due to the difficulty in its preparation.[43] Mixed phase commercial TiO$_2$ (P25), which has an anatase: rutile component ratio of about 3:1, is still a common control material for TiO$_2$ synthesis studies, both for DSCs and other applications (photo-catalysis, batteries, etc.). [44, 45]
although P25 is known to result in DSC devices with low efficiencies.[46] While there are some reports of high efficiency devices with P25, these are not common.[47] P25 has been widely applied as a photoanode for DSCs, but it is well known to show poor performance in them. The most common explanation for the poor performance of P25 is that it is due to the rutile phase because of the offset in the conduction band between the rutile and anatase phases which can affect the open circuit value ($V_{oc}$) depending on their flat-band potentials.[48, 49] Even though anatase TiO$_2$ is the preferred phase to use in photoanodes rather than rutile TiO$_2$ due to the poor performance of devices based on rutile TiO$_2$ (as claimed previously)[48, 49], some reports have confirmed that the performance of rutile TiO$_2$ as a photoanode material is comparable to that of anatase TiO$_2$ that is sensitized with either an organometallic dye (N719) or an organic dye (D149), indicating similar performance of anatase and rutile phases in P25.[50, 51]

For example, Park et al. reported that DSC based rutile photoanode showed 30% lower $J_{sc}$ than a device based on anatase photoanode while the $V_{oc}$ was the same for the two devices.[50] The lower $J_{sc}$ of rutile was attributed to the lower surface area and lower dye packing density as compared to anatase, resulting in a lower $J_{sc}$ due to lower dye loading on rutile. In addition, even with the offset in the conduction band and the slow diffusion of electrons in rutile compared to anatase, the quantum efficiency was similar.

Lin et al. also reported hierarchically three-dimensional (3D) rutile nanorods with high surface area as a photoanode for DSCs sensitized with D149 dye, which has a high extinction coefficient, to realize closer performance to that of anatase photoanode. The DSC based 3D rutile nanorods achieved 5.5% efficiency, which is comparable to that of anatase nanoparticles at 5.8%. The differences in $J_{sc}$ and $V_{oc}$ were much less than previously reported, which indicated similar light harvesting of rutile and anatase (meaning that the charge transport in rutile is not a big issue).[51] These two studies suggested that $V_{oc}$ and FF values are not inherently low for rutile phase.

Even though electron transfer between rutile and anatase nanoparticles can be enhanced through highly interconnected anatase and rutile nanoparticles [52], the composition of commercial TiO$_2$ (P25) consists of a mixed phase of anatase/rutile that is partially interconnected due to the content of amorphous TiO$_2$.[53]

Recently, it has been observed that P25 contains a quite sizable amorphous content, which can affect the charge separation and decrease the photocatalytic activity.[54] It is believed that this amorphous TiO$_2$ may affect the DSC performance. For example,
Kurian et al. used a post-water treatment to convert an amorphous TiO$_2$ layer, deposited by atomic layer deposition, to crystalline thin layers, which resulted in improved electron transport of crystalline TiO$_2$ nanotubes as a photoanode based DSC.[55] There is no report, however. That has directly investigated the role of amorphous TiO$_2$ in DSC performance. Thus, getting rid of this amorphous content with maintaining a high surface area is a challenge that needs to be considered in DSCs.

1.2.2.1 Zinc oxide (ZnO) based photoanode
Zinc oxide (ZnO) is another commonly used photoanode material which has a similar conduction band and working function to TiO$_2$ but with higher carrier mobility. Nevertheless, the instability of ZnO in acidic dyes and the formation of dye aggregates negatively affect its performance.[56] Some other semiconductor materials have been applied as photoanodes for DSCs, although the efficiency of such DSC devices is still uncompetitive with TiO$_2$ based DSCs.

Table 1.1: Some selected high-performing DSCs with different, photoanode materials, dyes, and electrolytes.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Sensitizer (dye)</th>
<th>Electrolyte</th>
<th>PCE %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Co-sensitizers, alkoxyisilyl anchor dye (ADEKA-1) and a carboxy-anchor organic dye (LEG4)</td>
<td>I/I$_3^-$ [Co(phen)$_3^{3+/2+}$]</td>
<td>11.2</td>
<td>14.3</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Donor-$\pi$-bridge-acceptor zinc porphyrin (YD2-o-C8) Co-sensitizers, YD2-o-C8 and YD2 organic dye</td>
<td>[Co(bpy)$_3^{3+/2+}$]</td>
<td>9.1</td>
<td>12.3</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Ruthenium dye (C106)</td>
<td>I/I$_3^-$</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Organic dye (C219) Ruthenium dye (Z907)</td>
<td>I/I$_3^-$</td>
<td>10.3</td>
<td>9.3</td>
</tr>
<tr>
<td>ZnO</td>
<td>Organic dye (D149)</td>
<td>I/I$_3^-$</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>Ruthenium dye (N719)</td>
<td>I/I$_3^-$</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Zn$_2$SnO$_4$</td>
<td>Organic dye (SJ-ET1) Ruthenium dye (N719)</td>
<td>I/I$_3^-$</td>
<td>6.3</td>
<td>3</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>Ruthenium dye (N719)</td>
<td>I/I$_3^-$</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>
1.2.2 The main challenges for TiO$_2$ photoanode based DSC
Sensitized photoanode film-based commercial TiO$_2$ nanoparticles normally show high transparency and poor light scattering due to their nanometer size, resulting in low light-harvesting efficiency in the visible region (visible light transmitted rather than scattered and absorbed by the dye).[36] Furthermore, the crystallinity or the presence of amorphous TiO$_2$, the surface area, the dye binding and dye packing density, and the porous structure can affect the dye loading, charge injection efficiency, and charge recombination in TiO$_2$ photoanode based DSCs.[62] Typically, the dye binding mechanism depends on the dye structure and the photoanode materials, which affects the charge injection from the dye to the photoanode. For example, there is a different trend in the charge injection efficiency for TiO$_2$ and Zn$_2$SnO$_4$ sensitized with ruthenium dye or organic dye.[60, 63] Recently, a mass transport issue related to the charge recombination in cobalt electrolyte based DSCs has been reported in TiO$_2$ nanoparticle based photoanode.[14, 16]

1.2.2.3 Charge recombination
Surface defects of TiO$_2$ nanoparticles which are usually located at the TiO$_2$/electrolyte interface or at the grain boundaries along with energy surface states located below the conduction band of TiO$_2$ can limit the electron transportation.[62] These defects and surface states serve as trap centers to obstruct electron transportation. Photogenerated electrons can recombine with the oxidization state of the sensitizer or electrolyte in DSCs through trapping and de-trapping processes (i.e. electron transport in DSCs is a trapping-detrapping mechanism, and deep traps will enhance recombination).[64] Charge recombination can be suppressed at fluorine doped tin oxide (FTO)/TiO$_2$ photoanode or TiO$_2$ photoanode /electrolyte interfaces by applying a pre or post TiCl$_4$ treatment, respectively.[65] TiCl$_4$ post-treatment can also reduce the surface defects of the photoanode and thus enhance the dye loading.[66] Charge recombination has also been successfully reduced by applying one-dimensional (1D) nanostructured TiO$_2$ photoanode in such forms as nanowires, nanorods, and nanotubes due to excellent electron transport of 1D structures.[67] DSCs based on TiO$_2$ photoanodes with such nanostructure showed limited efficiency (9%) [68-70], however, compared with that of TiO$_2$ nanoparticle film due to the low surface area resulting from the collapse of the nanostructure and the lack of porosity, which lead to low dye adsorption and eventually to low light harvesting.[71] It remains a challenge to improve the light scattering and the electron transport without affecting the surface area of photoanode nanostructures.
1.2.2.4 Light Harvesting Efficiency (LHE)

Even though TiO$_2$ nanoparticles have a high specific surface area (50 -100 m$^2$/g), their low light-scattering ability can affect the overall performance of DSCs. This concept is particularly relevant when dyes with low extinction coefficients are used and also when making very thick films is not an option. [12] TiO$_2$ films based on nanoparticles (10-20 nm in size) are thinner than the wavelength of visible light, so that they are transparent for most of the visible light spectrum rather than being scattered through the photoanode to increase the probability of being absorbed by the dye. This can contribute to low light harvesting efficiency. [72] To overcome this issue, an approach based on a bilayer structure with a scattering layer has been proposed by using TiO$_2$ with a large particle size (400-500 nm) as the scattering layer. This bilayer structure could enhance the light harvesting of the photoanode by capturing the incident light through scattering or diffracting it backward (Figure 1.4). [29, 73, 74] Employing large particles for the scattering layer may result in a decreased photocurrent, however, since thick films limit the electron diffusion and thus affect the charge transport (i.e. affect the electron density and hence the quasi-Fermi level ($qE_f$)). [75] Therefore, TiO$_2$ photoanode materials with multifunctional morphology, offering both high light scattering and large specific surface area for dye loading, should be synthesized for further optimization of DSC performance. [76]

![Figure 1.4: Improving the light scattering efficiency by applying a scattering layer, taken with permission from Hore et al. and Usami. [73, 74]](image)

1.2.2.5 Light Scattering and Mie scattering theory

There are two theoretical approaches to describe the light scattering by particles, the Rayleigh scattering and Mie scattering theories. [77, 78] The Rayleigh scattering theory involves elastic light scattering and is only valid in the case of non-absorbing spherical
particles (with a small dielectric constant) when the particle size is much less than the wavelength of incident light (particle size < 50 nm < $\frac{1}{10} \lambda$). The conditions of Rayleigh scattering are ($\frac{2\pi r}{\lambda} << 1$) and ($|N| \frac{2\pi r}{\lambda} << 1$) where, $r$ is the particle radius, $N$ is the complex refractive index of the scattering particle, $N = n - ik$, where $n$ is the refractive, and $ik$ is a complex term related to the absorption coefficient, ($k = \frac{\alpha \lambda}{4\pi}$), where $\alpha$ is the absorption coefficient. [77, 78]

The Rayleigh scattering cross-section ($\sigma_{\text{Rayleigh Scattering}}$) can be expressed as:

$$\sigma_{\text{Rayleigh Scattering}} = \frac{2\pi^5 (2\pi)^6}{3\lambda^4} + \frac{|N^2 - 1|^2}{|N^2 + 2|^2} \ldots \ldots \ldots 1-5$$

As can be seen from the equation, Rayleigh scattering depends on the particle size and the wavelength.

As can be seen from the equation, Rayleigh scattering depends on the particle size and the wavelength.

Mie theory scattering involves inelastic scattering of light due to a spherical particle when the particle size is comparable to the wavelength of incident light [$\frac{1}{10} \lambda < \text{particle size} (50 - 500 \text{ nm}) < \lambda$]. There is no limit to the particle size in Mie scattering theory, which is also valid for large particle sizes. The Rayleigh scattering theory limited to small particle sizes is a special case of Mie theory.) When the (particle size > 1 µm) > \lambda, Mie scattering is called optical scattering. [77, 78]

Mie scattering can be given as:

$$\sigma_{\text{Mie Scattering}} = \frac{\lambda^2}{2\pi} \sum_{n=0}^{\infty} (2n + 1) (|a_n|^2 + |b_n|^2) \ldots \ldots \ldots 1-6$$

Where $a_n$ and $b_n$ are parameters that can be determined by the Riccati Bessel functions $\psi$ and $\xi$. [77, 78]

The Mie scattering efficiency $Q_{\text{Mie Scattering}}$ can be written as:

$$Q_{\text{Mie Scattering}} = \frac{\sigma_{\text{Mie Scattering}}}{\pi r^2} \ldots \ldots \ldots 1-7$$

Mie scattering shows the dependence of light scattering from spherical TiO$_2$ particles on the particle size and the wavelength of light. For example, spherical TiO$_2$ particles larger than 200 nm can effectively scatter visible light in a range of ~400 - ~650 nm, as shown in Figure 1.5 a,b. [79, 80] It is expected that, by taking in the account the refractive index and the absorption of the electrolyte in the DSC system, TiO$_2$ spherical particles with comparable size to the visible light wavelength can achieve efficient light
scattering and thus enhance the light harvesting efficiency. [77, 78] The well dispersed TiO$_2$ nanoparticle (~25 nm) based photoanode film cannot participate in the light scattering and is transparent for most visible light, as shown in Figure 1.6. [78]

![Figure 1.5](image1.jpg)

**Figure 1.5:** The dependence of light scattering on (a) the particle size; and (b) the wavelength of incident light, taken with permission from Holik and Pulker. [79, 80]

![Figure 1.6](image2.jpg)

**Figure 1.6:** The light scattering of a photoanode film based on well dispersed TiO$_2$ nanoparticles, taken with permission from Zhang et al. [78]

To solve the problem of low scattering by TiO$_2$ nanoparticles, scattering particles with size comparable to the wavelength of the visible light can be either incorporated on top of the crystalline TiO$_2$ nanoparticles (25 nm) (bi-layer photoanode) or incorporated in a mixture with the TiO$_2$ nanoparticles to act as scattering centers. The bi-layer approach can increase the path length of the incident light through the photoanode materials,
enabling more light adsorption by the dye molecules and thus enhancing the light harvesting efficiency, but applying large scattering particles as a top layer on top of the TiO₂ nanoparticles (underlayer) can increase the photoanode thickness, which gives rise to charge recombination issues due to the limited electron diffusion in a such thick film. On the other hand, the mixture approach including large-size particles as scattering centers can affect the surface area of the TiO₂ nanoparticles and thus affect the dye loading capability. [77, 78]

Sub-micrometer size hierarchical or aggregated structures of TiO₂ spheres have shown a significant enhancement in DSC performance due to their multifunctional properties such as efficient light scattering capability, electrolyte penetration, dye loading (high surface area), and charge transport.

Figure 1.7 a-e shows the three photoanode configurations to enhance the light scattering in DSCs. [78, 81]

![Figure 1.7: Three photoanode configurations for enhancing the light scattering in DSCs: (a) bilayer, (b) a mixture of scattering particles and nanoparticles, (c) aggregated or hierarchical structures; (d) and (e) schematics illustrations of the light scattering through the aggregated nanoparticles, taken with permission from Zhang et al and Cao et al. [78, 81]](image)

Mie scattering is valid for describing single scattering and multiple scattering. Some simulated theoretical studies have indicated that efficient light scattering depends on the mixture weight ratio or volume ratio of TiO₂ scattering particles to TiO₂ nanoparticles. For example, a 5% weight ratio of scattering particles (125-150 nm or 250-300 nm) mixed with TiO₂ nanoparticles (~20 nm) was proposed to achieve effective light...
In another example, a 25% volume fraction of the scattering particles (~250) was predicted to maximize the light scattering.

Further, a simulation model for a bi-layer photoanode including large scattering particles predicted that the optimum particle size for the maximum back scattering can be calculated as \[ \text{[~1.3-1.4}\pi \text{/wavenumber}]. \]

There has been much research on designing TiO$_2$ photoanodes with high light scattering ability.

A bi-layer photoanode in a nanostructure-based DSC significantly improved the light scattering ability in the visible wavelength range.

Higher conversion efficiency of 9.43% with high $J_{sc}$ was achieved by using hollow spherical TiO$_2$ particles as the scattering layer as compared to commercial scattering particles (8.96%).

Microstructured TiO$_2$ hollow spheres can improve the dye adsorption and light scattering ability simultaneously, compared to the commonly used commercial TiO$_2$ large particle scattering layer that only provides light scattering ability.

Also, a DSC prepared with such beads as a scattering layer also showed similar results.

Moreover, mesoporous hierarchical microspheres for scattering light on top of commercial Dyesol TiO$_2$ nanoparticles as an underlayer achieved high efficiency of 10.30%.

This indicates that bilayer structured photoanodes with aggregated monocrystalline particles for light-scattering are a promising approach to enhance the efficiency of DSCs, as shown in Figure 1.8 a,b. The thickness in the case of bi-layer structured films should be controlled, however, to reduce the charge recombination losses.

**Figure 1.8:** Low (a) and high (b) magnification SEM images of TiO$_2$ hollow spheres as a scattering layer, taken with permission from Koo et al. [72]

### 1.2.3 Recent progress in TiO$_2$ photoanode based DSCs

Good photoanode properties, including high surface area, fast electron transport, and
high light scattering ability are required for high-efficiency DSCs. Recently, developments on TiO$_2$ photoanode have been focused on optimizing the specific surface area in 1D nanostructures by introducing nanocomposites, hierarchical structures, and alternative nanostructures of the scattering layer as a replacement for the conventional large-particle TiO$_2$ based scattering layer. For instance, 3D mesoporous nano/microsphere structures with higher surface area (100 m$^2$/g), exhibited better light scattering properties and thus higher PCE compared to P25 or bi-layer P25/microsphere photoanodes.[87]

1.2.3.1 Nanocomposite photoanode structure
Nanocomposites of TiO$_2$ 1D nanostructured materials with TiO$_2$ nanoparticles have been successfully used to enhance the performance of DSCs with photoanodes based only on nanoparticles by increasing the surface area, charge transport, and dye adsorption. For example, a mixture of TiO$_2$ nanotubes with TiO$_2$ nanoparticles (2% P25) achieved the high efficiency of 8.43% compared with either P25 (5%) or only TiO$_2$ nanotubes (7.83%).[88] Moreover, a composite including TiO$_2$ nanoparticles aggregated into microspheres with a surface area of 55.24 m$^2$/g was prepared by electrospaying P25 precursor solution with anatase TiO$_2$ nanoparticles (82.82 m$^2$/g) in a weight ratio of (0.7/0.3) achieved an efficiency of 7.59% compared to 5.80% and 5.35% for only anatase nanoparticles or or only nanoparticles aggregated into microspheres, respectively. This was attributed to enhanced light scattering and charge transport.[89] Furthermore, multiwall carbon nanotube/ TiO$_2$ nanoparticle nanocomposite achieved an incredible enhancement in efficiency, reaching 10.29%, compared to TiO$_2$ nanoparticles with 6.31% due to the enhanced charge transport achieved by using carbon nanotubes.[37]

1.2.3.2 Hierarchical Photoanode Structure
Hierarchical structures such as TiO$_2$ microspheres or 1D micro/nanoscale aggregated nanoparticles have attracted much research interest as photoanode materials. Photoanodes with hierarchical structure provide high light harvesting and better electron transport properties with a high surface area (Table 1.2).[90] Normally, hierarchical structures consisted of assemblies of nanostructured units, such as nanoparticles, nanorods, nanowires, nanoplates, etc., which can provide high dye loading and better light scattering compared to nanoparticle based photoanodes due to their high surface areas and hierarchical structures, as shown in Figure 1.9.a,b. [19, 91]
Photoanodes based on spherical nanoparticle aggregates could exhibit higher efficiencies than those made with nanoparticles because they provide high light scattering without affecting the surface area, have high electrolyte penetration through the mesoporous structure, and improve the electron transport resulting from highly connected nanoparticles.[75] High interface resistance can arise, however, from poor interface contact with the FTO resulting from large uncovered space on the FTO glass.[92] Therefore, for better efficiency, combining hierarchical structure with nanoparticles, which have high contact with the FTO glass, as a bi-layer film electrode is a promising approach.[93] Kim prepared nanoporous spheres 250 nm in size that were assembled from TiO$_2$ aggregated nanoparticles with a size of about 12 nm. DSC devices based on these hierarchical nanoporous spheres showed efficiency as high as 10.44% due to their higher specific surface area (117.9 m$^2$/g). The higher performance was attributed to the higher electrolyte diffusion through the larger mesoporous structure and higher dye adsorption compared to nanoparticle based devices (Figure 1.10 a-c).[92]

Figure 1.9: (a) High magnification and (b) low magnification SEM images of hierarchical TiO$_2$ photoanode structures (nanorods and nanoparticles) assembled into microspheres for high efficiency DSCs, taken with permission from Liao et al. [91]
Table 1.2: Performance of different hierarchical nanostructured TiO$_2$ based DSCs.

<table>
<thead>
<tr>
<th>Hierarchically assembled photoanode structures</th>
<th>PCE % Hierarchical vs. nanoparticles</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanorods +Nanoparticle assembly (TiO$_2$ microspheres)</td>
<td>10.34/8.10</td>
<td>[91]</td>
</tr>
<tr>
<td>Nanoparticle assembly (TiO$_2$ beads)</td>
<td>9.05/7.56</td>
<td>[94]</td>
</tr>
<tr>
<td>Nanoparticle assembly (TiO$_2$ nonporous microspheres)</td>
<td>8.44/7.30</td>
<td>[92]</td>
</tr>
<tr>
<td>Nanoribbons assembly (mesoporous hierarchical microspheres)</td>
<td>10.3/6.6</td>
<td>[75]</td>
</tr>
</tbody>
</table>

Figure 1.10: (a and b) SEM and TEM images of TiO$_2$ spheres, and (c) Schematic diagram shows the electrolyte diffusion through the mesoporous structure of TiO$_2$ spheres, taken with permission from Kim et.al. [92]

1.2.4 The effect of the isoelectric point (IEP) on the dye loading

The isoelectric point (IEP) means the pH values where there is zero net surface charge of a material.[95] If the IEP of a metal oxide is equal to or higher than that of the immersing dye, the surface of the metal oxide will have more positive charge, which enables the adsorption of more dye molecules. [63, 95] The isoelectric point (IEP) is
one factor that affects the dye binding on photoanode semiconductor materials (TiO$_2$, ZnO, Zn$_2$SnO$_4$, SnO$_2$, etc.). Since the sensitizers (dyes) can bind to the photoanode materials through the effective negative carboxylic groups, materials with higher IEP can adsorb (or bind) more negative carboxylic groups due to having higher positive surface charges. Thus, increasing the IEP at the dye/metal oxide interface is an effective way to enhance the light harvesting efficiency by enhancing the dye loading capability. [96, 97]

The approach of increasing the IEP can be used successfully to enhance the performance of other photoanode materials that have low dye loading in spite of their high surface areas.[96-98] Also, the IEP of photoanode materials can be increased by using a surface treatment or doping process with other materials that have higher IEP. A ZnO thin layer deposited by atomic layer deposition (ALD) was also used to increase the dye loading capability of low surface area TiO$_2$ nanowires due to the higher IEP of ZnO.[97] On the other hand, even though materials with high IEP values, such as ZnO, MgO, ZrO$_2$, and Al$_2$O$_3$, can be used to increase the dye binding, dye aggregation or the mismatching of the energy levels with the dye can affect the charge injection efficiency.[97]

Acidic surface treatment is another approach that can be used to increase the dye loading on TiO$_2$ in DSCs by increasing the positively charged surface area of TiO$_2$ (increasing the surface acidity and thus the IEP) due to increasing the amount of adsorbed H$^+$ ions. [40, 99, 100]

Also, it was reported that using acids as solvents in a solvothermal reaction can result in TiO$_2$ materials with high IEP, which can increase the dye adsorption. [101]

Furthermore, there was another report that exposed facets of synthesised TiO$_2$ with higher surface energy can affect the IEP and the thus the surface reactivity to better adsorb the dye molecules [102] Since acidic solvents have been widely used to control the TiO$_2$ morphology and crystal facets,[103] it is expected that using appropriate acidic solvents to synthesize TiO$_2$ with favourable exposed facets (e.g. 001) can enhance the IEP and thereby the dye loading capability. [51, 104]

Although the surface treatment of TiO$_2$ using acids or other metal oxides with higher IEP can enhance the dye loading or binding on the TiO$_2$ surface, it could make the DSC processing more complicated and increase the fabrication time.[105]

Since the IEP of synthesized materials is strongly dependent on the their synthesis approach, using a solvothermal approach based on acidic solvent could result in a
product with higher IEP,[101] This needs more investigation for a further understanding of the effects of the synthesis approach on the IEP and thus on the dye packing density in DSCs.

1.2.5 Effects of the paste preparation approach on DSC performance

DSCs have promising features such as tunable color and high transparency (architectural design) that can be used in applications such as windows in integrated buildings or building roofs. Also, the DSC performance is only slightly affected by changing the angle of incident light or the ambient temperature compared to the conventional silicon solar cells. (DSCs can perform efficiently even with low light intensity and in a wider range of ambient temperature).[106, 107]

As is well known, since 1991 there have been a large numbers of publications on optimizing DSC components and enhancing their overall performance.[12] Synthesizing and optimizing an efficient photoanode material takes up the largest proportion of research development, about 41%.[12] On the other hand, a photoanode film should have a highly connected mesoporous network with appropriate porosity and pore size distribution in order to ensure high dye loading and also to enhance the charge transport through the photonode film. Most photoanode films are usually printed using a powder or paste material after drying and/or calcination mixed with organic binders to obtain uniform and mesoporous film. [108-110] A few other works suspensions that had not been dried to obtain a high dispersion paste, which enabled them to print highly transparent films.[8, 111, 112]

Even though DSCs have such promising features[10, 113], the cost of ruthenium dyes and excessive film thickness should be reduced to ensure high transparency and large-scale production. As is well known, the complicated processing and the high cost of organometallic based ruthenium dyes are partly responsible for the increased production cost of DSCs. [114] Therefore, there is a trend towards developing metal-free organic dyes as an alternative to ruthenium based dyes.[115] DSC based organic dyes have achieved efficiency of over 10% using iodide electrolyte and over 14% using cobalt based electrolyte,[16, 115, 116]. Therefore, there is a need to further investigate the effects of using both preparation paste approaches (mentioned above) on DSCs performance, especially based on thin photoanodes sensitized with metal-free organic dyes.
1.2.6 Preparation methods for photoanodes materials for DSC

Different methods have been used to synthesize TiO$_2$ materials, such as precipitation, flame spray, microwave, sol-gel, etc., in order to control their crystallinity, polymorph phases, and morphology.\[117\] Hydrothermal or solvothermal synthesis is widely used as facile and cost-effective approach to prepare highly crystalline metal oxides by controlling the reaction conditions, such as the synthesis temperature (generally $< 250 ^\circ C$) and short reaction time.

Hydrothermal reaction can be efficiently used to produce crystalline TiO$_2$ with phase purity, high dispersion, and well-controlled crystallinity.\[118, 119\] Similarly, by controlling the hydrothermal conditions (such as, molar ratio, additives, temperature, reactant concentration and solvent pH), crystalline products with different morphologies, compositions and sizes can be obtained.\[120\] The calcination process is also applied for obtaining the TiO$_2$ crystalline structure. Even though the calcination process is important for the transformation from the amorphous phase to single or polycrystalline phase, it can be eliminated in some procedures.

Nanostructured TiO$_2$ is usually synthesized from the hydrolysis of a titanium precursor, which is normally achieved using an acid-catalyzed hydrolysis step including titanium (IV) alkoxide (e.g., titanium isopropoxide, TTIP) or a halide precursor (e.g., TiCl$_4$) followed by condensation. The properties of the resultant TiO$_2$ nanomaterials, including the structure size, crystallinity, surface area, morphology, degree of dispersion, porosity and crystal phase, are strongly related to the reaction conditions, including the reaction time, type of precursor, reaction temperature, solvent pH, post-treatment and drying conditions.\[121, 122\]

Solvothermal is the generic term, hydrothermal is specific for when water is used as the solvent (i.e. hydrothermal reactions are a subset of solvothermal ones).\[123\] Accordingly, higher reaction temperature and pressure can be obtained in some solvothermal reactions compared to hydrothermal reactions, depending on the boiling points of the organic solvents. Typically, the solvothermal method shows better control over the particle size, nanostructure, degree of crystallinity, and particle size distribution of TiO$_2$ nanomaterials compared to the hydrothermal method. \[119, 121\]

The hydrothermal reaction parameters significantly affect the chemical and physical properties of the synthesized materials, which provide a wide range to optimize and design the desired nanostructure, as shown in Figure 1.11 and Figure 1.12. For example, Wu et al. controlled the morphology of solvothermally synthesized anatase TiO$_2$
nanosheets and rhombic-like nanocrystals by using titanium isopropoxide in mixed solvents, including benzyl alcohol and oleylamine or benzyl alcohol, oleylamine and water respectively. [123] These nanosheets and nanocrystals showed a high percentage of specific exposed crystal facets, (001) and (010), unlike the common thermodynamically stable TiO$_2$ (101) facets (e.g. P25), which, in turn, showed higher dye adsorption and photocatalytic activity compared to commercial P25.[123] This was attributed due to the use of the mixed solvents, resulting in high energy (001) and (010) facets, which have high reactivity towards dye adsorption compared to (101) facets.

Lin et al. synthesized and controlled the morphology and crystal growth facets of different 3D hierarchical rutile TiO$_2$ microstructures by hydrothermal reaction, using titanium butoxide in water and different concentrations of hydrochloric acid.[51] One of these series, 3D hierarchical nanorod rutile TiO$_2$, showed higher DSC performance compared to commercial scattering particles sensitized with organic dye when applied as scattering layer on top of a photoanode made from commercial anatase nanoparticles. This is attributed to the higher facet surface area and better light scattering. [51]

Lin used the solvothermal reaction of titanium butoxide in acetic acid to synthesize mesoporous anatase single crystals with different pore facets for efficient DSCs based on cobalt electrolyte.[124]

Controlling the pH of the solution in the hydrothermal reaction can be used to change the polymorph phase of TiO$_2$. For example, Li and Xu used hydrothermal reaction to transform mixed phase anatase: rutile TiO$_2$ (P25) to anatase TiO$_2$ single crystals with tetragonal faceted nanorods by controlling the pH value in a basic solution containing Na-TiO$_2$.[125]

The morphology and crystalline phase depend on the precursor and solvents used in the solvothermal reaction. For example, Liu and Aydi used a hydrothermal reaction of titanium butoxide in a mixed solvent of water and hydrochloric acid with an optimized reaction temperature and additive ratio to grow single crystal rutile nanorods for DSC application. [126] Yandong Duan et al. used titanium tetrachloride in a mixed solvent of ethanol and water to synthesize mesoporous anatase TiO$_2$ microspheres for the scattering layer in DSCs.[127]

Using an anionic surfactant in the hydrothermal reaction can also control the morphology and crystalline phase. For example, Sheng-Cai Zhu and Ling Fu used the hydrothermal reaction of sodium dodecyl sulfate and titanium tetrachloride in water with hydrochloric acid to synthesize mixed crystalline phases of anatase hollow spheres
with rutile nanopins for photocatalytic application.[128] Other cation salt additives can be used to control the hydrothermal reaction and obtain a hierarchical TiO$_2$ structure. For example, Ye et al. used a hydrothermal reaction of titanium isopropoxide with hydrochloric acid to synthesize hierarchical TiO$_2$ flowers as DSC photoanode material.[129] Controlling the solvothermal reaction pressure can be used to control the particle size and crystalline phase of the synthesized TiO$_2$. For example, Mario et al. used a hydrothermal reaction of titanium isopropoxide with acetic acid and water with different autoclave pressures to control the TiO$_2$ particle size. The particle size of the synthesized TiO$_2$ increased from 9-13.8 nm when the pressure increased from 1-71 atm (23-210 °C).[130] In another example, Hsiao et al. synthesized TiO$_2$ by a solvothermal reaction of titanium isopropoxide in a mixed solvent of acetic acid and water using different autoclave pressures, 57, 100, and 120 bar. All the synthesized TiO$_2$ samples grown using the three pressure values during crystallization showed crystalline anatase TiO$_2$ mixed with amorphous TiO$_2$. The optimum coordination number of TiO$_2$ was at 100 bar, which enhanced the electron transport in DSCs. The coordination number of TiO$_2$ can be optimized by controlling the reaction pressure during the synthesis.[131] Figure 1.12 shows some typical structures prepared by hydrothermal or solvothermal reaction.[119, 132, 133]
1.2.7 Dye degradation on TiO$_2$ photoanode

Dye degradation, which affects device stability under visible light irradiation, has been widely investigated for ruthenium dyes (e.g. N719) and some other organic dyes. [134, 135] The devices containing them showed good lifetime stability under simulated sunlight using ultraviolet (UV) filtered light and temperatures less than 60 °C. Devices based on an organic coumarin dye using a UV filter (less than 420 nm) showed stable performance under visible light soaking for 1000 h, and no dye degradation was observed.[136] The photostability of DSCs devices based on MK-2 organic dye was also investigated using simulated light with/without a UV filter. Devices based MK-2 showed performance stability under the filtered light for 60 days, but the performance was decreased significantly using the simulated light without a UV filter. This was attributed to the dye degradation under UV exposure.[134, 137] In spite of this problem, many DSC devices have been developed and designed to overcome the photostability issue and enhance the device stability, but with the inherent UV photoactivity of TiO$_2$ resulting in free radical species remaining as a reason for dye degradation.[138, 139] Natural dyes have also been used recently as sensitizers in DSCs to be more stable against the UV photoactivity of TiO$_2$ photoanode.[139] Designing other metal oxides with lower UV photoactivity as alternative photoanode materials for TiO$_2$ can enhance the DSC photostability based on organic dyes under long-term irradiation. For example,
wide-band-gap metal oxides that are photocatalytically inactive, such as Zn$_2$SnO$_4$, are expected to show lower organic dye degradation compared to TiO$_2$ and thus enhanced device stability without using encapsulation or UV filters.[140] In photocatalytic application, many metal oxides (including TiO$_2$) are used specifically for degrading organic compounds.

1.2.8 Ternary metal oxide based DSCs

Binary semiconducting metal oxides such as ZnO, TiO$_2$, and SnO$_2$, have attracted intensive research interest for photoanode based DSCs. Nevertheless, alternative photoanode semiconductor materials with better physical and chemical properties, such as stability in acidic dye, charge transport, dye adsorption or packing density in term of IEP and surface reactivity, and photostability, are required. Ternary metal oxides have been reported as promising photoanode materials for DSCs, such as BaSnO$_3$, SrTiO$_3$, ZnFe$_2$O$_4$, and Zn$_2$SnO$_4$, due to their promising electronic, optical, and photovoltaic properties, such as a more negative conduction band edge, better charge mobility, and a wider optical band gap.[141-144] Among these ternary oxide semiconductors, zinc tin oxide, Zn$_2$SnO$_4$ (ZTO), has attracted more attention recently.[145-147] ZTO is a promising material for use in working electrodes for DSCs. There are a few reports on controlling the morphology of ZTO nanostructures such as cubes, spheres, anisotropic rods, etc by using different mineralizers and additives [148-150]. ZTO with a band gap of (3.6-3.7 eV) and electron mobility of (10-15 cm$^2$ V$^{-1}$ s$^{-1}$), which are higher than those of TiO$_2$ (3.2 eV, 0.1-1 cm$^2$ V$^{-1}$ s$^{-1}$), is an important ternary metal oxide. Also, ZTO exhibits high electron mobility, high electrical conductivity, and low absorption in the visible range [145, 151]. It is considered as a promising material for DSC applications with efficiency up to 6%.[73] It also has better stability in acidic dyes compared to ZnO photoanode and much higher performance compared to SnO$_2$ photoanode.[152] ZTO shows better photostability against UV radiation than TiO$_2$ photoanode, [153] while the electron-transport properties of ZTO oxide are similar to those of TiO$_2$. The main issues affecting the performance of ZTO photoanode structures, including nanoparticles [69, 72], single-crystal micro-octahedra [75], nanowires [76], and nanoflowers,) with commercial dye (N719) and iodide based electrolyte are: short electron diffusion length, low short-circuit current, low electron injection efficiency, high recombination with electrolyte, and low open-circuit voltage. The low surface area also observed in ZTO results in low dye loading and hence affects the LHE in DSCs.
Nevertheless, improvement in $V_{oc}$ and reducing recombination have been achieved by applying ZTO-ZnO in the form of core-shell nanostructures composing a thin film with an overall efficiency of 6% [154], as shown in Figure 1.13. Also, employing a bi-layer structure containing microporous ZTO nanoparticles (pore size = 180 nm) as an overlayer resulted in an enhanced LHE and hence enhanced efficiency of the DSC to 6.1% compared to devices based on ZTO nanoparticles (4.47%), as shown in Figure 1.13. [151] This was attributed to the enhanced light scattering while maintaining high dye loading (surface area = 101 m$^2$/g) of the microporous ZTO based bi-layer photoanode. The highest efficiency to date achieved in a DSC based on ZTO photoanode is 6.3%, using hierarchical ZTO mesoporous microspheres sensitized with organic dye. [143, 151]. ZTO is, therefore, an interesting mesoporous material for DSC photoanodes based on a metal-free organic dye.

The higher efficiency achieved by using organic dye was attributed to the high absorption and extinction coefficients of the organic dye and the high surface area, which enabled efficient dye adsorption [152], along with the light scattering capability of the ZTO hierarchical mesoporous microspheres assembled from nanobeads, as well as the efficient diffusion of iodide redox mediator, as shown in Figure 1.14 a,b. [60]

![Figure 1.13: (a) and (b) SEM images of ZTO-ZnO thin film core-shell structure; (c) reducing recombination in the ZTO-ZnO core-shell structure, taken with permission from Shin et al. [154]](image)
A survey of the progress in ZTO photoanode based DSCs is summarized below in Table 1.3 and Figure 1.15.

Table 1.3: Survey of progress in ZTO photoanode based DSCs (all works were conducted with commercial organometallic dye (N719) and iodide electrolyte, except for Ref. 60, which used organic dye (SJ-E1 and SJ-ET1). NP: nanoparticle.

<table>
<thead>
<tr>
<th>Zn$_2$SnO$_4$ photoanode structure</th>
<th>Thickness (µm)</th>
<th>Preparation method</th>
<th>PCE %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoparticle</td>
<td>5.6</td>
<td>Hydrothermal</td>
<td>2.5</td>
<td>[148]</td>
</tr>
<tr>
<td>Nanoparticle</td>
<td>4.3</td>
<td>Hydrothermal</td>
<td>3.8</td>
<td>[152]</td>
</tr>
<tr>
<td>Single crystal hexagonal nanoplate/micro-octahedron</td>
<td>9</td>
<td>Hydrothermal + solid-state reaction</td>
<td>3.1</td>
<td>[155]</td>
</tr>
<tr>
<td>Nanowires</td>
<td>20</td>
<td>Chemical vapor deposition</td>
<td>2.8</td>
<td>[156]</td>
</tr>
<tr>
<td>Nanoflower</td>
<td>15</td>
<td>Hydrothermal</td>
<td>3.35</td>
<td>[157]</td>
</tr>
<tr>
<td>Hierarchically mesoporous microspheres (nanobead assembly)</td>
<td>10</td>
<td>Electro-spray</td>
<td>6.3</td>
<td>[60]</td>
</tr>
<tr>
<td>ZTO + ZnO thin films (core-shell structure)</td>
<td>0.5</td>
<td>Pulsed laser deposition</td>
<td>6</td>
<td>[154]</td>
</tr>
<tr>
<td>Bi-layer Nanoparticle/macroporous</td>
<td>15</td>
<td>Hydrothermal</td>
<td>4.47 NP vs. 6.10 bi-layer</td>
<td>[151]</td>
</tr>
<tr>
<td>Bi-layer ZTO Nanoparticle/TiO$_2$</td>
<td></td>
<td>Hydrothermal</td>
<td>3.47 NP vs. 5.72 bi-layer</td>
<td>[63]</td>
</tr>
</tbody>
</table>
Further research and more investigation should be conducted to explore the promising properties of ZTO and other ternary metal oxides as photoanodes for DSCs. Even though these materials can be optimized as alternative photoanode materials, there are a few reports related to DSCs and other applications.

1.2.9 Recent progress in DSC sensitizers

Ruthenium-based dyes that are commonly used as the sensitizer in DSCs show outstanding performance due to offering a wide range of light absorption from ultraviolet to near-infrared light, compatibility in energy levels with TiO$_2$ based photoanodes and iodide redox-based electrolyte, and high molecular stability.[158] High efficiency up to 10.0% was recorded using an N3 ruthenium dye based DSC.[159] In 2005, further improvement in efficiency to 11.2% was achieved with N719 ruthenium dye [160] and 11.7% in 2010 with C106 ruthenium dye (Figure 1.16) [57], while efficiency as high as 10.7% achieved with black dye in 2012.[161] In the case of ruthenium dye based DSCs, however, no significant progress has been reported for over ten years.[121] This can be attributed to the complicated synthesis process and low extinction coefficients (10,000-20,000 M$^{-1}$ cm$^{-1}$) of ruthenium dyes as sensitizers. Even though some synthesized ruthenium dyes (such as CYC-B11) showed higher light harvesting efficiency with thin photoanode film due to their higher extinction
coefficients,[162] the complicated synthesis process for ruthenium-based dyes is still the greatest challenge in large-scale applications.

Metal-free organic dyes are promising sensitizers for DSCs.[163] Some organic dyes have shown promising properties such as high molar extinction coefficient (50,000–200,000 M⁻¹ cm⁻¹), simple and cheap synthesis processes, and high flexibility of their molecular structures, which can reduce the DSC fabrication requirements.[164] Organic dyes can extend the light absorption from the visible region to the near infrared region, which enhances the light harvesting efficiency. [163] 9%-10% efficiencies have been achieved using D149 organic dye with a controlled photoanode thickness.[111, 116] An efficiency of over 10% has been achieved for DSCs based on organic dyes (C219 and JF419 organic dyes) (Figure 1.16). [58, 165]. Also the co-sensitizer approach, which incorporates organic dye with other dyes, has achieved the highest DSC efficiency to date (over 14%). [16, 166] Nevertheless, dye aggregation and instability are the greatest obstacles to further improvements of organic dye based DSCs.

The research progress in modification and optimization of photosensitizers (dyes) has been continuous, leading to efficient light harvesting and better stability of their chemical structures.[167]

Figure 1.16 a,b shows the chemical structures of some typical ruthenium dyes and metal-free organic dyes. [168-171]

Figure 1.16: The molecular structures of some typical ruthenium and organic dyes, taken with permission from Lund et al, Willinger et.al, and Le Bahers et al. [168-171]
Intensive studies have been conducted to develop other efficient dyes to use as sensitizers with metal oxide semiconductor photoanodes. Porphyrin dye is a metal complex with a cyclic structure that involves four pyrroles.[172] The porphyrin dye is typically a complex consisting of a porphyrin organic ring (tetrapyrrole ring) surrounding a metal ion.[173] Typically, the porphyrin molecular structure contains two position anchoring points, four meso and eight β position points Figure 1.17.[174] These positions in porphyrin can link to single or multiple anchoring groups such as carboxylic acid or 8-hydroxylquinoline that are normally used to bind the dye with the TiO$_2$ photoanode in the DSC. [174] The organic porphyrin ring can efficiently absorb visible light enabling its use as a complex metal ion for efficient light harvesting in DSCs. Figure 1.17 shows the typical molecular structure of porphyrin and some efficient porphyrin dye-based DSCs. [174]

The porphyrin metal complex based dyes have shown excellent performance as photosensitizers due to their high absorption in the range of 400-750 nm (Soret band 400-500 nm and Q-band 500-750), high extinction coefficient (100,000-200,000 M$^{-1}$ cm$^{-1}$), excellent molecular stability, and appropriate energy levels with other DSC components.[167, 174] A study in 2000 showed efficient charge injection kinetics between the porphyrin dye and TiO$_2$, which was similar to that of ruthenium dyes.[175] Since then, many modifications of the chemical structure and synthesis procedures for porphyrin dyes have been conducted and resulted in high DSC efficiency. [167, 172] In 2010, a DSC efficiency as high as 11% was achieved by employing YD-2 dye (Figure 1.17).[176] In 2011, a further enhancement in efficiency up to 11.9% was reported through the use of YD-2-o-C8 porphyrin dye (Figure 1.17).[14] Previous research has shown, however, that in the case of porphyrin dye as sensitizer there is a challenge to light harvesting efficiency from the ultraviolet to the near-infrared regions and low photoelectron injection efficiency into photoanodes due to dye aggregation on the TiO$_2$ surface.[177] Thus, co-sensitization methods have been developed as an effective way to extend the light-harvesting range and enhance DSC performance.[14] In 2011, a record-breaking efficiency of 12.3% for DSCs was obtained using YD2-oC8 co-sensitized with an organic dye (Y123) (Figure 1.17).[14] Co-adsorbates with long chains (e.g. chenodeoxycholic acid or hexadecylmalonic acid) have also been used to overcome the dye aggregation and suppress the recombination at the TiO$_2$/electrolyte interface.[172, 178]

The highest efficiencies for DSCs with only one porphyrin dye have been achieved by
modifying the molecular structure of YD-2-o-C8 dye to synthesize either SM315 (13%) or GY50 (12.7%) using cobalt electrolyte. [179, 180] Figure 1.17 shows the molecular structure of some porphyrin dyes that have achieved high DSC efficiency.

![Molecular structures of porphyrin dyes](image)

**Figure 1.17:** The molecular structures of typical efficient porphyrin dyes, taken with permission from Yella et al., Mathew et al. and Yella et al. [14,179-180]

### 1.2.10 Recent progress in DSC electrolytes

Redox electrolytes in DSCs is used to transfer electrons from the counter electrode to the oxidized dye. The most important requirements for an effective redox electrolyte are solubility and ionic mobility of the redox couple in an organic medium, the driving force for the dye regeneration, and fast electron transfer kinetics with a minimal overpotential at the counter electrode. The type of electrolyte has a significant impact on both the efficiency and the stability of DSCs. [181, 182] The most used DSC liquid electrolyte is iodide-triiodide electrolyte (I$_3$-I), which has been known as the most common redox shuttle because of its suitable properties, such as fast oxidation of I$^-$ at the photoanode/electrolyte interface for efficient dye regeneration and slow reduction of (I$_3^-$) at the electrolyte/counter electrode interface for high electron collection, high diffusion, relatively high stability, low cost, and easy preparation.[181] To date, the recorded PCE of iodide electrolyte-based DSCs has been about 11%. [57] There are some limitations affecting the iodide electrolyte performance, however, such as absorption of visible light at 430 nm, corrosion of the noble metal counter electrode.
(e.g. Pt), and an upper limit on $V_{oc}$ of 0.9 V. These limitations significantly restrict further development of DSCs based on iodide redox electrolyte mediator.[164] As a result, several alternative electrolytes have been investigated, including the Co(II/III) polypyridyl complex, the ferrocenium/ferrocene (Fc/Fc+) couple, the Cu(I/II) complex, and thiolate/disulfide mediator.[181] In 2011, a Co$^{2+/3+}$ based DSC achieved an incredible efficiency of (12.3%) for a liquid electrolyte-based DSC with a high $V_{oc}$ of 0.935 V.[14] Currently, many related studies on Co$^{2+/3+}$ complex electrolytes have been performed. [183, 184] To date, the highest efficiency of a cobalt electrolyte based DSC is 14% using co-sensitizer dyes (the alkoxyisilyl anchor dye ADEKA-1 and the carboxy anchor organic dye LEG4).[16] Further optimization and improvement are required, however, to overcome the challenges associated with a Co$^{2+/3+}$ electrolyte based DSCs, including the slow diffusion into photoanode films and the fast recombination of photoelectrons with the oxidized redox species, along with instability concerns. [164]

Even though the highest efficiencies to date have been obtained in DSCs by employing cobalt based electrolyte, [16, 179] DSCs based on cobalt electrolyte suffer from high electron recombination from the TiO$_2$ conduction band to the oxidation state of cobalt electrolyte and insufficient electrolyte diffusion into the mesoporous TiO$_2$ photoanode. To reduce the charge recombination, a blocking layer has been employed on the TiO$_2$ surface.[185] Cobalt redox electrolyte requires large pores to ensure mass transport of the mediator into TiO$_2$ photoanode material. In 2013, Yella overcame the problem of mass transport in cobalt electrolyte based DSCs by increasing the TiO$_2$ pore size (up to 32 nm) and reducing the thickness of TiO$_2$ film.[14] Also, high porosity of the TiO$_2$ morphology combining macropores and mesopores has been successfully introduced to improve the penetration of bulky cobalt. [186] Thus, the pore size of TiO$_2$ nanoparticles with particle size of 20 nm is not efficient for ionic diffusion in cobalt electrolyte based DSC due to the high charge recombination rate. Therefore, the TiO$_2$ film porosity and thickness should be optimized to enhance the performance of cobalt-based DSCs. Combining a high surface area with improved charge-carrier transport and efficient light harvesting in a high-efficiency device is still a challenge.[23]

1.3 Structure of this thesis

In this thesis, each experimental results chapter is a publication. This thesis discusses the synthesis approaches to photoanode materials for DSCs and investigates some limitations related to the photoanode materials (TiO$_2$ and ZTO) that are not comprehensively addressed. These include the effects on DSC performance of
amorphous content, the nanostructure of the scattering particles in term of light scattering capability, the dye packing density in term of the isoelectric point, the paste preparation methods and the dye binding mechanism in terms of charge injection efficiency. Standard commercially available dyes, N719 as an organometallic dye or D149 as a metal-free organic dye, have been used with previously reported iodide based electrolytes. The performances of different configurations of photoanode materials, including a commercial TiO$_2$ product (P25), TiO$_2$ nanoparticles (Dyesol NR18-T) and scattering particles (Dyesol WER2-O), synthesized TiO$_2$, and Zn$_2$SnO$_4$ as an alternative photoanode materials have been investigated.

Regarding the changing requirements on photoanodes, in spite of massive amounts of research, there are some aspects that have been largely ignored due to focusing only on investigating the charge transfer rate, surface area, and porosity. However, the target applications have changed, and as such, the material requirements have changed. This thesis is important because it acknowledges these changes and their impact on requirements for photoanodes in future research (and hopefully, ultimately commercial products). Below is a highlight of each chapter that achieves these aims.

**Chapter 1:** This chapter presents the general background of DSCs, and the aims and objectives of this thesis. In addition, this chapter presents a brief literature review on recent progress on DSCs and the common challenges for and limitations of the photoanode materials.

**Chapter 2:** This chapter describes the characterization methods and equipment with a brief overview of their theoretical principles, as well as the materials synthesis and DSC device assembly.


This chapter also provides in depth understanding to the role of amorphous TiO$_2$ in the photovoltaic performance of DSCs. This is important, as P25 continues to be commonly used by researchers as a control material. Furthermore, the performance of DSCs and
other devices made using other synthesized TiO\textsubscript{2} nanoparticles may be impacted, as amorphous content may go unnoticed.

**Chapter 4:** This chapter reports on the synthesis of two types of mesoporous aggregated TiO\textsubscript{2} nanoparticles (sub-micron size, 300 nm and 700 nm), synthesized by a facile solvothermal approach, and their application as a scattering layer for DSCs. The DSC with these scattering layers incorporated on the top of commercial transparent TiO\textsubscript{2} nanoparticles (NR18-T), showed improved DSC performance compared to that with a commercial scattering layer (WER2-O) due to their higher dye loading and better light scattering capabilities. Two types of sub-micron sized particles were initially produced, using a range of acetic acid: ethanol ratios. These particles, TiO\textsubscript{2}-700 (1:5) and TiO\textsubscript{2}-300 (1:3), were suitable for application as scattering layers as they have high surface areas and good light scattering capability in the wavelength range of 300-800 nm. Fine tuning around the above ratios will allow for fine tuning of sizes, which may be considered as future optimization work. *This chapter is based on a publication (K. Al-Attafi, A. Nattestad, Y. Yamauchi, S.X. Dou, and J.H. Kim, Aggregated mesoporous nanoparticles for high surface area light scattering layer TiO\textsubscript{2} photoanodes in Dye-sensitized Solar Cells. Scientific Reports, 2017. 7(1): p. 10341).*

**Chapter 5:** This chapter shows the production of solvothermally synthesized anatase TiO\textsubscript{2} nanoparticles (SANP) by a facile solvothermal approach and their application as a photoanode, sensitized with either N719 or D149 for DSCs. The DSCs with SANP photoanode showed improved performance compared to the standard photoanodes, either with only commercial anatase nanoparticles (NR18-T) or with a commercial scattering layer (WER2-O) as well due to their higher dye loading and light scattering capabilities. *This chapter is based on a manuscript submitted to the journal Science and Technology of Advanced Materials. (K. Al-Attafi, A. Nattestad, H. Qutaish, L. K. Shrestha, Y. Yamauchi, S.X. Dou and J.H. Kim, Solvothermally synthesized anatase TiO\textsubscript{2} nanoparticles for photoanodes in dye-sensitized solar cell. Submitted to Science and Technology of Advanced Materials).*

**Chapter 6:** Typically, researchers first dry their synthesised nanoparticles (often calcining to get good crystallinity) before making a paste and using said paste to make films. This chapter compares the performances of DSCs using two TiO\textsubscript{2} paste preparation methods for solvothermally synthesized anatase nanoparticles. Dried solvothermally synthesized anatase TiO\textsubscript{2} nanoparticles resulted in a scattering photoanode film (SANP-S) and non-dried solvothermally synthesized anatase
nanoparticles resulted in a transparent photoanode film (SANP-T). SANP-T showed higher transparency and higher surface area with more uniform surface morphology than SANP-S. SANP-S showed higher efficiency than SANP-T, however, when sensitized with either N719 or D149 dye due to higher light scattering resulting from its aggregated nanoparticles. It was also the case that the differences in D149 sensitised devices were small, whereas they were more substantial for N719. *This chapter is based on a publication (K. Al-Attafi, A. Nattestad, S.X. Dou, and J.H. Kim, A Comparative Study of TiO$_2$ Paste Preparation Methods Using Solvothermally Synthesised Anatase Nanoparticles in Dye-Sensitised Solar Cells. Applied Sciences, 2019. 9(5): p. 979).*

**Chapter 7:** This chapter describes the synthesis of crystalline Zn$_2$SnO$_4$ (ZTO) nanoparticles, formed into cubic aggregate structures by a solvothermal reaction. Cubic aggregates of ZTO nanoparticles were applied as a photoanode for DSCs, using either a high extinction coefficient organic (D149) or an organometallic (N719) dye. ZTO|D149 showed a promising PCE of 4.9%, close to that of TiO$_2$|D149, but the same was not true for N719. This is due to low injection yields in the non-TiO$_2$ system, which appears to be tied to a different binding mechanism. This is a major issue for the prospects of ZTO and other ternary metal oxides, as many have been abandoned due to low PCE and IPCE when using N719. In addition, experiments were performed using ZTO and TiO$_2$ in aqueous dispersions to degrade Rhodamine B, suggesting that ZTO based DSCs should be more stable. This chapter can provide significant insights in the following areas: (1) the mechanism for the synthesis of cubic aggregated ZTO; (2) the mechanism of dye binding (N719 and D149) on TiO$_2$ and ZTO, and its impact on charge injection; (3) the performance of ZTO sensitized with organic dye; and (4) dye photodegradation. *This chapter is based on a publication (K. Al-Attafi, F.H. Jawdat, H. Qutaish, P. Hayes, A. Al-Keisy, K. Shim, Y. Yamauchi, S.X. Dou, A. Nattestad, and J.H. Kim, Cubic aggregates of Zn$_2$SnO$_4$ nanoparticles and their application in dye-sensitized solar cells. Nano Energy, 2019. 57: p. 202-213).*

**Chapter 8:** This chapter contains the overall conclusion of the thesis and some recommendations for the future work.
1.4 References


78. Zhang, Q., D. Myers, J. Lan, S.A. Jenekhe, and G. Cao, Applications of light scattering in dye-sensitized solar cells. Physical Chemistry Chemical Physics,


2 Experimental Methods

2.1 Introduction

The characterization methods are important for studying and understanding the physical and chemical properties of the synthesized materials. In this chapter, the equipment and experimental techniques that were used in the synthesis and characterization of photoanode materials are briefly described. The theoretical principles of the characterization techniques and the practical equations used to obtain the data are also described. In addition, the general steps in materials synthesis and DSC device assembly are included. The characterization method that were used in this thesis are: X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), surface area analysis (Brunauer-Emmett-Teller (BET)), UV-visible spectroscopy, Fourier transforms infrared spectroscopy (FTIR), zeta potential measurements, Mott-Schottky analysis, and cyclic voltammetry.

2.2 Synthesis procedure of photoanode materials

Simple and effective-cost solvothermal methods were used to design and synthesize nanoparticles to make efficient photoanode nanostructures for DSC application. The diagram below (Figure 2.1) describes the synthesis procedure steps for the synthesised materials in Chapters 4, 5, 6, and 7. The a photoanode material used in Chapter 3 (H-P25) was hydrothermally treated by our group (Yusuke Ide and Yusuke Yamauchi, World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS).[1]

![Flowchart of synthesis procedure used to prepare nanomaterials.](image)

Figure 2.1: Flowchart of synthesis procedure used to prepare nanomaterials.
A Teflon-lined stainless steel autoclave bomb, 45 mL (Parr Instrument Company) (Figure 2.2) was used to synthesize the nanomaterials with optimized heating temperatures. The solvothermal reaction conditions, including the time and temperature of the reaction, the ratios of solvents and starting materials, and the times for calcination and drying, are detailed in each chapter.

![Image of solvothermal reactor](image_url)

**Figure 2.2**: The solvothermal reactor used to synthesize the nanomaterials

### 2.3 Characterization methods

#### 2.3.1 X-Ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) is one of the important techniques, which is basically used to determine the crystal phase of the synthesized materials. In this technique, the specimen can be prepared either as a powder or as a film on a quartz substrate. The X-ray beams are reflected through the crystal planes according to Bragg’s law [2], and the resulting diffraction pattern or spectrum functions as a fingerprint for the material under study (Figure 2.3a).[3] XRD provides important fundamental information such as the phases of compositions and the nature of the crystal structure (amorphous, polycrystalline, or single crystal). It can also provide quantitative analysis such as the crystal size and the lattice constants of the crystal structure, and the amount of crystalline or amorphous content in the synthesized materials.[2]

The peaks in the diffraction pattern of the sample can be described by Bragg’s law, Equation (2-1);

\[ n\lambda = 2d_{hkl}\sin\theta \]  \hspace{1cm} \text{(2-1)}

Where \( \lambda \) is the wavelength of X-ray, \( d_{hkl} \) is the interplanar spacing of the crystalline plane with the corresponding Miller indices \( (hkl) \), and \( \theta \) is the diffraction angle.
The crystal size \((D_P)\) can be estimated using the Scherrer equation,

\[
D_P = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta}
\] ……….. (2-2)

Where, \(D_P\) is the crystal size, \(\beta_{1/2}\) is the full width at half maximum of a particular peak in the XRD pattern. The lattice constants for the cubic and tetragonal structures can be calculated using Equations (2-3) and (2-4), respectively.

\[
\frac{1}{d_{hkl}^2} = \frac{\hbar^2 + k^2 + l^2}{a^2} \quad \ldots \ldots \quad (2-3)
\]

\[
\frac{1}{d_{hkl}^2} = \frac{\hbar^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad \ldots \ldots \quad (2-4)
\]

The phase structure of synthesized materials was determined by using Bruker Advance or GBC MMA instruments with Cu Ka radiation (Figure 2.3b). The powders of synthesized materials were diluted with ethanol and placed on a quartz substrate after being dried. The XRD diffraction scan was carried out under the scan conditions of 20°-80° diffraction angles, 0.02° step size, 1°/min scan rate, 1.54 Å X-ray wavelength, and 40 kV and 25 mA power supply for the equipment.

![Figure 2.3: (a) Working principle of XRD, taken with permission from Andrei et.al [3]; (b) GBC MMA instrument used for structural phase analysis of synthesized materials.](image)

2.3.1.1 Reference Intensity Ratios (RIR) method

Reference Intensity Ratios (RIR) is a quantification method which can be used to approximately quantify the elemental ratios of the phases in mixed elemental materials or to quantify the amorphous and crystalline phases in the synthesized materials using X-ray powder analysis. For the synthesized materials containing amorphous content, it is not possible to quantify the amorphous phase in a direct way.\[4\] It can be quantified by using an internal or external reference material such as well crystalized \(\text{Al}_2\text{O}_3\) (Corundum). The reference material either can be mixed with the sample of material...
under study in a known weight ratio (1:1 weight ratio) or used as an external standard measured under the identical conditions. The internal reference method can be used to assess the approximate compositional weight ratio of the material. The actual amorphous or crystalline phase weight ratios in the material can be quantified subsequently from the difference in the weight ratio obtained from the integrated intensities of the sample, $I_S$(XRD), and the standard material (high crystallinity $\text{Al}_2\text{O}_3$, Corundum), $I_C$(XRD), obtained from the XRD traces in comparison with the standard calculated ratio obtained from the XRD database (Equation (2-5)).[4, 5]

$$\frac{I_S}{I_C} = \frac{I_S}{(\text{standard})} \text{ ... 2-5}$$

This method can only be used to quantify the compositional crystalline phase or the amorphous content for materials that have a known standard ratio, and it is not valid as a quantification method for newly synthesized materials. Also, the standard internal reference for quantitative analysis ($\text{Al}_2\text{O}_3$, Corundum) is expensive and may be not available in most laboratories.

2.3.1.2 Phase quantification method (Spike-In)

In this method, a well crystallized internal reference ($\text{Al}_2\text{O}_3$ or Si) can be mixed with the sample under study in a known weight ratio. The Spike-In technique is a phase quantification method to assess the amount of amorphous content in crystalline sample by comparing the initial mass of the sample ($S_{\text{mass}}$) and the crystalline standard reference mass ($R_{\text{mass}}$) with their values obtained from the integrated intensities of their XRD spectra, which are $S_{\text{XRD}}$ and $R_{\text{XRD}}$ respectively. Thus the amount of amorphous content in the sample can be quantified using Equations (2-6) or (2-7) for any synthesized material.[6-8]

If the sample contains amorphous content ($S_{\text{Amorphous}}$), the integrated intensities of the XRD peaks of the sample ($S_{\text{XRD}}$) will decrease compared to those of the standard reference ($R_{\text{XRD}}$). The decrease in the intensity of the crystalized internal reference ($R_{\text{XRD}}$) will affect the original weight percentage of the sample ($S_{\text{mass}}$) mixed with a certain percentage of the internal reference ($R_{\text{mass}}$). Thus, the mass ratio of the sample ($R_{\text{XRD}}$) will decrease with an increase in the internal reference ratio ($R_{\text{XRD}}$). This means that a decrease in $R_{\text{XRD}}$ will cause a decrease in the relative ratio of the standard internal reference ($R_{\text{mass}}$) / ($R_{\text{XRD}}$), which determines the amount of amorphous content in the sample ($S_{\text{Amorphous}}$).

$$S_{\text{Amorphous}}(\text{wt\%}) = 100 \text{ (wt\%)} - \left[ R_{\text{mass}}(\text{wt\%}) + \frac{R_{\text{mass}}(\text{wt\%})}{R_{\text{XRD}}(\text{wt\%})} \times S_{\text{XRD}}(\text{wt\%}) \right]$$
This method was used to quantify the amount of amorphous content in all the synthesized materials using XRD equipment (PW1130 model with Cu tube and DF3 Spellman generator). The measurements range was between 20-80° (measurements carried out by Prof. Brian Jones).

Software used for XRD analysis:

- MATCH (phase identification from XRD powder diffraction-version 2)
- Siroquant for quantification analysis-version 3
- VESTA (Visualization for Electronic and Structural Analysis-version 4)

### 2.3.2 Scanning Electron Microscopy (SEM)

An SEM is an electron microscope that provides low and high magnification, from 10 to $5 \times 10^5$ times with a resolution up to 10 nm, of three-dimensional images of surface topography using electrons rather than light. An electron can behave as a particle or a wave, and hence, the electron beam can be concentrated on the sample surface within a few microns.[9] The principle of SEM depends mainly on the focusing of a beam of electrons on the sample surface using electromagnetic lenses to scan the sample area to be studied under vacuum. The image is then formed by the collection and processing of the secondary backscattered electrons by a detector to produce a topographical image of the sample, as shown in Figure 2.4 a.[10, 11]

Field emission SEM, FE-SEM (JEOL JSM 7500FA), was used to determine the morphology and the particle size of the synthesized materials (Figure 2.4b). The powdered sample was diluted in ethanol and dropped onto a conductive carbon tape or Lacey/Carbon 200 Mesh, Copper (Electron Microscopy Sciences, Australia). After drying, the samples were coated with a 10 nm layer of platinum using the sputtering method (Edwards E302A) to avoid the effects of charge accumulation. The operation of SEM was set up as: accelerating voltage = 5 kV; current emission =10 µA; probe current= 8 mA; and the working distance = 8 mm).
Sputter coating is used to coat a sample of metal or semiconductor film or powders by bombarding with a metal such as gold, platinum, or aluminium by using high current through the metal substrate (cathode) under vacuum, resulting in the formation of a coating layer over the sample surface (anode).[12]

An Edwards Auto 306 instrument (Figure 2.5) was used to coat the samples for SEM measurements with 10 nm of platinum using the sputter coating method to avoid the effects of charge accumulation while collecting SEM images.
2.3.3 Transmission Electron Microscopy (TEM)

A TEM is an electronic microscope that is similar in principle to an SEM but with higher energy electrons up to 400 keV that are focused on the sample by electromagnetic lenses to enable the electrons to be transmitted through thin sections of the sample under vacuum, as shown in Figure 2.6 a.[13] The transmitted electron beam can be detected and forms a two-dimensional image showing the internal structure of the nanomaterial, including the porosity and the particle size, while the diffracted beams can be collected to produce diffraction patterns that are distinctive fingerprints for the crystal structure of materials. Selected area electron diffraction (SAED) patterns are created by a parallel electron beam focused on the selected sample area by a controllable aperture in the range of hundreds of nanometres. The diffraction patterns obtained from SAED can provide important information about the degree of crystallinity of the materials and the crystal properties such as the interplanar lattice spacings. The crystallographic nature of the sample can be determined from the diffraction pattern spots (bright parallel spots indicating a single crystal structure, bright spots in the form of separate rings indicating a polycrystalline structure, concentric rings without spots indicating an amorphous structure). [14] This information can be used to confirm the XRD analysis. TEM can also provide high resolution images (HRTEM) to view the actual interplanar distances or the lattice fringes of the crystal structure of the nanomaterials under study. The transmitted and diffracted electron beams can be collected to form low or high magnification images on a fluorescent screen using bright or dark field imaging modes respectively. Meanwhile, the transmitted and diffracted electron beams can be combined together to form an HRTEM image (Figure 2.6a).[13, 15, 16]

TEM (JEOL JEM-2010) (Figure 2.6 b) was used to study the nanostructure of the synthesised materials. Information about the particle size, the porosity, internal the structure and the distances between the lattice fringes of the synthesized nanomaterials were obtained using HRTEM images. The diffraction patterns of the synthesized materials were obtained by using SAED. The nanostructure analysis obtained from TEM was used along with that obtained from XRD analysis to confirm the phase structure of the synthesized materials.
The operation settings of JEOL JEM-2010 were set as: accelerating voltage = 200 keV; beam current emission = 105 µA; and column pressure > 5 × 10⁻⁵ Pa).

2.3.4 X-ray Photoelectron Spectroscopy (XPS)

XPS is an important technique that can be used to study the chemical composition of a wide range of compounds and elements and provides a quantitative analysis of their chemical structures. Typically, XPS is used to quantify the chemical structure of a sample by scanning the sample surface using a focused X-ray beam, with an average depth of analysis of about 2-5 nm. [17, 18] The quantified surface analysis obtained from XPS is important in photovoltaic and photocatalysis applications, where the materials’ surface compositions strongly affect their performance. The basic principle of this technique depends mainly on the excitation of electrons from the sample surface by X-rays, and the obtained spectrum of these photoexcited electrons is then analyzed in terms of their binding energy and intensity, which is considered as a fingerprint of their chemical composition (Figure 2.7 a). [19] The XPS technique is similar to energy-dispersive X-ray spectroscopy (EDS), which uses a focused X-ray beam on the sample, as shown in Figure (2.6). XPS uses secondary electrons excited from the sample surface, however, with depth of analysis around 2-5 nm, while EDS uses the finely focused electron beam with depth of analysis around 1-3 µm. Therefore, XPS is normally used for surface compositional analysis. [20]

A SPECS PHOIBOS 100 XPS analyser was used with a high-vacuum chamber with its pressure below 10⁻⁸ mbar. The X-ray beam was produced using an Al Kα radiation
source with energy of 1486.6 eV, a high voltage of 12 kV, and a power of 144 W. The XPS binding energy spectra of SANP and NR18-T samples were recorded at the pass energy of 20 eV with step width of 0.05-0.1 eV in the fixed analyser transmission mode. Full survey scans of the SANP and NR18-T samples were collected at the pass energy of 60 eV and step width of 0.5 eV. The Casa XPS software package was used for analysis of the XPS data.

Figure 2.7 b shows the XPS instrument used to examine the compositional structures of the synthesized SANP and commercial NR18-T samples discussed in Chapter 6.

Figure 2.7: (a) XPS working principle; (b) XPS instrument. [19]

2.3.5 Surface Area Analysis (BET)

Brunauer-Emmett-Teller (BET) analysis was used to calculate surface areas, based on adsorption-desorption isotherms of the synthesized materials. The specific surface area ($S_A$) of a nanomaterial can be evaluated by using automatic analyser or by collecting the isotherm for the adsorption and desorption of nitrogen gas (multilayer) and plotting it versus a relative pressure. The measured surface area (in m$^2$/g) provides useful information about the material’s capability to adsorb liquids or gases, which is important for many applications.[21]

Barrett-Joyner-Halenda (BJH) analysis is also used to estimate the pore volume or the pore area of nanoparticles using adsorption-desorption isotherms. The pore size distribution value depends on the particle size of the materials, but it doesn’t depend on the external sample area.[21]

- The average pore size distribution can be determined depending on the adsorption-desorption isotherm type, as shown in Figure 2.8.
- An average pore diameter greater than 50 nm (type II isotherms), indicates a macroporous structure of the materials.
- An average pore diameter between 2-50 nm (type IV isotherms) indicates a
mesoporous structure.

An average pore diameter less than 2 nm (type I isotherms) indicates a microporous structure.[22]

The specific surface area can be calculated from the adsorption-desorption isotherm of N\textsubscript{2} gas as a function of relative pressure (P/P\textsubscript{0}), using Equations (2-8) and (2-9): [21]

$$\frac{1}{V_g \left(\frac{P}{P_0} - 1\right)} = \frac{1}{V_m S} + \frac{S-1}{V_m S} \left(\frac{P}{P_0}\right) \ldots \ldots (2-8)$$

Then;

$$S_A (\text{total}) = \frac{V_m N_A}{M \cdot 22400} \ldots \ldots (2-9)$$

Where \(V_g\) is the volume of gas adsorbed at standard temperature and pressure (STP); \(V_m\) is the theoretical monolayer capacity of the gas; \(P/P_0\) is the relative pressure of the gas; \(S\) is a constant related to specific adsorbent/adsorbate interaction between the solid and the gas; \(M\) is the powder mass; and 22400 in mL represents the volume occupied by 1 mole of the adsorbent gas at STP.

Microtrac Belsorp-mini and Tri star 3020 nitrogen adsorption-desorption equipment were used to obtain the specific surface area and pore volume values (Figure 2.9 a,b).
Thermogravimetric analysis (TGA) is one of the methods utilized to provide complementary and supplementary characterization information on the materials. TGA measures the amount and rate of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. This method can analyze the material’s mass loss or gain due to decomposition, oxidation, or loss of volatiles. Loss of water, solvents, or residue remaining in synthesized materials can be determined by TGA measurements using a range of temperatures. [23]

TGA measurements were carried out on Mettler Toledo thermal analysis instrument (Figure 2.10) using 35 mg sample weight, 10 °C/min heating rate, and a 25-900 °C temperature range under air.

Figure 2.9: Specific surface area and pore size equipment (a) Microtrac BELSorp-mini II and; (b) Tri-Star 3020.

Figure 2.10: Mettler Toledo thermal analysis instrument used to carry out the TGA measurements.
2.3.7 Ultraviolet-visible spectrophotometer (UV-Vis)

UV-Vis absorption spectroscopy is a simple technique to measure and characterize the optical properties of materials in powder or film form, including their transmittance, absorbance, and reflectance. UV-Vis spectroscopy can provide useful qualitative or quantitative information regarding the optical parameters of the materials through analysis of the spectra obtained from measuring the light intensity as a function of wavelength.

A Shimadzu UV-Vis-1800 (Figure 2.11 a) was used for quantitative assessment of the amount of dye loading on the photoanode films (per projected area or volume) using the Beer-Lambert law (Equation (2-10)) and the dye loading quantification method.[24]

\[ A = \varepsilon_m c l \] ........... (2-10)

\( A \) is the absorption of the desorbed dye solution; \( \varepsilon_m \) is the molar extinction coefficient of the dye; \( c \) is the dye concentration; and \( l \) is the path length.

The dye packing per nm² was calculated using Equation (2-11):[25]

\[ \text{Dye packing} = \frac{S_A}{N_A \times \text{Dye loading per projected area}} \] ........... (2-11)

Where \( S_A (\text{nm}^{-2}) = S_A (\text{nm}^2 \text{ g}^{-1}) \times V (\text{nm}^{-3}) \times \rho (\text{g nm}^{-3}) \) ........... (2-12)

\( V \) is the volume; \( \rho \) is the density, and \( N_A \) is Avogadro number’s \( (6.022140857(74) \times 10^{23} \text{ mol}^{-1}) \)

A Shimadzu UV-Vis-3600 (Figure 2.11 b) with an integrated sphere (ISR-3100) was used to measure the transmittance and the diffuse reflection, and to calculate the optical band gap using Tauc plots for all the synthesized materials using Equation (2-13).

\[ (a h \nu)^{1/r} = \gamma (h \nu - E_g (\text{metal oxide})) \] ........... (2-13)

\( \alpha \) is the absorbance coefficient; \( h \nu \) is the photon energy; \( E_g (\text{metal oxide}) \) is the Optical energy gap; \( r = 2 \) for indirect allowed transitions; and \( \gamma \) is a constant.

At \( (a h \nu)^{1/2} = 0 \) by extrapolating the straight line after correction for the light scattering effect, the intercept with the x-axis represents the optical band gap of the indirect allowed transitions \( (E_g ) \), which can be obtained using Equation (2-14),

\[ E_g (\text{metal oxide}) = h \nu \] ........... (2-14)
Fourier Transform Infrared Spectroscopy (FTIR)

An FTIR spectrometer is an important instrument that is used to identify organic compounds with polar chemical bonds, for example, -OH, -CH, -NH, etc., with strong dipoles that have powerful charge separation. In this technique, electromagnetic radiation in the infrared region of the spectrum is used in order to study the vibration modes of molecules in materials for bending, stretching, etc., as the energy that has been absorbed is used to modify their levels of energy.

FTIR can be used to determine the existence of a specific functional group in a certain organic compound. There is a unique vibrational energy for each functional group, and therefore, the IR spectra may be considered as fingerprints.

The IR technique that is used extensively to examine the surface properties of materials as thin film instead of their bulk properties is known as attenuated total reflectance (ATR). FTIR gives molecular information through collecting the transmitted IR spectrum, while the ATR identifies the surface chemical properties through collecting the reflected IR at the surface. This method is more efficient and provides accurate outcomes and a low signal to noise ratio without using a KBr disk reference. In addition, a small amount of sample, around 0.5-1 micron in size, is required for this analysis.[26]

A Shimadzu IR prestige-21 and its ATR measurement accessory (Figure 2.12 a, b) were used to collect ATR-IR spectra of dyed/undyed TiO₂ and ZTO films (3 µm thickness) and for N719 and D149 dye powders.

Figure 2.11: (a) Shimadzu UV-Vis -1800 and (b) Shimadzu UV-Vis -3600 used to measure the optical properties of the synthesised materials.
Raman spectroscopy is a simple technique to identify the chemical composition, polymorph phase, impurity, contamination, degree of crystallinity of a material, and the molecular bond interactions. This information can be obtained mainly from the interaction of the laser light with the chemical bonds of the material. In Raman spectroscopy, a laser source with high intensity can be used to scan and identify the chemical structure of materials.[27] Most of the laser light is scattered by the molecules of the material with the same wavelength as the incident laser according to Rayleigh scattering, while a minimal amount of laser light is scattered with different wavelengths from the laser source according to Raman scattering, which depends on the chemical nature of the material. A Raman spectrum has spectral peaks that represent the relationship between the incident laser light intensity and the inelastically scattered light according to the Raman scattering, as shown in Figure 2.13.a.[28] The peak positions of this spectrum correspond to specific vibrations of individual or group molecular bonds identifying the chemical structure of materials.[29, 30]

A Horiba Jobin Yvon HR800 confocal Raman spectrometer with a 632.8 nm laser (Figure 2.13 b) was used to measure the Raman shift of material films (3 μm) (in Chapter 5 and chapter 6). The Raman spectra were measured in the wavenumber range of 100-800 cm\(^{-1}\).

**Figure 2.12:** (a) Shimadzu IR prestige-21 and; (b) accessory part used for ATR measurements of ZTO and TiO\(_2\) dyed films.
2.3.10 Film thickness measurements

A surface profiler uses the contact or stylus profilometry technique to measure the thickness of thin or thick films. It can provide accurate thickness measurements of the deposited films and also can provide two-dimensional images of the surface roughness and topography, which enable us to detect the defects on the film materials. It also provides cost-effective film thickness measurements and analysis.[31]

A Veeco Dektak 150 Surface Profiler (Figure 2.14) was used for the film thickness measurements on photoanodes for DSCs.

Figure 2.13: (a) Raman basic principles [27]; (b) Raman spectroscopy instrument.

Figure 2.14: Veeco Dektak 150 profilometer used for film thickness measurements.
2.3.11 Zeta potential measurements

The isoelectric point (IEP) is a critical factor that affects the surface properties of the metal oxide. The IEP is basically the value of pH at which no net electric charge is carried by the metal oxide surface (i.e. IEP is the point where the net zeta potential on the surface is equal to zero). The zeta potential is defined as the electrokinetic potential of the dispersed particles in a solution (e.g. water), which represents the difference in potential between the total charges on the particle surfaces and the total charge of the surrounding solution (slipping plane). There are various factors that influence the zeta potential, such as the chemical configuration of the surrounding solvent, the experimental pH value, and the ions inside the metal oxides.[32] A higher IEP of metal oxide nanoparticles indicates higher positive surface charge, while a lower IEP indicates a lower positive surface charge.[33, 34] The IEP value of nanoparticles can be determined experimentally by calculating the zeta potential in their dispersed solution (Figure 2.15 a, b).[35, 36] It was found that when the IEP is high, the dye loading amount is also high, which suggests that it is mainly the dye loading at the dye-metal oxide interface that is influenced by the IEP.[37]

A Zetasizer Nano-ZS (Figure 2.16) was used to measure the zeta potentials of 0.01 M of TiO₂ or ZTO in aqueous solutions with different pH values (2-12), which were adjusted using 0.25 M NaOH and 35-37 vol% HCl.

Figure 2.15: (a) Zeta potential principle, taken with permission from Li et al. [35]; (b) Isoelectric point IEP measurements. [36]
2.3.12 Mott-Schottky measurements

During an interaction of a semiconductor (e.g. n-type) with a redox electrolyte, when the Fermi level of the semiconductor has greater energy ($E_F$) than that of the redox electrolyte, it is possible to attain an equilibrium by transferring electrons from the semiconductor to the redox electrolyte resulting in equal Fermi levels for the two phases.[38] The Fermi energy is the highest energy level occupied by electrons at absolute zero temperature, while the Fermi level has a 50% possibility of occupancy of electrons with respect to the Fermi energy level at finite temperature.[39] This leads to positive charging of the semiconductor, and as the density of the semiconductor carriers is extremely low compared to that within the solution, there is counterbalancing of the diffuse charge in the semiconductor by the charges in the electrolyte. When the semiconductor potential is altered unnaturally by using a potentiostat, the Fermi levels of the semiconductor and the redox couple become different, and this modifies the degree of band bending due to decrease in the electron density within the semiconductor, on the basis of the voltage that has been applied. When band bending or charge depletion is not exhibited by the applied voltage, then the semiconductor has a flat-band potential ($E_{fb}$), as shown in Figure 2.17 a, b.[39, 40]

The $E_{fb}$ of the semiconductor can be obtained from the Mott-Schottky equation (2-15).

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 A^2 e N_d} \left( E - E_{fb} - \frac{k_B T}{e} \right) \quad \ldots (2-15)$$

$C$ is the capacitance; $\varepsilon$ is the dielectric constant; $\varepsilon_0$ is the vacuum permittivity; $A$ is the area; $e$ is the electron charge; $N_d$ is the donor charge density; $E$ is the applied potential; $E_{fb}$ is the flat band potential; $k_B$ is the Boltzmann constant; and $T$ is the absolute
By plotting \((1/c^2)\) versus applied potential \((E)\), the intercept of the straight line with \((E)\) represents the flat band potential \((E_{fb})\). The donor density \((N_d)\) in the dark can be also calculated from the slope using the dielectric constant \((\varepsilon)\) and the area \((A)\) [39], as shown in Figure 2.17 c.

Figure 2.17: The energy band diagram of the TiO\(_2\)/electrolyte interface: (a) applied voltage = \(E_{fb}\); (b) applied voltage > \(E_{fb}\) [40]; (c) Mott-Schottky plot.

A VSP-300 potentiostat workstation (Biologic Science Instruments) was used to carry out Mott-Schottky measurements (conducted at 1 kHz) to determine the flat band potential of TiO\(_2\) and ZTO films (3 µm) deposited on FTO glass. 0.1 M Na\(_2\)SO\(_4\) was used as the electrolyte, saturated calomel electrode (SCE) as the reference electrode, and a platinum counter electrode (Figure 2.18).

Figure 2.18: VSP-300 potentiostat workstation used to carry out Mott-Schottky measurements of TiO\(_2\) and ZTO films.
2.3.13 Cyclic Voltammetry measurements (CV)

The cyclic voltammetry technique is a common electrochemical method that can be used to determine the electrolyte potential or the oxidisation potential of dyes in DSCs.[41] Characterization is normally carried out on dye molecules that are immersed in an inert non-redox active liquid, but when the dye is bound to a metal oxide surface, there can be a decrease in its reduction and oxidation potentials.[42] Methods such as differential pulse voltammetry and square wave voltammetry can be used to obtain better resolution. (They can be used to measure many more things, but these are two examples which have direct relevance to this thesis to avoid capacitive artefacts.) The CV measurement method was used to examine the energy levels of dyes employed in DSCs.

The oxidation and reduction potentials were measured using an eDAQ potentiostat system controlled by eDAQ EChem software (Figure 2.19), which were then approximated to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of N719 and D149 dyes. The oxidation potential values ($E_{ox}$) of N719 and D149 were obtained from CV measurements. A pseudo reference setup containing Ag/Ag$^+$ as a quasi-reference electrode and Pt mesh as a counter electrode was used, which was then calibrated against 1 mM ferrocene /ferrocenium ($F_c/F_{c^+}$) as an inert internal reference electrolyte to determine the oxidation potential ($E_{ox}$) for N719 and D149 dyes on TiO$_2$ or ZTO films (3 μm thickness) as a working electrode deposited on FTO.[43] 0.1 M tetrabutylammonium perchlorate in anhydrous acetonitrile was used as supporting electrolyte. The solution in the system was degassed prior to the CV measurements.

HOMO of dye (V) = $E_{ox} - E_{ox} (F_c/F_{c^+})$ ………. (2-16)

Using the onset of the absorption of the dyed film, the optical band gap of a dye can be calculated as,

$E_g (eV) = 1240/\lambda$ (nm) ………. (2-17)

Then, the LUMO values of dyes can be calculated as, [43]

LUMO of dye (eV) = [HOMO (V) + 5.13] $E_g$ (eV ………. (2-18)
2.4 Preparation of photoanode (working electrode) and device assembly

Screen printing and doctor blade methods are commonly used to fabricate photoanode films for DSCs using the procedure. These methods can be simply used to fabricate large area films with lower production cost. The screen printing method is standard technique to fabricate high efficiency DSCs while the doctor blade method is used to control or optimise the film thickness manually, as shown in Figure 2.20 a,b and Figure 2.21.[44]

**Figure 2.19:** eDAQ potentiostat system used for CV measurements.

**Figure 2.20:** Screen printer (Keywell-500FH, Taiwan) and doctor blade method used to fabricate the photoanode films.
In order to study the operating functions of a DSC and the interactions of its components, it is important to comprehend the characterization of the DSC as a whole system, along with investigations of individual components. The main characterization techniques applied in this thesis are photocurrent-voltage measurements (J-V), Incident photon to current conversion efficiency spectroscopy (IPCE), and electrochemical impedance spectroscopy (EIS). Information on these techniques are discussed briefly in the following sections.
2.5.1 Photocurrent density-voltage (J-V) measurements

J-V measurements were carried out using a solar simulator with an AM1.5 filter; set to 1 sun (100 mW·cm$^{-2}$, PV Measurements, Colorado) or an Oriel solar simulator (Figure 2.22). The J-V measurement process included applying a bias; allowing the device to equilibrate; measuring the current; dividing the measured current by the photoanode area; and repeating the measurement in dark/light. The measurement settings were set as voltage range (0.02-1 V), voltage step (0.005 V), cell area (0.16 cm$^2$), mask area (0.25 cm$^2$), settling time (0.04 s), current compliance (0.1 A), and maximum light power (100 mW cm$^{-2}$). Four or at least three devices were used for each condition, with average values of PCE, $V_{oc}$, $J_{sc}$, and FF reported ±1 standard deviation.

Figure 2.22: (a) Colorado (b) Keithley 2400 solar simulators used to measure J-V response for DSC devices.

2.5.2 Incident photon to current conversion efficiency (IPCE)

All the work in this thesis used liquid state electrolytes and dyes in DSCs, which have been shown to have a linear current response to light intensity, at least up to 1 sun.

A QEX10 system from PV Measurements (Figure 2.23) was used to measure the IPCE for DSC devices by sequentially measuring the IPCE across a range of wavelengths (300-800 nm) in 5 nm steps using the DC mode. The IPCEs were measured for four or at least three devices for each configuration, and then the IPCEs were plotted using the representative devices.
2.5.2 Electrochemical impedance spectroscopy (EIS)

EIS measurements can add more depth to our understanding of charge transport or recombination kinetics provided by steady-state I-V measurements on DSCs (usually performed under open circuit conditions). EIS is a useful type of electrochemical spectroscopy, which is essentially required to comprehend the mechanism of charge transport in a DSC system.

EIS is widely used, including for DSCs, where it involves perturbing the potential given to the DSC system, producing a sinusoidal wave of alternating potential, and the corresponding sinusoidal alternating current is determined with respect to a change in the modulation frequency.[42] The ratio of voltage to current in the frequency domain is known as the impedance, and it includes real as well as imaginary parts. There is a real value of the impedance of a resistor, which is independent of the frequency. In contrast, there are imaginary values of the impedances of the capacitor and inductor, which change with frequency.

It is possible to consider a DSC electrically as a mix of resistances and capacitances. Hence, EIS helps in recognizing the resistors and capacitors (also a Warburg diffusion element) at the component interfaces in the DSC (sensitized working electrode/electrolyte or electrolyte/counter electrode) while the charge transfer process is in progress (i.e. it relies on the transfer rate being on the same time scale as the perturbation). The equivalent circuit model (Figure 2.24 a) was used to study the charge transport and recombination losses in the DSC devices based on an optimised photoanode. In the equivalent circuit, $R_S$ is the series resistance, including the sheet resistance of the charge collector (FTO) and the device connection resistance, $R_{ct1}$ and
Rct2 are the charge transfer resistances, and \((CPE_1)\) and \((CPE_2)\) are their corresponding constant phase elements at the counter electrode/electrolyte and photoanode/electrolyte interfaces, respectively. \(CPE_2\) also represents the chemical capacitance \((C_p)\) of the photoanode. [42, 45].

\(R_S, R_{ct1}, R_{ct2}, CPE_1,\) and \(CPE_2\) can be calculated from the Nyquist plot, while the electron recombination lifetime \((\tau_n)\) and the electron transfer lifetime \((\tau_d)\) can be obtained from the corresponding Bode plot using the equation:

\[
\tau_n = \frac{1}{2\pi f_{max}} \quad \ldots \ldots \quad (2-19)
\]

Where, \(\tau_n\) is the electron recombination lifetime; \(f_{max}\) represents the frequencies at the local impedance maxima \((f_{max}, \text{low frequencies})\).

\[
\tau_d = \frac{1}{2\pi f'_{max}} \quad \ldots \ldots \quad (2-20)
\]

Where, \(\tau_d\) is the electron transit lifetime, and \(f'_{max}\) represents the frequencies at the local impedance maxima \((f_{max}, \text{high frequencies})\).

The lower bound estimation of the collection efficiency \((\phi_{cc})\) can be calculated using the following equation:[46]

\[
\phi_{cc} = 1 - \frac{\tau_d}{\tau_n} \quad \ldots \ldots \quad (2-21)
\]

EIS can be applied under different conditions for the DSC (dark, light, at \(V_{oc}\) or \(V_{max}\), or other bias) as well as for modelling and reporting in different ways.

A Reference 600 Potentiostat (GAMRY Instruments) (Figure 2.24 b) was used for electrochemical impedance spectroscopy measurements (EIS) which were carried out on DSCs containing different photoanodes under 1 sun illumination at \(V_{oc}\) in the frequency range of \(0.1–10^6\) Hz and AC voltage of 10 mV. These conditions were applied to investigate the charge recombination kinetics in the DSC under simulated sunlight conditions as in real operation, in order to determine the recombination losses of electrons photogenerated by the dye, and the charge density and chemical capacity of the photoanode materials.
2.6 Photocatalytic degradation measurements of organic dye

Photocatalytic measurement is a common technique that is widely used to determine the photoactivity of materials, depending on the reactions which take place subsequently between the simulated sunlight (air mass 1.5 AM filter, 1 sun illumination) and the energy gaps of these materials. Standard dyes such as Methyl blue or Rodamine B are usually used to measure the degree of photoactivity of the materials dispersed in an aqueous solution of the standard dye by measuring the photodegradation of the dye due to the effective charge separation of the materials.[47]

Simulated solar illumination (Oriel LCS-100, 100 mW/cm²) (Figure 2.25) was used to measure the photocatalytic degradation of organic dye on ZTO and TiO₂ materials dispersed in an aqueous solution of Rhodamine B dye. The experiments were run three times across the full solar range (i.e. UV, Vis, and near infrared (NIR)) to obtain the average values and the standard deviation for the absorption spectra and degradation rate.
2.7 References


15. *Basic Principles of Transmission Electron Microscopy* 18/09/2018; Available from: [http://www.hk-phy.org/atomic_world/tem/tem02_e.html](http://www.hk-phy.org/atomic_world/tem/tem02_e.html).


18. *X-Ray Photoelectron Spectroscopy in Analysis of Surfaces* Update based on the


Chapter 3

3 The effect of amorphous TiO$_2$ in P25 on Dye-Sensitized Solar Cell performance

This chapter is based on a published work [K. Al-Attafi, A. Nattestad, Q. Wu, Y. Ide, Y. Yamauchi, S.X. Dou, and J.H. Kim, The effect of amorphous TiO$_2$ in P25 on dye-sensitized solar cell performance. Chemical Communications, 2018. 54(4): p. 381-384], with contributions of other co-authors as follows: K.Al-Attafi, A. Nattestad, and J. Kim designed experiments. K. Al-Attafi performed TEM, SEM, XRD and DSC measurements and wrote the manuscript. K. Al-Attafi and Q. Wu interpreted and revised the EIS measurements. K. Al-Attafi and Y. Yamauchi performed and analyzed BET measurements. Y. Ide treated P25 nanoparticles and quantified the amorphous content. K.Al-Attafi, A.Nattestad, and J. Kim. Analyzed the data and revised the manuscript. A.Nattestad, J. Kim, and S. Dou supervised the work. All authors discussed the results and contributed to revisions.

P25 is one of the most widely used forms of Titanium (IV) oxide (TiO$_2$), including being routinely utilized in DSCs, where it is often employed as a control, in spite of its poorly defined nature and the typically low resulting device efficiencies (or possibly because of this). Work by Park in 2000 [1] and later by Lin et al.[2] suggested that the rutile component might not be to blame for this, as has often been claimed. Recently it has been observed that P25 can contain quite a sizable amorphous content.[3] A method to selectively remove this non-crystalline material has been developed by our collaborator,[4] allowing for scrutiny of the role this amorphous material plays. In this Chapter, the effect of amorphous TiO$_2$ in P25 on DSC performance was investigated. Hydrothermally treated P25 (H-P25) was expected to show higher dye loading and better charge injection in DSCs compared to untreated P25. Devices based on H-P25 showed higher efficiency compared to the as-received P25 material, realizing 5.3% and 3.2% respectively. More importantly, this reveals important information about the detrimental effect of amorphous TiO$_2$ on DSC performance, with broader implications, as most researchers do not actively examine their synthesized materials for the presence of an amorphous component.
3.1 Introduction

P25 has been adopted as a cheap source of TiO$_2$ nanoparticle and has been widely used in photocatalysis and DSCs applications.[5, 6] As an integral component of a DSC, the photoanode provides a high surface area for adsorption of the sensitizer and serves as a medium for transferring electrons injected from the sensitizer to the charge collector and is commonly made of TiO$_2$ nanoparticles.[7] The crystal structure of TiO$_2$ is, therefore, an important factor to be considered in designing efficient photoanodes for DSCs.[8] P25 is a commonly employed control and understanding its chemistry is important and may have broader implications for DSCs and in other technologies (such as catalysis, batteries, and super-capacitors, among others).

Even though P25 has been widely applied in photoanodes for DSC,[9] it is well known for its comparatively poor performance. The poor performance has often been attributed to the rutile component, with the conduction band edge of rutile being below that of anatase phase by ∼0.2 V. As a first approximation, this could be expected to affect the open circuit value ($V_{oc}$). Anatase is usually the preferred form of TiO$_2$, with record efficiencies all attained using this crystal phase.[10, 11] It has however been seen that DSCs based on rutile photoanodes, display similar ($V_{oc}$) and fill factors (FF) to those obtained using anatase TiO$_2$. The short circuit current densities ($J_{sc}$) of rutile based devices are however typically lower,[2, 12] with Park reporting that the DSCs based on rutile photoanodes have $J_{sc}$ values of around 70% of devices based on the anatase photoanode. This was attributed to the lower dye loading in the rutile sample. More recently, our group reported the application of high surface area, hierarchically assembled, 3D rutile nanorod assemblies as photoanodes for DSC, utilizing a high extinction coefficient organic dye (D149) to realize a similar performance to that of anatase photoanodes with a similar total surface area (5.5% versus 5.8% efficiency).[2]

The difference in $J_{sc}$ values here was only 13% with the FF and $V_{oc}$ again being close to one another. In light of these studies, which suggest that the solar-to-electric conversion efficiency is not inherently low for rutile based DSCs, the question remains as to why P25 shows such poor performance in DSCs and what the broader implications are.

Some studies have shown that the electronic structure of amorphous TiO$_2$ is similar to that of anatase and rutile phases.[13, 14] On the other hand, amorphous TiO$_2$ has localized trap states near both the valence and conduction band edges, due to disordered positions of O and Ti atoms, resulting from network distortions[13, 14]. Studies have also shown that the adsorption of dye molecules on TiO$_2$ surfaces is strongly correlated
to surface facets. Particles without well-defined facets are more likely to show worse surface dye packing, also resulting in an exposed surface, which is susceptible to charge recombination reactions.[15-17] Faceted surfaces can also enhance light scattering which again contributes to improving the light harvesting efficiency.[18] It is seen that amorphous TiO$_2$ leads to a low dye packing density compared to other phases.[19, 20] Thus, it is postulated that removing this amorphous TiO$_2$ will improve DSC performance.

It has been observed that P25 has a substantial amorphous content [21] (which cannot be observed directly from XRD diffraction patterns). Recently a hydrothermal treatment process was developed by our group to remove this amorphous material by selective dissolution and recrystallization.[22] This modified TiO$_2$ material showed a remarkably enhanced charge separation and photocatalytic efficiency as a result of the removal of recombination sites/barriers for charge separation. Getting rid of this amorphous content, while maintaining the high surface area, is, however, a challenge which needs to be considered. In another study, Kurian used a water treatment to convert an amorphous TiO$_2$ layer (15 nm), deposited by atomic layer deposition, to crystalline anatase nanoparticles, which resulted in improving the electron transport in TiO$_2$ nanotubes. These were then used as a photoanode in a DSC,[23] where the PCE was 3.9% and 4.9% for untreated and treated photoanode respectively.

Herein, we use the recently developed amorphous content free analogue of P25 (H-P25) in a photoanode to investigate the effect of amorphous TiO$_2$ on DSC performance, through comparison with devices based on P25 (N.B. TiCl$_4$ surface treatment is explicitly omitted from the photoanode preparation). Significantly, DSC devices based on H-P25 photoanode, sensitized with N719, showed a power conversion efficiency (PCE) of 5.3%, compared to 3.2% for the untreated P25 photoanode.
3.2 Experimental

3.2.1 Synthesis of modified P25 nanoparticles

P25 (supplied by Nippon Aerosil), tetra propylammonium hydroxide (TPA, ca. 40% in water, purchased from Tokyo Chemical Industry Co., Ltd.), water and ammonium fluoride (NH₄F, purchased from Kanto Chemical Co., Inc.) were mixed at a molar ratio of P25:TPA:H₂O:NH₄F = 1:0.8:5:0.2 in a Teflon-lined stainless-steel autoclave and the mixture treated at 443 K for seven days. The product was recovered by centrifugation and repeatedly washed with water.

3.2.2 Preparation of H-P25 and P25 photoanodes and DSC assembly

H-P25 and P25 photoanodes were prepared as follows: pastes of each material was made by grinding 1 g of either treated or untreated P25 powder rigorously with (25 ml) absolute ethanol, (1 ml) distilled water, (0.2 ml) acetic acid. After that, 5 g of a binder solution (10 wt% ethyl cellulose in ethanol) and 5 g terpinol were added to the mixture. The formed slurry was stirred and then sonicated for an hour. Following this, the ethanol, water, and acetic acid were evaporated using a rotary evaporator.

FTO glass was sonicated three times (20 minutes) in each of soapy water, acetone, and ethanol. A dense TiO₂ blocking layer was deposited on FTO substrate by spray pyrolysis of a solution of diluted titanium diisopropoxide bis (acetylacetonate) (75% in isopropanol) (Aldrich), in absolute ethanol (1:9 v/v). To form the mesoporous structure of photoanodes, H-P25 and P25 pastes were cast in thickness (11.5 ± 0.3 µm) using a Dr Blade method on pre-cleaned FTO glass. The deposited photoanodes were sintered using sequential annealing process to remove organic components. After cooling down to 110 °C, photoanodes were sensitized with a commercial organometalic dye (N719 Solaronix), by immersion in a 0.5 mM dye bath using a mixture of solvents (1:1) acetonitrile (HPLC, Lab-scan):tert-butanol (LR, Ajax Chemicals). After 24 hours dying time, the films were rinsed with acetonitrile and dried. Another a piece of FTO glass, with a Ø=1 mm port, was coated with a drop of (10 mM) platinic acid solution (H₂PtCl₆) in ethanol which was thermally decomposed by heating at 400 °C for 20 min to form the counter electrode. Sensitized working electrode and platinum counter electrode were sealed together using a spacer of 25 µm Surlyn (Solaronix) by a hot-press. A liquid electrolyte consisting of acetonitrile and valeronitrile [85:15 vol%] with 30 mM iodine (I₂), 0.5 M 4 tertbutyl pyridine (4-tBP), 0.6M 1-butyl-3-methylimidazolium iodide (BMII) and 0.1 M guanidinium thiocyanate (GuSCN) was introduced between the sealed working and counter electrodes using a vacuum back-
filling technique. Finally, a piece of Aluminum foil backed Surlyn was used to seal counter electrode port.

3.2.3 Characterizations
X-ray diffraction patterns of the crystalline structure of treated and untreated P25 were examined by using RIGAKU Smart Lab in range (2° - 40°) using 1°/min scan speed. The surface morphologies and internal structure were obtained transmittance electron microscopy (JEOL JEM-6500F). Brunauer-Emmet-Teller (BET) measurements including specific surface area and adsorption-desorption data, were conducted using (MicrotracBel Belsorp-mini). Optical properties of photoanodes including (absorption, transmittance, the diffuse reflection) was obtained using Ultraviolet-Visible-NIR light spectroscopy (Shimadzu UV-3600) with an integrating sphere attachment. Dye-sensitized H-P25 and P25 photoanodes immersed for (5 minutes) into a (0.1 M) NaOH solution (mixed solvent water and ethanol 1:1 v/v) and the amount of desorbed dye molecules was quantified by measuring the absorption spectrum of desorbed dye solution (on three films for each) by photospectroscopy (Shimadzu UV-1800). Film thicknesses were measured using a Surface Profiler (Veeco Dektak 150). Photocurrent density-voltage (J-V) was measured using a PV Measurements (Colorado) solar simulator with AM1.5 filter; set to 1 sun (100 mW/cm²). A QEX10 system, also from PV Measurements, was used for Incident Photon to charge carrier Conversion Efficiency (IPCE) measurements. Electrochemical impedance spectroscopy (EIS) including Nyquist and Bode plots was measured using a Reference 600 Potential/Galvanostat/ZRA (GAMRY INSTRUMENTS) under 1 sun illumination and at Voc in the frequency range of 0.1 – 106 Hz using 10 mV perturbation.

3.3 Results and Discussion
Transmission electron microscope (TEM) images show that the primary particle size and shape of H-P25 were similar to those of P25 (Figure 3.1 a,b). On the other hand, H-P25 has a large number of extended interfaces compared to P25, as indicated by the yellow arrows in Figures 3.1 a,b. The number of interfaces between crystalline particles was estimated for H-P25 and P25 by counting the crystalline particles interfaces across multiple (>3) high-resolution TEM images (HRTEM). Enlarged TEM images (HRTEM) for P25 and H-P25 (as shown in Figure 3.1 c,d) show a significant decrease in the amorphous material after treatment. For P25 the charge transport will occur either through amorphous TiO2 and/or longer routes. The TEM and HRTEM images show that the amorphous component removed during the hydrothermal treatment was
converted to acrystalline material. As a result, H-P25 undergoes more aggregation and has more crystalline particle interfaces compared to P25 (see reference 19). In addition to the crystal phase changes, the morphology is expected to impact the performance. The surface area of H-P25, obtained from nitrogen isotherm measurements, is around 20% lower than that of P25 (47 m$^2$ g$^{-1}$, compared to 57 m$^2$ g$^{-1}$, as shown in Figure 3.1e and Table 3.1). The lower surface area of H-P25 can be attributed to increased interparticle contact and a greater degree of agglomeration resulting from the redeposition of the dissolved amorphous TiO$_2$. The inset in Figure 3.1e shows that the pore size distribution of H-P25 is significantly changed after removal of the amorphous content, with the average size being substantially larger than that of P25. This leads to a slightly lower porosity than that of P25 (Table 3.1). XRD analysis shows that diffraction peaks related to the anatase and rutile in H-P25 were more intense, indicating higher crystallinity (or larger amount), than for P25 (Figure 3.1 f). The compositional analysis was reported previously, showing P25 to be 76 wt% anatase:13 wt% rutile:11 wt% amorphous and H-P25 to be 81:19:0.[22]

**Table 3.1:** Porosity and Specific surface area data for P25 and H-P25

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)$^a$</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>71</td>
<td>57</td>
</tr>
<tr>
<td>H-P25</td>
<td>63</td>
<td>47</td>
</tr>
</tbody>
</table>
Figure 3.1: TEM images (a) and (b) and HTEM images (c) and (d) of P25 and H-P25 respectively; (e) N$_2$ adsorption/desorption isotherms; (f) XRD patterns. (*) indicates the diffraction peak of Al$_2$O$_3$, used as a standard for XRD normalization.
The dye loading was quantified using a desorption method to compare the light harvesting efficiencies for both photoanodes (Figure 3.2 and Table 3.2). In spite of the lower specific surface area of the materials, which is explained by the substantially higher packing density of these dyes on H-P25 compared to P25 (30±1 and 24±1 nmol cm$^{-2}$) and (61±1.5 and 48±2.3 µmol cm$^{-3}$) respectively. This higher density of the dyes is attributed to more sites being available for dye binding on faceted surfaces, as opposed to amorphous (see Figure 3.3).

![Absorption spectra of desorbed dye solution of N719 dye-sensitized H-P25 and P25 photoanodes (two films for each).](image)

**Figure 3.2:** Absorption spectra of desorbed dye solution of N719 dye-sensitized H-P25 and P25 photoanodes (two films for each).

**Table 3.2:** Dye loading measurements of H-P25 and P25 sensitized with N719 dye, (two films for each, thickness=5.5 ±0.25 µm, Area=1 cm$^2$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of dye (nmol cm$^{-2}$)</th>
<th>Amount of dye (µmol cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25.1</td>
<td>25</td>
<td>49.5</td>
</tr>
<tr>
<td>P25.2</td>
<td>23</td>
<td>46.3</td>
</tr>
<tr>
<td>H-P25.1</td>
<td>31</td>
<td>62.0</td>
</tr>
<tr>
<td>H-P25.2</td>
<td>30</td>
<td>59.9</td>
</tr>
</tbody>
</table>
The current-voltage responses of DSC devices based on either H-P25 or P25 photoanodes are plotted as shown in Figure 3.4 a. The key photovoltaic parameters are given in Table 3.3. Three devices for each were made (Table 3.4). DSCs incorporating H-P25 photoanodes exhibited photocurrent conversion efficiencies of 5.3 ± 0.5%, substantially higher than those of the P25 based devices 3.2 ± 0.3% (Table 3.3 and Table 3.4). The higher performance is mainly due to improvement in fill factor (FF) and $J_{sc}$. The $V_{oc}$ was consistent between the two sets of devices.

$J_{sc}$ enhancements were further investigated by incident photon to current conversion efficiencies (IPCE) measurements (Figure 3.4 b). The IPCEs of the H-P25 based devices are higher than those of P25 over the 400-725 nm range, consistent with the higher value of $J_{sc}$ resulting from an enhanced light harvesting efficiency and thereby an increased the photocurrent value. The higher $J_{sc}$ obtained from H-P25 devices can be attributed to the better light harvesting efficiency resulted from higher dye loading.

Due to the major difference in the observed photovoltaic responses related to the FF, Electrochemical Impedance Spectroscopy (EIS) was employed. EIS measurements were carried out under 1 sun illumination, to compare the electron transfer rates and lifetimes, with Nyquist and Bode plots shown in Figure 3.4 c and d respectively. These were analyzed based on the model proposed by Bisquert and co-workers.[24, 25] Parameters from the fitted data are shown in Table 3.5, with $R_s$ referring to the series resistance, $R_{ct1}$ and $R_{ct2}$ to charge transfer resistance at the counter and the working electrode respectively. $CPE_1$ and $CPE_2$ represent the constant phase elements associated with the counter and working electrodes respectively. $CPE$s are used in this EIS model instead of

![Figure 3.3](image-url): Inhibition of electron recombination at TiO$_2$/I$_3^-$ interface by a densely packed N719 layer on clean total interfaces (right), and irregularity spaced on P25 by amorphous (left).
a simple capacitor as interfaces between the electrolyte/photoanode, and the electrolyte/counter electrode, which form double layer capacitance, are not ideal due to the diffuse electrolyte layer (leaky capacitor), surface roughness and nonuniform current distribution.[25] Two semicircles were observed in Nyquist plots, as seen in Figure 3.4 c, which were fitted using an equivalent circuit shown in the inset (see Figure 3.5). The first semicircle originated from higher frequencies and represents the electrochemical impedance of electron transfer at the counter electrode/electrolyte interface. As expected this was very similar for both devices tested. Meanwhile, the second semicircle at mid-range frequencies is related to the impedance of the interface between the photoanode material and the liquid electrolyte in competition with the transfer of injected electrons through photoanode material [24, 26]. Devices based on H-P25 exhibit a lower electrochemical impedance to charge transport through photoanodes (36.5 Ω cm\(^{-2}\)) compared to that of P25 photoanodes (45 Ω cm\(^{-2}\)) which indicates better charge transport through H-P25. As shown in Figure 3.4 d, the frequencies of the local impedance maxima \(f_{\text{max}}\), low frequencies) in the devices were 79 Hz and 100 Hz respectively. The electron lifetime, calculated using \(\tau_e = \frac{1}{2\pi f_{\text{max}}}\),[27] in the H-P25 based cells was therefore observed to be longer than that in the P25 based photoanode, again indicating that electron recombination losses have been mitigated, increasing the FF of the device. Furthermore, devices based on H-P25 exhibit a higher chemical capacitance \(C_p\) value compared to P25, indicating higher densities of shallow traps that receive more electrons generated from the excited dye (higher electron density).[2] It has previously been seen that the amorphous material may form electronic barriers.[19, 28]
Table 3.3: Photovoltaic parameters and the amount of dye loaded for H-P25 and P25 photoanodes based DSCs.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>7.3±0.1</td>
<td>0.78±0.0</td>
<td>56±5</td>
<td>3.2±0.3</td>
</tr>
<tr>
<td>H-P25</td>
<td>10.2±0.7</td>
<td>0.79±0.0</td>
<td>67±9</td>
<td>5.3±0.5</td>
</tr>
</tbody>
</table>

Figure 3.4: (a) J-V characterizations of DSCs based on H-P25 and P25 photoanodes (thickness 11.5 ± 0.3 µm and area 0.16 cm$^2$); (b) Incident photocurrent conversion efficiency (IPCE); electrochemical impedance spectroscopy; (c) Nyquist plot; (d) Bode plot of device based on H-P25 and P25 photoanodes.
Table 3.4: J-V parameters of measured DSC devices based H-P25 and P25 photoanodes

<table>
<thead>
<tr>
<th>Devices</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25.1</td>
<td>7.2</td>
<td>0.78</td>
<td>59</td>
<td>3.4</td>
</tr>
<tr>
<td>P25.2</td>
<td>7.3</td>
<td>0.80</td>
<td>58</td>
<td>3.4</td>
</tr>
<tr>
<td>P25.3</td>
<td>7.3</td>
<td>0.77</td>
<td>50</td>
<td>2.8</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>7.3</td>
<td>0.78</td>
<td>56</td>
<td>3.2</td>
</tr>
<tr>
<td>STDEV</td>
<td>0.1</td>
<td>0.02</td>
<td>5</td>
<td>0.3</td>
</tr>
<tr>
<td>H-P25.1</td>
<td>9.6</td>
<td>0.79</td>
<td>69</td>
<td>5.0</td>
</tr>
<tr>
<td>H-P25.2</td>
<td>11.0</td>
<td>0.79</td>
<td>57</td>
<td>5.0</td>
</tr>
<tr>
<td>H-P25.3</td>
<td>9.9</td>
<td>0.80</td>
<td>74</td>
<td>6.0</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>10.2</td>
<td>0.79</td>
<td>67</td>
<td>5.3</td>
</tr>
<tr>
<td>STDEV</td>
<td>0.7</td>
<td>0.01</td>
<td>9</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 3.5: Electrochemical impedance data for devices based on H-P25 and P25 photoanodes.

<table>
<thead>
<tr>
<th>Device</th>
<th>$R_S$ (Ω cm$^{-2}$)</th>
<th>$R_{ct1}$ (Ω cm$^{-2}$)</th>
<th>$R_{ct2}$ (Ω cm$^{-2}$)</th>
<th>$C_p$ (µF m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>6.1±0.2</td>
<td>10±0.6</td>
<td>45±0.7</td>
<td>112±5</td>
</tr>
<tr>
<td>H-P25</td>
<td>6.1±0.1</td>
<td>7.3±0.6</td>
<td>36.5±0.6</td>
<td>178±6</td>
</tr>
</tbody>
</table>

Figure 3.5: Fitting data of Nyquist plots of DSC devices based on H-P25 and P25 photoanodes sensitized with N719 dye.

Figure 3.6 a shows the light transmitted by the undyed H-P25 photoanode is lower than that of undyed P25 photoanode in the wavelength range of 400-800 nm. This is because H-P25 has slightly less porosity, due to larger agglomeration particles leading to the more dense film which has slightly lower transmittance. Also, the larger pore size in H-
P25 (inset Figure 3.1 e) should enhance longer wavelength scattering. Similarly, the transmittance of dyed H-P25 photoanode is lower than that of the P25 one in the wavelength range 400-800 nm. Figure 3.6 b shows the diffuse reflectance spectrum of H-P25 and P25 photoanodes. Undyed H-P25 photoanode showed slightly higher diffuse reflection in the visible region. As for dyed photoanodes, both photoanodes showed similar diffuse reflection in the wavelength range 400-700 nm with a slight increase in diffuse reflectance of H-P25 in the near infrared range 700-800 nm. Figure 3.6 c shows the absorption of undyed H-P25 photoanode is slightly higher than that of P25 photoanode while after being dyed; the absorption values of dyed H-P25 photoanode are higher than that of dyed P25 photoanode across the entire wavelength range. This means that dyed H-P25 film has higher light harvesting in the entire wavelength range due to owing higher dye loading along with slightly higher diffuse reflection than that of dyed P25. Figure 3.6 d shows higher adsorbed dye on H-P25 photoanode compared to P25 which is in good agreement with dye loading measurements resulting in enhanced photocurrent.

The optical properties of P25 and H-P25 films including transmittance, diffuse reflection, absorbance and absorbance of dye, measured and reported in Figure 3.6, show minimal differences in the transmittance and diffuse reflection measurements. This is in line with what would be expected, given the dye loading per unit area on both films was similar – the effects of higher dye packing density and lower surface area on H-P25 canceling one another out.
3.4 Conclusion

This study has investigated the effect of removal of amorphous TiO$_2$ in commercially available TiO$_2$ (P25) on DSC performance. Amorphous TiO$_2$ was dissolved and recrystallized to new anatase or rutile nanoparticles through selectively hydrothermal treatment. The efficiency of DSCs based on H-P25 was enhanced by 44% compared to that based on untreated P25, due to an increased $J_{sc}$, along with substantially better FF. The higher $J_{sc}$ was attributed to enhanced light harvesting due to higher dye loading on H-P25, in spite of the lower specific surface area. This is attributed to the surface construction of the crystalline material which is more favorable for the binding of the dye. The enhancement in FF results from the substantially longer electron lifetimes, higher electron densities and suppressed recombination losses due to the removal of the amorphous barriers and associated defect states. While it is seen that amorphous TiO$_2$ affects DSC performance negatively, the PCE of DSCs based on H-P25 is still low due
to the high density of shallow traps (which is expected for such mixed phase P25), in spite of anatase and rutile being good materials for photoanodes in their own right. This study sheds light on an issue that has not been widely studied and can provide a more detailed understanding of the effect of amorphous TiO$_2$ on the photovoltaic performance. P25 persists as a control for many research groups around the world, with quite variable performance. Furthermore, most researchers, ourselves included, have tended to ignore the role of amorphous TiO$_2$ in the DSC photoanode. These findings may also be useful to explain the performance of other TiO$_2$ samples, used in DSCs and other devices, where the impact of amorphous content may go unnoticed.

3.5 References


Chapter 4

4 Aggregated mesoporous nanoparticles for high surface area light scattering layer TiO$_2$ photoanodes in Dye-sensitized Solar Cells

This chapter is based on a published work [K. Al-Attafi, A. Nattestad, Y. Yamauchi, S.X. Dou, and J.H. Kim, Aggregated mesoporous nanoparticles for high surface area light scattering layer TiO$_2$ photoanodes in Dye-sensitized Solar Cells. Scientific reports, 2017. 7(1): p. 10341], with contributions of other co-authors as follows: K.Al-Attafi, A.Nattestad, and J. Kim designed experiments. K.Al-Attafi performed synthesis, TEM, XRD, SEM and DSC measurements and wrote the manuscript. K.Al-Attafi and Y. Yamauchi. Performed and analyzed BET measurements. K.Al-Attafi, A.N., and J. Kim. Analyzed the data and revised the manuscript. A. Nattestad, J. Kim, and S. Dou supervised the work. All authors discussed the results and contributed to revisions.

Even though using sub-micron scattering particles can enhance the light scattering ability of photodiodes as a result of capturing more light and hence increasing the light harvesting through photoanode materials in DSCs, their low surface area can affect dye loading and thus photocurrent. Meanwhile, hierarchically aggregated structures have shown properties such as high surface area, high light scattering, and a well-connected mesoporous structure that can ensure efficient dye loading, light scattering, and charge transport, respectively. Since, the light scattering ability of the particles is correlated with their particle size according to Mie theory, maintaining a high surface area is required to ensure efficient dye loading. In this Chapter, two sub-micron sizes of aggregated anatase TiO$_2$ nanoparticles (300 nm and 700 nm) have been synthesised by a facile one-step solvothermal reaction using mixed ethanol: acetic acid solvent. The performances of DSCs based on these scattering layers were investigated and compared to DSCs based on a commercial scattering layer.

These aggregated structures, TiO$_2$-700 and TiO$_2$-300, were found to be comprised of 8.5 nm and 10.5 nm anatase crystals, and possess specific surface areas of 138 and 106 m$^2$ g$^{-1}$ respectively. These particles were incorporated into DSCs as high surface area scattering layers, along with a layer of a transparent material. Solar-to-electric conversion efficiencies (PCE) of 9.1% and 8.2% were recorded using these aggregated particles as compared to those of commonly used large particles scattering layer 7.4%.
4.1 Introduction

Since the breakthrough report by O’Regan and Gratzel in 1991, DSCs have attracted a great deal of research attention, due to their anticipated low-cost, simple manufacturing processes and promising photocurrent conversion efficiency.[1-4] A DSC consists of a number of components. Firstly, light is absorbed by a sensitizer to generate an excited state dye, which is capable of injecting electrons into the conduction band of wide band gap metal oxide, with these electrons being then transported through the metal oxide to an external circuit. After charge injection, the cationic sensitizer is reduced back to its neutral form by electrons donated from a redox mediator. Balance in this mediator is maintained by the catalytic counter electrode. The most commonly used materials in DSC for the above four components are organometallic ruthenium complexes, titanium oxide (TiO$_2$), iodide/triiodide redox couple (I$_3$/I$_-$) and platinum nanoparticles respectively.[5, 6] To date, the highest efficiencies of DSC have been recorded using TiO$_2$ anatase nanoparticle photoanodes, [3, 4] due to excellent optoelectronic properties, [7-9] albeit with different sensitizers and redox electrolyte as compared to the above-mentioned system.

Meta-analysis shows that over 40% of research towards enhancing DSC performance has looked at modifying or developing an efficient photoanode nanostructure. [6, 10-12] In these studies it has been established that materials for efficient photoanodes should have (1) a large surface area to facilitate high dye loading, leading to high light harvesting efficiency, (2) have a well-connected network of pores for electrolyte diffusion,[13], (3) facilitate electron transfer (4) have a minimum of defects (both surface and bulk), including those formed at grain boundaries, to limit charge recombination energy losses.[14] These considerations are however somewhat contradictory. For instance, while decreasing the size of TiO$_2$ nanoparticles increases the surface area, the average pore size is also decreased; limiting diffusion as well as leading to increased numbers of grain boundaries based defects. [15]

Another strategy to enhance the light harvesting efficiency is the use of light scattering effects as increasing the average path length of light as it travels through the TiO$_2$ film, improving the probability of it being captured by dye molecule (particularly in the wavelength range where the dye extinction coefficient is the lowest). According to Mie theory, the size of the scattering particle will determine the wavelengths of light which will be scattered efficiently.[16]

This is typically exploited by employing a bi-layer photoanode structure consisting of a
transparent (weakly scattering), underlayer comprised of small particles and a layer of larger (scattering) particles on the top.[12] Sub-micrometre sized TiO\(_2\) spheres have been prepared by sol-gel methods by controlling the hydrolysis reaction and crystallized by subsequent calcination. This procedure has successfully obtained spherical TiO\(_2\) structures. However, their low surface area limits their application in DSCs.[17-19] Recently there has been a trend towards the production of hierarchical TiO\(_2\) structures, with large dimensions (effective scattering) consisting of nanoparticles (high dye loading).[15, 20-22] Such previous solvothermal approaches used to synthesize hierarchically aggregated TiO\(_2\) nanoparticles had long synthesis procedures to control the morphology and/or crystalline phase.[15, 17, 21, 23-25] These recent studies motive us to synthesize hierarchical mesoporous structures, with different aggregate sizes (300 ± 65 nm and 700 ± 150 nm, TiO\(_2\)−300 and TiO\(_2\)−700 respectively) composed TiO\(_2\) nanoparticles (~10.5 nm and ~8.5 nm respectively) in a facile solvothermal approach. We report a new and facile one-step solvothermal approach using titanium isopropoxide (TTIP) as a precursor in a solvent mixture containing acetic acid (AA) and ethanol (EtOH). Subsequently, we investigate their performance in DSCs, which is enhanced as compared to the commonly used, commercially available, light scattering layer (WER2-O). This is explained in terms of high surface area and relatively high light scattering, along with efficient electrolyte penetration through the highly interconnected mesoporous structure.

4.2 Experimental

4.2.1 Synthesis of TiO\(_2\)−700 and TiO\(_2\)−300

TiO\(_2\)−700 and TiO\(_2\)−300 were synthesized by a facile one-step solvothermal process. Briefly, Titanium isopropoxide (TTIP) (0.5 ml) was added dropwise to an acetic acid-ethanol mixed solvent under vigorous stirring for (1 h) at room temperature. A clear solution was formed which was transferred into a Teflon-lined stainless steel autoclave, 45 mL (Parr Instrument Company) heated to 180 °C (ramp time of 1 °C/min) for 9 h, after cooling down to room temperature the resulting white precipitate was collected and washed with distilled water and ethanol three times and then dried overnight at 90 °C. Finally, the samples were calcined at 400 °C (ramp time of 1 °C/min) in air for three hours. The morphologies, particle size and surface area of TiO\(_2\)−700 and TiO\(_2\)−300, were controlled by adjusting the acetic acid-ethanol volume ratio (AA:EtOH v/v) with keeping other solvothermal reaction conditions constant. The typical volume ratio of (AA: EtOH v/v) were used to synthesize TiO\(_2\)−700, and TiO\(_2\)−300 were (1:5 in ml) and
4.2.2 Preparation of photoanodes and DSCs assembly

Fluorine-doped tin oxide (FTO) glass was sequentially cleaned using soapy water, acetone, and ethanol in an ultrasonic bath for 20 min per solvent. A blocking layer of TiO$_2$ was deposited on the cleaned FTO substrate using spray pyrolysis of titanium (IV) diisoproxide-bis-acetylacetonate (75 wt.% in isopropanol, Aldrich) solution (1:9 v/v in ethanol) at 450 °C. Scattering pastes (WER2-O, Dyesol Australia, TiO$_2$-700 and TiO$_2$-300 or as described below) were printed on the top of a single transparent layer (18NR-T, Dyesol Australia) using a Keywell screen printer with a custom mesh (43 T) to form 4 mm × 4 mm (0.16 cm$^2$) photoanodes. The printed transparent layer (18NR-T) was dried at 125 °C before scattering layers were deposited. Pastes of TiO$_2$-700 and TiO$_2$-300 were prepared using 1.0 g of TiO$_2$ ground in a mixture of ethanol (25 ml), distilled water (1 ml), and acetic acid (0.2 ml). After that terpineol (5 g) and ethyl cellulose (0.5 g) were added to form slurry which was sonicated and stirred for (2 h). [26, 27] A viscous white paste was finally obtained after an evaporation process to remove water and ethanol. TiO$_2$-700 and TiO$_2$-300 scattering pastes were printed (thickness = 5.5 μm) on the top of a single transparent layer (18NR-T, Dyesol Australia) (thickness = 6.5 μm). For comparison, the photoanode including a single transparent layer (18NR-T) and a commercial scattering layer [Dyesol Australia WER2-O reflective Titania paste (thickness = 5.5 μm)] was printed. After that, the printed photoanodes were sintered using a multi-step program (up to 550 °C). Finally, the photoanodes were surface treated by soaking the photoanodes in (20 mM) aqueous solution of TiCl$_4$ (Sigma) for 30 min at 70 °C, then washed and re-sintered at (500 °C for 30 min).

After cooling down to 110 °C, the photoanodes were immersed in an N719 dye solution (0.5 mM, Solaronix). The dye solution was a mixture of tert-butanol (LR, Ajax Chemicals) and acetonitrile (HPLC, Lab-scan) [1:1 v/v], the photoanodes were taken out from dye solution after 24 h and washed with acetonitrile and then dried. Counter electrodes were prepared by first drilling holes in a separate piece of FTO glass, to be used as a filling port for the electrolyte solution. One drop of (10 mM) H$_2$PtCl$_6$ solution (in ethanol) was smeared on the cleaned pre-FTO counter electrode and heating to 400 °C for 20 min. The counter electrodes are cooled before being sandwiched together with the photoanode, using a 25 μm Surlyn (Solaronix) spacer, by a hot press. The electrolyte solution [acetonitrile/Valeronitrile (85:15 vol %), iodine (I$_2$) (0.03 M), 4-tertbutyl pyridine (4-tBP) (0.5 M), 1-butyl-3-methylimidazolium iodide (BMII) (0.6 M), and
guanidinium thiocyanate (GuSCN) (0.1 M)] was introduced into the filling port by the vacuum back-filling technique, and the filling port was then closed with a piece of Surlyn laminated to aluminium foil.

4.2.3 Material Characterizations

The crystalline structures of TiO$_2$-700 and TiO$_2$-300 were examined using X-ray diffractometer (Bruker Advance, 40 kV, 30 mA) (Cu Kα, λ = 1.5406 Å) in range (2θ = 20°–80° with scan rate (1°/min). The morphology and internal structure of samples were examined by field-emission scanning electron microscopy (FE-SEM) (JEOL JSM-7500) and transmittance electron microscopy TEM (JEOL JEM-2010). Brunauer-Emmet-Teller (BET) surface area, as well as BHJ porosity and pore volume values, were determined from data collected on (Microtrac Belsorp-mini) nitrogen adsorption-desorption equipment. The amount of dye on the different scattering layers was calculated by measuring the absorbance of dye desorbed from the films (thickness = 4 μm, area = 1 cm$^2$) in (4 ml) of (0.1 M) NaOH solution (distilled water: ethanol 1:1 v/v) using a Shimadzu UV-3600 spectrophotometer. The light scattering properties (diffuse reflectances) were measured using an integrating sphere (ISR-3100) and the above spectrophotometer. A Veeco Dektak 150 Surface Profiler was used for the film thickness measurements. Photocurrent density-voltage (J-V) measurements were measured using a solar simulator with AM1.5 filter; set to 1 sun (100 mW/cm$^2$, PV Measurements, Colorado). A QEX10 system from (PV Measurements) was used for the incident to photocurrent conversion efficiency (IPCE) measurements in 5 nm steps. The measured currents were referenced to a calibrated Si photodiode. A Reference 600 Potentiostat (GAMRY instrument) was used for electrochemical impedance spectroscopy measurements (EIS) which were carried out for DSCs based on different photoanodes under 1 sun illumination at $V_{oc}$ in a frequency range (0.1–106 Hz) and AC voltage 10 mV.

4.3 Results and Discussion

The morphologies and internal structures of the aggregated particles were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in the high and low magnification (SEM) images (Figure 4.1 a, b, e and f). Hierarchical mesoporous structures, with different aggregate size (700 nm and 300 nm designated TiO$_2$-700 and TiO$_2$-300 respectively) composed TiO$_2$ nanoparticles, were formed using mixtures of acetic acid and ethanol as a mixed solvent. SEM images also confirmed that (TiO$_2$-700) and (TiO$_2$-300) show highly connected mesoporous structure
as a result of assembling TiO$_2$ nanoparticles into hierarchical spheres and clusters shapes.

TEM images (Figure 4.1 c, d, g and h) show that both (TiO$_2$-700) and (TiO$_2$-300) have mesoporous structures, consisting of tightly interconnected and highly crystallized TiO$_2$ nanoparticles with average sizes of (~8.5 nm) and (~10.5 nm) respectively.

![Figure 4.1: Structural (internal and morphological) characterizations of the calcined TiO$_2$-300 and TiO$_2$-700: (a-d) low and high magnification SEM and TEM images of TiO$_2$-300; (e-h) low and high magnification SEM and TEM images of TiO$_2$-700.](image)

X-ray diffraction patterns (XRD) for the two aggregate materials are shown in (Figure 4.2). Both possess polycrystalline tetragonal anatase phase without any impurities or other phases (JCPDS no. 21–1272, a = 3.785 Å, b = 3.785 Å, and c = 9.514 Å) [this is even true before calcination]. The average crystallite sizes of TiO$_2$-700 and TiO$_2$-300 were ~8.5 nm and ~10.5 nm respectively, based on the Scherrer equation [28]. The high-resolution TEM (HRTEM) images [Figure 4.3 a-d] confirmed that (TiO$_2$-700) and (TiO$_2$-300) are composed of nanocrystalline TiO$_2$ with a fringe spacing of approximately (3.5 Å), corresponding to the (101) plane of the TiO$_2$ anatase phase which is consistent with XRD analysis.
Figure 4.2: XRD diffraction patterns of synthesized TiO$_2$-700 and TiO$_2$-300 before and after calcination.

Figure 4.3: High magnification TEM and high resolution HTEM images: (a,b) of TiO$_2$-700; (c and d) of TiO$_2$-300.
The commercial transparent NR18-T, scattering particles WER2-O, and synthesised \( \text{TiO}_2 \)-300; and \( \text{TiO}_2 \)-700 aggregated nanoparticles were spiked with about 10% silicon to act as an internal standard to assess the degree of crystallinity using the reference intensity method (RIR) for quantification analysis and Siroquant software. The spiked (actual) weight ratio for \( \text{TiO}_2 \): Si and the calculated weight ratios obtained from the integrated intensities (after subtracting the background) of all samples shown in Table 4.1 and Figure 4.4 a-d. The percentage decrease of crystallinity degree of \( \text{TiO}_2 \) samples, which represents the amorphous \( \text{TiO}_2 \) weight ratio, can be quantified as:

\[
\text{Amorphous } \text{TiO}_2 (\text{wt})\% \quad = \quad 100 (\text{wt})\% - [\text{Si}_{\text{mass}} (\text{wt})\% + \frac{\text{Si}_{\text{mass}} (\text{wt})\%}{\text{Si}_{\text{XRD}} (\text{wt})\%}] \times \text{crystalline } \text{TiO}_2_{\text{XRD}} (\text{wt})\%]
\]

All samples consist entirely of anatase, however, all the peaks are broader than for well crystalline anatase (best fitting) except WER2-O. No other mineral phases were recorded and none of the samples shows an amorphous hump suggesting that the materials are all crystallines with approximately no amorphous phase (very little amount of amorphous was approximately quantified). The calculated amount of amorphous phase (less than 4%) which is very little or ignorable can be resulted from the broadened peaks compared to the best fitting due to the nanosize effect with different grain size ranges or very finely crystalline phase (different full-width half-maximum- FWHM). These little amount of amorphous \( \text{TiO}_2 \) should not affect the dye loading and thus the photocurrent of DSC devices.

**Table 4.1**: Quantification analysis of crystallinity degree (estimated amorphous phase) of synthesized and commercial \( \text{TiO}_2 \).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Spiked weight ratio with Silicon (%)</th>
<th>Calculated weight ratio with Silicon (%)</th>
<th>Quantified amorphous ( \text{TiO}_2 ) phase ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{TiO}_2 )-700</td>
<td>90.5:9.5</td>
<td>90.2:9.8</td>
<td>3</td>
</tr>
<tr>
<td>( \text{TiO}_2 )-300</td>
<td>90.8:9.2</td>
<td>90.5:9.5</td>
<td>3</td>
</tr>
<tr>
<td>WER2-O</td>
<td>90.7:9.3</td>
<td>91.4:8.6</td>
<td>0</td>
</tr>
<tr>
<td>18NR-T</td>
<td>90.7:9.3</td>
<td>90.3:9.7</td>
<td>4</td>
</tr>
</tbody>
</table>
XRD, SEM and TEM analyses clearly demonstrated that both (TiO$_2$-700) and (TiO$_2$-300) have a hierarchical structure consisting of nano-sized TiO$_2$ anatase nanoparticles, providing a highly interconnected mesoporous structure. This is verified by nitrogen adsorption/desorption measurements in (Figure 4.5 a and Table 4.2), which showed a type IV isotherm and H3 hysteresis loops at high relative pressures (P/P$_0$ = 0.60–0.95). This indicates the presence of significant mesoporous structures in both (TiO$_2$-700) and (TiO$_2$-300) compared to (WER2-O) and is comparable with that of (18NR-T). Moreover, the hysteresis loops observed for the isotherms, even higher relative pressures (P/P$_0$ = 0.85–0.95), indicate more condensed N$_2$ in the pores and large voids of (TiO$_2$-700) and (TiO$_2$-300) compared to those of (WER2-O) and (18NR-T) leading to the conclusion that the overall surface area is larger for the aggregated particles. Barrett-Joyner-Halenda (BJH) analysis of pore size distribution (Figure 4.5 b) showed that the

**Figure 4.4:** XRD analysis of integrated intensities of synthesized and commercial TiO$_2$ samples to calculate approximately the TiO$_2$: Si weight ratio to assess the TiO$_2$ crystallinity degree (estimated amorphous phase) using RIR method.
internal pore size (formed by aggregation nanoparticles) of \((\text{TiO}_2-700)\) and \((\text{TiO}_2-300)\) are (6.2 nm and 9.2 nm) respectively which are smaller than that of transparent layer (18NR-T) due to the smaller nano-size of their primary nanoparticles. However, the observed peak pore size of the Dyesol scattering layer (WER2-O) is around (2.7 nm). Due to the solid structure, this is assumed to arise from surface roughness. The external pore size related to the voids among (WER2-O) and \((\text{TiO}_2-300)\) particles are around 180 nm and 120 nm respectively due to owing approximately similar particle size. The external pore size of \((\text{TiO}_2-700)\) is expected to be around 350 nm, however, it is not observed here due to equipment limitations. Brunauer-Emmett-Teller (BET) calculations were conducted and summarized in Table 2. It is therefore expected that \((\text{TiO}_2-700)\) and \((\text{TiO}_2-300)\) would be capable of hosting a larger amount of dye, which can lead to higher photocurrent compared to those of (WER2-O). The internal and external pores of \((\text{TiO}_2-700)\) and \((\text{TiO}_2-300)\) can provide facile channels for the efficient electrolyte diffusion.[15, 29]

In addition, the aggregate size of around 700 nm and 300 nm, provide good scattering, while having high surface area true in undyed films, however, light travels in the film, hence increasing the probability of absorption light by the dye especially at wavelengths where the dye extinction coefficient is lower.

Figure 4.5: (a) Nitrogen adsorption-desorption isotherms measurements; (b) Pore size distribution calculated from the adsorption branch of a nitrogen isotherm by the Barrett-Joyner-Halenda (BJH) method.
Table 4.2: Porosity (P), Specific surface area ($S_A$) and Surface roughness factor ($R_F$) of 18NR-T, WER2-O, TiO$_2$-700 and TiO$_2$-300 particles. $^a$ The porosity calculated as: $P = P_V/\rho - 1 + P_V$, where $P_V$ is the cumulative pore volume (cm$^3$ g$^{-1}$) and $\rho^{-1}$ is the inverse of the density of anatase TiO$_2$ ($\rho^{-1} = 0.257$ cm$^3$ g$^{-1}$). $^b$ The estimated value of the surface roughness factor ($R_F$) is calculated by $R_F = \rho(1-P)S_A$. [26]

<table>
<thead>
<tr>
<th>Samples</th>
<th>Porosity (%)$^a$</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>Roughness factor (µm$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-300</td>
<td>63</td>
<td>106</td>
<td>154</td>
</tr>
<tr>
<td>TiO$_2$-700</td>
<td>56</td>
<td>138</td>
<td>235</td>
</tr>
<tr>
<td>WER2-O</td>
<td>35</td>
<td>15</td>
<td>38</td>
</tr>
<tr>
<td>18NR-T</td>
<td>67</td>
<td>79</td>
<td>103</td>
</tr>
</tbody>
</table>

DSCs based on a bi-layer photoanode structure, incorporating a 18NR-T transparent layer, with either WER2-O, TiO$_2$-700 or TiO$_2$-300 as scattering layers, designated as (18NR-T/WER2-O), (18NR-T/TiO$_2$-700) and (18NR-T/TiO$_2$-300) respectively, along with a single layer (transparent only) (18NR-T) were prepared to investigate the effect of the scattering layers on the photovoltaic properties of the DSC. The current density-voltage characterisations (J-V) and key photovoltaic parameters are summarized in (Table 4.3) with representative J-V curves in Figure 4.6. a. DSC based on (18NR-T/TiO$_2$-300) and (18NR-T/TiO$_2$-700) photoanodes showed a significant enhancement in the photocurrent conversion efficiency compared to these using (18NR-T) or (18NR-T/WER2-O) photoanodes, with efficiencies of 8.2%, 9.1%, 7.2%, and 7.4% respectively. The higher efficiency of DSC devices based on (18NR-T/TiO$_2$-300) and (18NR-T/TiO$_2$-700) photoanodes is mainly due to enhanced $J_{sc}$ while $FF$ and $V_{oc}$ are fairly consistent (Table 4.3). Dye loading on the (TiO$_2$-700 and TiO$_2$-300) films is significantly higher than that of (WER2-O) and comparable to that of Dyesol transparent layer (18NR-T) as seen from desorption experiments (Figure 4.6 b and Table 4.4). The hierarchical mesoporous structure of (TiO$_2$-700) and (TiO$_2$-300) based on high surface area aggregated nanoparticles can host more dye molecules, leading to higher $J_{sc}$ while the very low surface area of (WER2-O) can result in lower $J_{sc}$ due to the poor dye loading.
Table 4.3: J-V characterizations of DSC devices.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18NR-T/TiO$_2$-300</td>
<td>14.1±0.4</td>
<td>0.79±0.01</td>
<td>69±1</td>
<td>8.2±0.2</td>
</tr>
<tr>
<td>18NR-T/TiO$_2$-700</td>
<td>16.1±0.1</td>
<td>0.80±0.01</td>
<td>71±1</td>
<td>9.1±0.1</td>
</tr>
<tr>
<td>18NR-T/WER2-O</td>
<td>13.8±0.3</td>
<td>0.79±0.01</td>
<td>67±1</td>
<td>7.4±0.3</td>
</tr>
<tr>
<td>18NR-T</td>
<td>12.9±0.7</td>
<td>0.83±0.01</td>
<td>70±1</td>
<td>7.2±0.4</td>
</tr>
</tbody>
</table>

Table 4.4: The amount of dye on TiO$_2$-300, TiO$_2$-700, WER2-O and 18NR-T films.

<table>
<thead>
<tr>
<th>Films</th>
<th>Dye loading ($10^{-7}$ mol cm$^{-2}$)</th>
<th>Dye loading ($10^{-5}$ mol cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-300</td>
<td>0.55</td>
<td>14</td>
</tr>
<tr>
<td>TiO$_2$-700</td>
<td>0.63</td>
<td>16</td>
</tr>
<tr>
<td>WER2-O</td>
<td>0.32</td>
<td>4</td>
</tr>
<tr>
<td>18NR-T</td>
<td>0.61</td>
<td>15</td>
</tr>
</tbody>
</table>

The enhancement in photocurrent densities and its relationship to enhanced light harvesting efficiency was also further investigated with an incident photon to current conversion efficiencies (IPCE) measurements. In Figure 4.6 c, devices based on (18NR-T/TiO$_2$-300) and (18NR-T/TiO$_2$-700) showed higher IPCE values in the entire measured wavelength range (300–800 nm) along with a broader shape around than those of (18NR-T) and (18NR-T/WER2-O), (Figure 4.6 c and Figure 4.7), even though (WER2-O) itself was more scattering than the aggregates. Peak IPCE values were nearly identical, while more marked differences in the red part of the spectrum were seen, where the dye absorption is lower.

The light-scattering effect can be evaluated by measuring the diffuse reflection of photoanode films. Figure 4.6 d shows the reflectance spectra of different photoanode films in the range of (400–800 nm). (18NR-T/WER2-O) photoanode showed the strongest diffuse reflection (65–85%) which is higher than that of (18NR-T/TiO$_2$-700) and (18NR-T/TiO$_2$-300) photoanodes respectively which are in turn, have higher diffuse reflection (40–60%) than that of transparent layer (18NR-T) (20–30%). The lower diffuse reflection of (18NR-T/TiO$_2$-700) and (18NR-T/TiO$_2$-300) (40–60%) compared to (18NR-T/WER2-O), is probably due to owning high porosity structure resulting in the less dense film (not being solid particles) (Table 4.1) and (Figure 4.8).
Figure 4.6: (a) J-V characteristics of DSC devices measured under 1 sun illumination with an area of 0.16 cm$^2$; (b) absorbance spectra of the dye solution desorbed on the different scattering layers; (c) Incident photon to current conversion efficiency (IPCE) curve of DSCs.

Figure 4.7: Broadening shape of (IPCE) spectra of DSC devices based on 18NR-T, 18NR-T/TiO$_2$-700, 18NR-T/TiO$_2$-300 and 18NR-T/WER2-O photoanodes.
Electrochemical Impedance Spectroscopy (EIS) measurements were carried out to compare electron transfer and lifetime of devices based on bi-layer photoanodes. Nyquist plots of all the devices showed similar electrochemical interface impedance response. However, device based on (18NR-T/WER2-O) showed a more depressed arc in the second semicircle (lower frequencies) which is related to electron transfer at the TiO$_2$ interface with FTO and the electrolyte (Table 4.5 and Figure 4.9 a). Fittings for all these devices use $CPE$, as opposed to capacitive elements, in the model as the double layer interfaces between the electrolyte/photoanode are non-ideal and act as a leakage capacitor.[30] Bode plots were used to estimated lifetime ($\tau = 1/2\pi f_{\text{max}}$) [31] of injected electrons from dye through photoanode to the charge collector (FTO). (Figure 4.9 b) showed that the maximum value of frequency of devices based on (18NR-T/TiO$_2$-700) and (18NR-T/TiO$_2$-300) photoanodes were located at (20 Hz) and (25 Hz) respectively which is lower than that of (18NR-T/WER2-O) (38 Hz), implying that the lifetimes of electron transfer through (18NR-T/TiO$_2$-700) and (18NR-T/TiO$_2$-300) photoanodes are longer than in (18NR-T/WER2-O) due to reduced electron recombination and/or faster electron diffusion through high surface area hierarchical crystalline structure (there are more boundaries in the aggregates and increased surface area).
Table 4.5: Electrochemical impedance spectroscopy data of DSCs based on 18NR-T/WER2-O, 18NR-T/TiO$_2$-700 and 18NR-T/TiO$_2$-300 photoanodes.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$R_s$ ($\Omega$)</th>
<th>$R_{ct1}$ ($\Omega$)</th>
<th>$R_{ct2}$ ($\Omega$)</th>
<th>$CPE_2$ ($\mu$F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18NR-T/TiO$_2$-700</td>
<td>3.9</td>
<td>2.2</td>
<td>23.5</td>
<td>786</td>
</tr>
<tr>
<td>18NR-T/TiO$_2$-300</td>
<td>3.9</td>
<td>1.8</td>
<td>24.3</td>
<td>585</td>
</tr>
<tr>
<td>18NR-T/WER2-O</td>
<td>3.9</td>
<td>2.4</td>
<td>23.3</td>
<td>924</td>
</tr>
</tbody>
</table>

Figure 4.9: Electrochemical impedance spectroscopy; (a) Nyquist plot; (b) Bode plot of DSC based on 18NR-T/WER2-O, 18NR-T/TiO$_2$-700 and 18NR-T/TiO$_2$-300 photoanodes.

4.4 Conclusion

High PCE has been realized through the use of aggregated TiO$_2$ structure as scattering layers. The sub-microsize hierarchical mesoporous spheres TiO$_2$-700 comprised of 8.5 nm TiO$_2$ nanoparticles, prepared by a simple one-step solvothermal method, provided the highest PCE of 9.1% in conjunction with a transparent TiO$_2$ layer. This resulted from combined effects of higher dye loading, efficient electrolyte diffusion through the highly connected mesoporous structure and good light scattering properties. To the best of our knowledge, this is the highest efficiency for aggregated nanoparticles hierarchical microsphere as scattering layers with a commercial transparent TiO$_2$ layer.[22, 24, 32, 33]
4.5 References


30. Bisquert, J., A. Zaban, M. Greenshtein, and I. Mora-Seró, Determination of rate constants for charge transfer and the distribution of semiconductor and electrolyte electronic energy levels in dye-sensitized solar cells by open-circuit


Chapter 5

5 Solvothermally-synthesized anatase TiO$_2$ nanoparticles for photoanodes in metal-free dye-sensitized solar cell

This chapter is based on a submitted work to the journal Science and Technology of Advanced Materials (SATM) [K. Al-Attafi, A. Nattestad, H. Qutaish, L. K. Shrestha, Y. Yamauchi, S.X. Dou and J.H. Kim, Solvothermally synthesized anatase TiO$_2$ nanoparticles for photoanodes in dye-sensitized solar cell, with contributions of other co-authors as follows: K. Al-Attafi, A. Nattestad and J. Kim designed the study and research plan. K. Al-Attafi synthesized the materials, prepared devices and characterized and analysed the results (J-V, EIS, SEM, TEM, XRD, BET, FTIR, TGA, Zeta potential, optical measurements, XPS measurements, and Raman measurements) and wrote the manuscript. K. Al-Attafi and H. Qutaish analysed the FTIR and Raman measurements. K. Al-Attafi, L. K. Shrestha and Y. Yamauchi measured and analysed BET measurements. K. Al-Attafi and A. Nattestad and J. Kim revised the manuscript. S. Dou, J. Kim and A. Nattestad supervised the study.

Many researchers working on the development of DSCs continue to focus on the synthesis of photoanode materials with high surface area, along with high light scattering ability to enhance light harvesting efficiency. On the other hand, dye packing density, which can also affect the light harvesting efficiency significantly, is often overlooked. In this Chapter, Solvothermally-synthesized Anatase TiO$_2$ Nanoparticles (SANP) were obtained by a new and simple approach using a mixed solvent, ethanol and acetic acid. SANP were applied as a photoanode material in DSCs using a metal-free organic dye (D149) or organometallic dye (N719). The dye loading (packing density) was examined in terms of the isoelectric point (IEP) and the contribution of this, in addition to light scattering effects were shown to control the photovoltaic efficiency of the devices; specifically when compared with ones employing commercially available titania nanoparticles (either transparent or a bilayer structure with a transparent layer and a scattering one). SANP photoanodes sensitised with D149 dye were optimised at 10 µm, yielding photovoltaic conversion efficiencies of 6.9% which was higher than for transparent or transparent + scattering films (5.6% and 5.9% respectively) Further to this, an efficiency of 7.7% was achieved using a SANP photoanode sensitized with N719 dye, with 7.2% seen for the transparent photoanode
and 7.9% with a scattering layer. The high efficiencies of devices based on SANP photoanode are attributed to the high dye loading capability in addition to good light scattering. A further point of interest is that even with the increased reactivity of the surface towards dye adsorption, we did not observe any significant increase in recombination with the redox mediator, presumably due to this increased dye loading providing better shielding.

5.1 Introduction
Titanium dioxide (TiO$_2$) has been used in sensitised photoanodes since the first report by Chen in 1979.[1] A significant increase in popularity followed the report of the first Dye-sensitized Solar Cells by O’Regan and Grätzel in 1991, [2, 3] typical architecture of the cell consisting of a high surface area TiO$_2$ film, deposited on a charge collector such as Fluorine-doped Tin Oxide (FTO) and sensitized with a dye which injects electrons into this TiO$_2$ film following photoexcitation. The subsequent regeneration of the dye is achieved by a redox shuttle which is, itself re-reduced by a catalytic counter electrode such as platinum. [2] The highest efficiency in such a system achieved to date is over 14%. [4] In spite of the advent of other technologies [5, 6] and price decreases of maturing photovoltaic technologies, DSC are still of interest to researchers, largely due to some of their distinct features, which provide promise for niche applications, such as flexible devices and/or indoor applications, where DSCs do not suffer as greatly from low light intensities, angle of incidence or partial shading as silicon does.[7-11]
It is well known that low extinction coefficients of dye monolayers necessitate high surface area and close packing of dyes on these surfaces. As such nanoscale TiO$_2$ particles are standard in DSC applications. Light scattering is another approach to increasing light harvesting, with the mean free path of a photon traversing the photoelectrode increased, thereby increasing the likelihood of it being absorbed by a dye. This poses a contradiction for photoanode development, as scattering is primarily controlled by particle (or void) size. [12, 13] As such bilayer photoanodes with one layer of TiO$_2$ nanoparticles, and one composed of larger particles (400-500 nm) are commonly used, to scatter/reflect the incident light backward through the high surface area nanoparticle region to increase the probability of absorption.[14] In general thick TiO$_2$ layers should be avoided as they lead to a lowering of the overall charge density in the film, which affects the quasi-Fermi level and subsequently the attainable device voltage. [15, 16]
The ruthenium complex N719 is still the most commonly employed dye in DSC research, and as such serves as an important benchmark, however, high production/purification costs and low molar extinction coefficients limit widespread commercial viability.[17, 18] Further to this, recent record device efficiencies (including the above mentioned 14%) have been attained using dyes employing more earth-abundant metals or metal-free organic compounds. [17, 19, 20] D149 was one of the first organic dyes to rival the performance of N719 and is widely used in research today as it is commercially available. Photovoltaic conversion efficiencies of up to 9% have been reported, [21]

Using D149 and photoanodes comprised of a mixture of particle sizes, which provided strong light scattering as well as high surface area. [22] In spite of the small particle size of SANP, even compared to the commercially available transparent source (NR18-T), it is expected to scatter light effectively due to aggregate formation.

The isoelectric point (IEP) refers to the pH at which there is zero net surface charge on the material.[23] With all other things being equal, the higher the IEP value a metal oxides surface has, the more it is able to adsorb negatively charged dye molecules, such as those with carboxylic functionality, [23, 24] and is a key factor in determining the total dye loading on photoanodes.[25, 26] Although not commonly addressed, this has been exploited by several researchers. This has previously been achieved most simply through the use of different semiconductors (i.e. not TiO$_2$), which possess high IEP, such as ZnO or SnO$_2$.[25, 26] This has also been achieved with surface post-treatments (such as TiCl$_4$ or acid washes).[25] While enhanced light harvesting due to this increased dye loading may result from high IEP values,[25-27], this may also lead to dye aggregation, which can negatively affect overall device performance. [26]

Furthermore, dye loading is important outside the specific field of DSC research. One recent report by Azeez et al. on the use of TiO$_2$ particles for photocatalytic applications showed a significant dependence of the IEP of TiO$_2$ nanoparticles synthesised at different pH values. In this, the use of acidic conditions (pH=1.6) was employed to reduce particles with a higher IEP, at pH=7.35, while those synthesised at pH=7 gave an IEP at 4.27 and those made at pH=10 slightly lower again at 4.15. [28] In spite of having a larger particle size, the particles synthesised at pH=10 gave the highest degradation rate of 1.08 hr$^{-1}$, compared to 1.02 hr$^{-1}$ for neutral and 0.36 hr$^{-1}$ for the particles synthesise in acid conditions, with the differences attributed to dye adsorption facilitating more effective photodegradation. The enhancement in the photocatalytic
activities of TiO$_2$ nanoparticles synthesised at pH=7 and 10 compared to that synthesised using pH=1.6, were attributed to the higher adsorption of cationic methylene blue dye to the higher negatively charged TiO$_2$ surface. [28] Thus, TiO$_2$ nanoparticles synthesised using pH=1.6 with (IEP=7.35) are expected to show higher surface adsorption to anionic dyes with carboxylic groups due to their higher surface positive charge. We have also previously reported the role IEP plays in photocatalytic dye removal vis-à-vis dye loading onto the surface.[29]

As mentioned above, acidic surface post-treatments have been expected to increase dye loading on TiO$_2$ through changes to the IEP. For example, Song et. al claimed that 50 mM hydrochloric acid surface treatment of TiO$_2$ could increase the dye loading on TiO$_2$ surface sites due increasing the adsorption of H$^+$ ions and thus increase the positive charge of TiO$_2$ surface. [30] Meanwhile acetic acid treatment of TiO$_2$ was also claimed to enhance N719 dye binding as well as reduce charge recombination between TiO$_2$ and the redox mediator, resulting in enhanced charge injection and charge collection efficiencies respectively. [31] The enhancement in charge injection efficiency after acetic acid treatment was explained as a result of changing the dye binding mode between COO$^-$ and Ti from monodentate and partially bidentate modes to the optimal bidentate chelating mode. [31] Meanwhile, Kim et. al reported that nitric acid (pH=1) surface treatment increased the positive charge density on TiO$_2$ photoanode and thus enhanced N719 dye loading rates with reducing the dying time to 30 min rather than 9 h for untreated TiO$_2$ photoanode, with attaining similar device efficiency and $J_{sc}$. [32] Interestingly, the total dye loading after long dying times appears to be similar for the treated and untreated samples here. In another slightly different approach, Subramanian and Wang used H$_2$O$_2$ vapor in argon in a tube furnace at 450 °C to increase the hydroxyl group concentration on TiO$_2$ surfaces, which also enhanced the dye binding/loading and thus the photocurrent.[33]

It has been widely reported that the dye adsorption capability is strongly affected by exposed facets of TiO$_2$ crystal structures.[34] Since the surface energy of the exposed facets for anatase TiO$_2$ are in order of (101) 0.44 J m$^{-2}$ < (010) (0.53 J m$^{-2}$) < (001) (0.90 J m$^{-2}$) < (110) (1.09 J m$^{-2}$) [35] while, for rutile TiO$_2$ are in order of (110) < (100) < (101) < (001) [36], increasing the surface energy of the exposed facets can enhance their reactivity to adsorb more dye molecules. Specifically, Nanostructured anatase or rutile TiO$_2$ with exposed facets (001) can adsorb more dye compared to those without specific facets and thus enhance DSC performance or photocatalytic activity. [36-40]. Many
researchers synthesized anatase or rutile TiO$_2$ particles with different morphologies (mostly by solvothermal reaction based acidic solvents) with a high percentage of specific exposed facets to enhance the dye loading in DSCs. Peng et al. synthesized hierarchically microspheres assembled nanosheets using mixed solvent water and hexane. [41] These hierarchical microspheres showed exposed (001) facets and, due to their nanosheets assembly, resulted in a high dye loading compared to TiO$_2$ nanoparticles, with 14% enhancement in DSC PCEs as compared to devices based nanoparticles. The enhancement was mainly attributed to the higher surface area and higher dye adsorption on exposed facets (001) of assembled nanosheets, as well as higher light scattering, compared to TiO$_2$ nanoparticles.[41] Du et al. also synthesized different TiO$_2$ morphologies with different exposed facets using hydrothermally treated tetratitanate nanoribbon precursor materials, by controlling the pH values in a hydrothermal reaction performed at 180 °C. Different anatase TiO$_2$ morphologies were formed with different exposed facets (rod-like at pH≤3, cuboidal and rhombohedral at pH=5, and spindles at pH=7-14). The morphologies with more facets, particularly (001) facets, such as nanocuboid, nanorrhombic and nanospindle showed higher photocatalytic and DSC performance compared to those with less exposed facets (nanorod and the reference commercial P25).[37] Similarly Yu et al. synthesized two morphologies of anatase TiO$_2$ by hydrothermal method using titanium butoxide as a precursor and hydrofluoric acid as a morphology control agent. The resulting morphologies were nanosheets and truncated octahedron with exposed (001) and (101) facets respectively. While the dominant exposed facets of nanosheets and truncated octahedron were (001) and (101) respectively, both morphologies showed higher DSC performance compared to devices using P25. This was attributed to higher dye adsorption on exposed (001) facets of nanosheets and truncated octahedron nanoparticles due to their higher surface reactivity to bind more dye molecules compared to those with exposed (101) facets which are a more thermodynamically stable facet.[39] In another study, Chu et al. synthesized truncated octahedral anatase TiO$_2$ nanoparticles with a high percentage of exposed (001) facets by two steps hydrothermal reactions. To do this, anatase TiO$_2$ nanowires were first prepared by a hydrothermal reaction of Ti powder in an aqueous solution of sodium hydroxide at 200 °C for 48 h and then, these were hydrothermally treated in an aqueous solution of ammonium fluoride at 200 °C for 48 h to obtain the truncated octahedron TiO$_2$ nanoparticles with exposed (001) facets. While a hydrothermal reaction of TiO$_2$
nanowires in only water resulted in a random morphology with other phases. Devices based on truncated octahedron anatase TiO$_2$ nanoparticles exposed (001) facets showed higher performance with an efficiency of 7.06% than those based on non-controlled TiO$_2$ morphologies. This was attributed to the higher dye adsorption on the exposed (001) facets of TiO$_2$ nanoparticles.[40] Maitani et al. also controlled the synthesis of anatase TiO$_2$ nanosheets and nanoparticles with exposed (001) and (101) facets, by adding hydrofluoric acid and water respectively. In spite of lower surface area of nanosheets compared to nanoparticles (87.78 vs. 117.6 m$^2$.g$^{-1}$), the nanosheets with dominant exposed (001) facets showed slightly higher (or comparable) DSC performance compared to nanoparticles based on only (101) facets. This was attributed to the enhanced charge injection and suppressed charge recombination of nanosheets with (001) facets as well as the higher packing density (0.96 vs. 0.86 dyes.nm$^{-2}$). [42]

From the above literature, it can be concluded that using acidic or basic solvents in the synthesis of TiO$_2$ nanostructures can significantly affect the morphology and exposed facets of synthesized materials. [34, 40, 43] To the best of our knowledge, there is only one report on the effect of the exposed facets orientation of rutile TiO$_2$ on the IEP. [44] Bullard and Cima studied the dependence of isoelectric point of polymorph rutile TiO$_2$ on the crystal orientations. They showed that the exposed crystal facets (001) exhibited the highest IEP in a range of (5.5-5.8) while the IEP of exposed facets (110) and (100) were in ranges (4.8-5.5) and (3.2-3.7) respectively. [44] This was explained in term of surface reactivity, according to the theory of surface adsorption, the surface acidity is a function of charge affinity and density of adsorption sites which are mostly the cationic positive sites. These positive adsorption sites can bond strongly to the hydroxyl groups in solvents due to having high IEP.[44, 45]

The exposed (001) facets have a higher coordinator number of Ti-O atoms with two-fold coordinated oxygen atoms compared with (110) and (100) facets, that have mixed two and three-fold coordinated oxygen atoms. This creates more base sites on (001) (Lewis sites) which enable the adsorption of more hydrogen ions. The hydrated TiO$_2$ surface can be more reactive to adsorb water and form two carboxyl groups through reacting with oxygen vacancies. [46, 47]

While most DSCs researchers synthesising new TiO$_2$ photoanode structures focus on creating high surface area and tailoring pores structure, in conjunction with enhancing light scattering, to attain good light harvesting efficiency, increasing the IEP, such as
with acid surface treatment can improve the dye loading, which also increases the light harvesting efficiency significantly. [30, 31] While post-treatments of TiO₂, like the ones described above, this adds an extra-step in production. On the other hand, facet control tends to employ either HF or NH₄F, bringing with them safety issues. To achieve high light harvesting efficiency in DSC with a relatively thin photoanode requires high extinction coefficient dyes, a highly connected mesoporous TiO₂ photoanode structure with high surface area and appropriate porous structure to ensure an efficient dye loading.[13, 48] Also, the particle size should be optimised to suppress the recombination losses associated with the smaller particle size of TiO₂ nanoparticles.[49] As organic dyes relax the requirements in TiO₂ photoanode design few reports, have been published regarding optimization of TiO₂ photoanodes sensitized with D149 for DSCs. [21, 50, 51]. In spite of there being a number of publications seeking to optimize devices for D149, these often focused on improving the electrolyte or the light harvesting of photoanode using a scattering layer. Therefore, increasing of dye loading along with reducing the film thickness and suppressing the recombination losses are required for efficient DSC based on free-metal organic dyes.

In this work, we investigate the effect of surface area, porosity, and IEP on the dye loading, as well as the dye packing density of N719 and D149 on TiO₂, using a newly synthesised material, produced in a solvothermal reaction with a mixture of ethanol and acetic acid. Mixed solvents, including acids, is commonly used in the hydrothermal reaction to control TiO₂ morphologies with specific exposed crystal facets that exhibit different dye loading. [34, 40, 43]

Also, if acetic acid can be used to control the exposed crystal facets, it would be much more scalable than using other solvents such as HF or NH₃F.[52, 53]

To the best of our knowledge, the effect of solvothermal reaction conditions on product IEP and subsequently on dye packing in such mixed solvent reactions has not been investigated. As such, we report here a new and facile solvothermal approach to synthesize high surface area anatase TiO₂ nanoparticles (20 nm) along with their performances in DSCs using either organometallic N719 dye or organic D149 dye. To more fully understand the differences as compared to using commercially available TiO₂, light scattering and dye packing density are investigated, with dye packing density seen to be dependent on IEP.
5.2 Experimental

5.2.1 SANP production
SANP were synthesized by a new and facile one-step solvothermal process. Briefly, Titanium isopropoxide (TTIP) (1.5 ml) was added dropwise to an acetic acid-ethanol mixed solvent (1:2 v/v) under vigorous stirring for (1 h) at room temperature. A clear solution was formed which was transferred into a Teflon-lined stainless steel autoclave, 45 mL (Parr Instrument Company) heated to 200 °C (ramp time of 1°C /min) for 9 h, after cooling down to room temperature the resulting white precipitate was collected and washed with distilled water and ethanol three times and then dried overnight at 90 °C. Finally, the samples were calcined at 500°C (ramp time of 1°C /min) in the air for three hours (in this procedure the calcination step can be eliminated from the synthesis procedure as the sample showed higher crystallinity even prior to calcination).

5.2.2 DSC devices assembly
A screen printing paste was prepared from SANP, using our previously reported method. [54-56] In brief, organic binders (ethyl cellulose), ethanol, terpineol, acetic acid and water were added to the SANP, mixed and then the low boiling point solvents were evaporated using a rotary evaporator (leaving terpineol).[54] Using this paste, 10 µm films of SANP were screen printed onto cleaned FTO glass for use as photoanodes, along with commercial transparent TiO₂ (Dyesol NR18-T) and in some cases also a scattering layer (Dyesol-WER2-O). Prior to this porous film, a dense layer was formed through the spray pyrolysis of titanium (IV) diisoproxide-bis-acetylacetone (75 wt.% in isopropanol, Aldrich) solution (1:9 v/v in ethanol) at 450 °C) After that, the printed photoanodes were sintered using a multi-step program (up to 500 °C). Finally, the photoanodes were surface treated by soaking the photoanodes in (20 mM) aqueous solution of TiCl₄ (Sigma) for 30 min at 70 °C, then washed and re-sintered at (500 °C for 30 min), the photoanodes were immersed in either a 0.5 mM N719 (Solaronix) dye solution of a mixture of tert-butanol (LR, Ajax Chemicals) and acetonitrile (HPLC, Lab-scan) [1:1 v/v], or 0.5 mM D149 (1-material, Canada) in a 1:1 (v/v) mixture of acetonitrile and tert-butanol. The photoanodes were taken out from the dye solution after 24 h and washed with acetonitrile and then dried.
Counter electrodes were prepared by first drilling holes in a separate piece of FTO glass, to be used as a filling port for the electrolyte solution. One drop of H₂PtCl₆ solution (10 mM in ethanol) was smeared on the cleaned pre-FTO counter electrode and heating to 400 °C for 20 min. The counter electrodes are cooled before being
sandwiched together with the photoanode, using a 25 μm Surlyn (Solaronix) spacer, by a hot press. The electrolyte solutions [acetonitrile=valeronitrile (85:15 vol %), 0.03 M iodine (I_2), 0.5 M 4-tertbutyl pyridine (4-tBP), 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), and 0.1 M guanidinium thiocyanate (GuSCN)] for N719 or [0.05 M iodine (Sigma), 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (Solaronix), 0.1 M lithium iodide (Sigma) in methoxypropionitrile (Sigma)] for D149 were introduced into the filling port by a vacuum back-filling technique, and the filling port was then closed with a piece of Surlyn laminated to aluminium foil.

5.2.3 Materials and devices characterizations
The crystalline structure of SANP and commercial transparent titania NR18-T were examined using X-ray diffractometer (MMA, GBC Scientific Equipment LLC, Hampshire, IL, USA, 40 kV, 30 mA, Cu Ka radiation, λ = 1.5406 Å) in the range of 2θ = 20-80°, with a scan rate of 1°/min. The morphology and internal structure were examined by transmittance electron microscopy TEM (JEOL JEM-2010). Microtrac Belsorp-mini nitrogen adsorption-desorption equipment was used to obtain specific surface area and pore volume values. The amount of N719 and D149 dyes on the different films was calculated by measuring the absorbance of dyes desorbed from the films (thickness = 5 μm, area = 1 cm²) in 4 ml of 0.1 M NaOH solution (distilled water: ethanol 1:1 v/v) for N719 or in 4 ml of 0.4 M NaOH in methanol for D149 [36, 54] using a Shimadzu UV-1800 spectrophotometer. The diffuse reflection and the optical energy gap were conducted using an integrating sphere attachment (ISR-3100) and a Shimadzu UV-3600 spectrophotometer. The isoelectric points of the materials (0.01 M aqueous dispersions with 2 < pH < 12, adjusted using either 0.25 M NaOH or 37% v/v HCl) were measured using Zetasizer Nano-ZS (MALVERN). A Shimadzu IR prestige-21 was used to measure FTIR spectra of undyed NR18-T and SANP films (3 μm thicknesses). The transmittance spectra of materials in FTIR measurements were normalized to make a reasonable comparison. A Horiba Jobin Yvon HR800, confocal Raman with a 632.8 nm laser was used to measure Raman shift of NR18-T and SANP films (3 μm). The Raman spectra were measured in the range of 100-800 cm⁻¹ wavenumber range. A SPECS PHOIBOS 100 XPS analyser was used with a high-vacuum chamber at the pressure below 10⁻⁸ mbar. X-ray beam was produced using Al Kα radiation source with energy 1486.6 eV, a high voltage of 12 kV and; a power of 144 W. The XPS binding energy spectra of SANP and NR18-T samples were recorded at the pass energies of 20 eV, step width of 0.05-0.1 eV in the
fixed analyser transmission mode. The full survey scans of SANP and NR18-T samples were measured at the pass energies of 60 eV and a step width of 0.5. Casa XPS software package was used for analysis XPS data. Thermogravimetric analysis (TGA) (STAR System, METTLER TOLEDO) was used to measure the weight loss of SANP and NR18-T powders (35 mg) in the temperature range (25-900 °C) under air. A Veeco Dektak 150 Surface Profiler was used to determine the film thicknesses. Photocurrent density-voltage (J-V) measurements were measured using a solar simulator with an AM1.5 filter; set to 1 sun (100 mW/cm², PV Measurements, Colorado). A QEX10 system from (PV Measurements) was used for the incident to photocurrent conversion efficiency (IPCE) measurements in 5 nm steps. A Reference 600 Potentiostat (GAMRY instrument) was used for electrochemical impedance spectroscopy measurements (EIS) which were carried out for DSCs based on different photoanodes under 1 sun illumination at $V_{oc}$ in a frequency range (0.1–$10^6$ Hz) and AC voltage 10 mV.

5.3 Results and discussion

5.3.1 Electron Microscopy and X-ray powder diffraction (XRD)

Images collected by Transmission Electron Microscopy (TEM, Figure 5.1 a,b) show the morphologies of solvothermally prepared nanoparticles (SANP) and commercial transparent titania nanoparticles (NR18-T). As can be seen, SANP have a more uniform, if aggregated, structure consisting of 20 ± 5 nm nanoparticles. Meanwhile, NR18-T are comprised of two particle shapes, including spindle-like particles 32 ± 6 nm long and 10 ± 2 nm diameter, as well as 10 ± 3 nm spherical nanoparticles. The insets in Figure 5.1 a,b show the shape morphologies of SANP and NR18-T. The shape of SANP is mainly attributed to the different degree of truncation of the octahedral structure during the solvothermal reaction.[57, 58] While NR18-T have two different shape morphologies, those being spindle and spherical particles. The percentage of high energy exposed (001) facets is expected to be higher for the truncated SANP shape compared to spindle NR18-T shape. These differences in SANP and NR18-T morphologies are mainly resulted from the difference in synthesis conditions.
The crystallinity of anatase phase was also confirmed by high-resolution TEM images (HRTEM) and selected area electron diffraction patterns (SAED) Figure 5.2.

The X-ray diffraction patterns (Figure 5.3) confirmed that SANP nanoparticles are phase pure anatase TiO₂ (JSPD.21-1272) with good crystallinity, which is quite similar to NR18-T. However, all the peaks of SANP are narrower than those of NR18-T indicating smaller particle size of the former.
It is noteworthy that SANP showed high crystallinity even prior to calcination and contain a significant number of micropores. Also, a uniform morphology of SANP with high surface area and appropriate pore size distribution are expected to enhance the dye loading compared to NR18-T as shown in Figure 5.4 a,b. This is suggesting it to be particularly useful in low-temperature manufactures, such as flexible DSCs. [49, 59]

In addition to being phase pure, neither sample shows any significant broad hump, which could be associated with the presence of amorphous material. This is further explored using the reference intensity ratio method (RIR). The SANP and NR18-T powders were spiked with about 10% silicon to act as an internal standard to assess the degree of crystallinity. The actual weight ratio was (90.7%:9.3%) for NR18-T: Si and
(90.3%:9.7%) for SANP: Si. While the calculated weight ratios obtained from the integrated intensities (after subtracting the background) of NR18-T: Si and SANP: Si were (90.3%:9.7 %) and (90 %:10 %) respectively (Figure 5.5). Thus, the percentage decrease of crystallinity degree, which represents the amorphous weight ratio, can be calculated as:

$$\text{Amorphous TiO}_2 \text{ (Wt\%)} = 100 \text{ (Wt\%)} - [ \frac{\text{Si}_{\text{mass}} \text{ (Wt\%)} + \text{Si}_{\text{mass}} \text{ (Wt\%)} \times \text{crystalline TiO}_2 \text{ XRD } \text{ (Wt\%)}}{\text{Si}_{\text{mass}} \text{ (Wt\%)} + \text{Si}_{\text{mass}} \text{ (Wt\%)} \times \text{crystalline TiO}_2 \text{ XRD } \text{ (Wt\%)}]}$$

Or,

\[(90.7 \%-90.3 %)/90.3 %=4 \% \text{ for NR18-T} \]

\[(90.3\%-90\%)/90\%=3 \% \text{ for synthesised SANP}\]

Both SANP and NR18-T only show XRD peaks corresponding to crystalline anatase TiO₂ and No other mineral phases were recorded, and neither sample shows any broad hump associated with amorphous material. This is confirmed using in Figure 5.5 a,b, with less than 3% amorphous determined to be present in SANP and 4% for NR18-T.[60] The quantification method used here is only to approximately estimate the amorphous material as a lower estimation method with expected errors.[61] It is therefore assumed this amorphous content would only slightly affect the dye loading capability and the charge injection on SANP or NR18-T.[62]

![Figure 5.3](image)

**Figure 5.3:** The quantification of the crystallinity degree of NR18-T and SANP using the reference intensity method (RIR).

Figure 5.6 shows the nitrogen adsorption/desorption isotherm measurements and the inset the pore size distributions of SANP, NR18-T and commercial reflector particles
WER2-O (used as scattering layer in photoanodes). SANP have a higher surface area and larger mesoporous structure observed from the larger isotherm loop compared to both NR18-T and WER2-O, while the total porosity of SANP is comparable to that of NR18-T, and these are both much higher than that of WER2-O (Table 5.1). The average pore size distribution of SANP is centred at 20 nm which is smaller than for NR18-T at 37 nm, while for WER2-O it is >120 nm which is not observed here due to equipment limitations.

![Figure 5.4: Nitrogen adsorption-desorption isotherms measurements and the inset is the pore size distribution of SANP and NR18-T samples, calculated by the Barrett-Joyner-Halenda (BJH) method.](image)

**Figure 5.4:** Nitrogen adsorption-desorption isotherms measurements and the inset is the pore size distribution of SANP and NR18-T samples, calculated by the Barrett-Joyner-Halenda (BJH) method.

**Table 5.1:** The porosity and Specific surface area of SANP, 18NR-T and WER2-O materials.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Porosity (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Surface Area (m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP</td>
<td>60</td>
<td>101</td>
</tr>
<tr>
<td>NR18-T</td>
<td>66</td>
<td>79</td>
</tr>
<tr>
<td>WER2-O</td>
<td>35</td>
<td>15</td>
</tr>
</tbody>
</table>

<sup>a</sup> The porosity calculated as \( P = \frac{P_V}{P_V + P^1}, \) where \( P_V \) is the cumulative pore volume (cm³·g⁻¹), and \( P^1 \) is the inverse of the density of anatase SANP (\( P^1 = 0.257 \) cm³·g⁻¹).[56]

It can be observed that SANP have more uniform particle distribution compared to NR18-T, resulting in the formation of a uniform porous structure compared to NR18-T as shown in Figure 5.7 a-d.
5.3.2 Solar performance for SANP sensitized with D149 organic dye
Photovoltaic performance of DSCs based on SANP photoanodes (10.0 ± 0.5 μm), were compared with those based on only NR18-T (also 10.0 ± 0.5 μm) or NR18-T (6.0 ± 0.5 μm)/WER2-O (5.0 ± 0.5 μm). 10 μm film thickness was selected as these were shown to provide the highest PCE performance in DSCs using D149 (Table 5.2, Table 5.3 and Figure 5.8). Figure 5.9 a,b; Table 5.4 and Table 5.5 show the higher PCE and IPCE maxima of DSCs devices based on SANP compared to those utilising NR18-T or NR18-T/WER2-O photoanodes. From ~400 nm to ~650 nm IPCE of SANP is consistently above the other two, in this region, LHE will be close to 100%. All devices here display similar open circuit voltages (V_{oc}). However the Fill Factors (FF) and current densities (J_{sc}, also seen in IPCE responses) are appreciably higher with the SANP photoanodes than with the other two systems tested here.
Table 5.2: Optimization of photoanode thickness based on SANP sensitized with D149.

<table>
<thead>
<tr>
<th>Device</th>
<th>( J_{sc} ) (mA·cm(^{-2}))</th>
<th>( V_{oc} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 µm SANP-D149</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>14.0</td>
<td>0.68</td>
<td>61.1</td>
<td>6.06</td>
</tr>
<tr>
<td>2</td>
<td>12.7</td>
<td>0.68</td>
<td>61.2</td>
<td>5.51</td>
</tr>
<tr>
<td>3</td>
<td>14.2</td>
<td>0.67</td>
<td>59.7</td>
<td>6.14</td>
</tr>
<tr>
<td>4</td>
<td>12.9</td>
<td>0.67</td>
<td>61.4</td>
<td>5.56</td>
</tr>
<tr>
<td>Average</td>
<td>13.5 ± 0.7</td>
<td>0.68 ± 0.01</td>
<td>60.8 ± 0.8</td>
<td>5.82 ± 0.33</td>
</tr>
<tr>
<td>10 µm SANP-D149</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>17.1</td>
<td>0.67</td>
<td>63.6</td>
<td>7.02</td>
</tr>
<tr>
<td>2</td>
<td>16.5</td>
<td>0.68</td>
<td>63.2</td>
<td>6.85</td>
</tr>
<tr>
<td>3</td>
<td>17.2</td>
<td>0.65</td>
<td>63.8</td>
<td>6.72</td>
</tr>
<tr>
<td>4</td>
<td>16.7</td>
<td>0.66</td>
<td>63.2</td>
<td>6.80</td>
</tr>
<tr>
<td>Average</td>
<td>16.9 ± 0.3</td>
<td>0.66 ± 0.01</td>
<td>63.5 ± 0.3</td>
<td>6.91 ± 0.12</td>
</tr>
<tr>
<td>12 µm SANP-D149</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15.3</td>
<td>0.68</td>
<td>55.8</td>
<td>6.15</td>
</tr>
<tr>
<td>2</td>
<td>16.3</td>
<td>0.68</td>
<td>59.2</td>
<td>6.15</td>
</tr>
<tr>
<td>3</td>
<td>15.8</td>
<td>0.67</td>
<td>60.3</td>
<td>6.00</td>
</tr>
<tr>
<td>4</td>
<td>15.9</td>
<td>0.67</td>
<td>55.3</td>
<td>6.00</td>
</tr>
<tr>
<td>Average</td>
<td>15.6 ± 0.4</td>
<td>0.67 ± 0.01</td>
<td>57.7 ± 2.5</td>
<td>6.08 ± 0.08</td>
</tr>
<tr>
<td>11 µm SANP/WER2-OD149</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>14.9</td>
<td>0.69</td>
<td>58.6</td>
<td>5.80</td>
</tr>
<tr>
<td>2</td>
<td>13.7</td>
<td>0.68</td>
<td>55.3</td>
<td>5.58</td>
</tr>
<tr>
<td>3</td>
<td>13.7</td>
<td>0.69</td>
<td>56.4</td>
<td>5.75</td>
</tr>
<tr>
<td>4</td>
<td>14.9</td>
<td>0.69</td>
<td>55.4</td>
<td>5.71</td>
</tr>
<tr>
<td>Average</td>
<td>14.9 ± 0.6</td>
<td>0.69 ± 0.01</td>
<td>56.4 ± 1.5</td>
<td>5.71 ± 0.10</td>
</tr>
</tbody>
</table>

Table 5.3: J-V parameters of devices based on optimized SANP sensitized with D149.

<table>
<thead>
<tr>
<th>Device</th>
<th>( J_{sc} ) (mA·cm(^{-2}))</th>
<th>( V_{oc} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP-8 µm</td>
<td>13.5 ± 0.7</td>
<td>0.68 ± 0.01</td>
<td>57.6 ± 2.5</td>
<td>5.82 ± 0.30</td>
</tr>
<tr>
<td>SANP-10 µm</td>
<td>16.9 ± 0.3</td>
<td>0.66 ± 0.01</td>
<td>63.5 ± 0.3</td>
<td>6.91 ± 0.13</td>
</tr>
<tr>
<td>SANP-12 µm</td>
<td>15.6 ± 0.4</td>
<td>0.67 ± 0.01</td>
<td>61.5 ± 0.7</td>
<td>6.10 ± 0.10</td>
</tr>
<tr>
<td>SANP/WER2-O-11 µm</td>
<td>14.9 ± 0.7</td>
<td>0.69 ± 0.01</td>
<td>56.5 ± 1.5</td>
<td>5.71 ± 0.10</td>
</tr>
</tbody>
</table>
$J_{sc}$ is determined by the combination of three factors, specifically, the charge injection efficiency ($\Phi_{inj}$), the charge collection efficiency ($\Phi_{cc}$) and the Light Harvesting Efficiency (LHE), which is itself dependent on dye absorption coefficients, dye loading and light scattering ability, as this affects the pathlength of light. It seems reasonable to assume that the charge injection efficiency ($\Phi_{inj}$) will be similar between dyes on SANP and NR18-T (of course there may be reasons for this not to be the case), while the charge collection efficiency ($\Phi_{cc}$) is assumed to be slightly higher for SANP photoanode based on Electrochemical Impedance Spectroscopy (EIS) results below.

The LHE of SANP, compared to NR18-T and WER2-O, sensitized with D149 was investigated by using the quantified amount of desorbed dye from the photoanodes films (area = 1 cm$^2$, thickness = 5 μm, which was desorbed in 4 ml of 0.4 M NaOH in methanol) (Figure 5.10 a, Table 5.6) (overnight dyeing time was employed to ensure the equilibrium was attained, c.f. Kim et al.).[32] Figure 5.10 a,b show a lower-bound estimate of the LHE, based on the dye loading results. According to this, the LHE of the dyed SANP films is higher than those of NR18-T or WER2-O (with more broadening toward 700 nm) which enable it to harvest more light in this range. SANP films show higher dye loading compared to NR18-T and NR18-T/WER2-O photoanodes, when normalised against the surface area to give dye packing (dyes nm$^{-2}$), SANP again was shown to have superior dye hosting abilities, compared to NR18-T and WER2-O. This is attributed to having a higher IEP, which favours the binding of negatively charged

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**Figure 5.6:** (a) J-V characteristics measured under 1 sun illumination with an area of 0.16 cm$^2$ and; (b) The incident photon to current conversion efficiency (IPCE).
dyes, as the surface is itself positively charged [25, 26]. IEP obtained from Zeta potential measurements as shown in (Figure 5.11 a). In addition to this, undyed SANP films showed higher diffuse reflection than that of NR18-T although lower than that of WER2-O films (Figure 5.11 b), indicating good light scattering, and extended pathlength of light though SANP films compared to NRA8-T. Figure 5.11 c shows the photographs of the three undyed photoanode configurations. This data was transposed to form Tauc plots (Figure 5.11 d), which shows no significant differences in terms of the optical bandgap of these materials.

**Table 5.4:** J-V parameters details of devices based on synthesized SANP, NR18-T and NR18-T/WER2-O sensitized with D149.

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP</td>
<td>D149 (10 µm)</td>
<td>1</td>
<td>17.1</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>16.5</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>17.2</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>16.7</td>
<td>0.66</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>16.9 ± 0.3</td>
<td>0.66 ± 0.01</td>
</tr>
<tr>
<td>NR18-T</td>
<td>D149 (10 µm)</td>
<td>1</td>
<td>14.0</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>15.0</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>15.1</td>
<td>0.67</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>14.7 ± 0.6</td>
<td>0.67 ± 0.01</td>
</tr>
<tr>
<td>NR18/WER2-O</td>
<td>D149 (11 µm)</td>
<td>1</td>
<td>16.0</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>15.6</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>16.1</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>15.1</td>
<td>0.68</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>15.7 ± 0.4</td>
<td>0.66 ± 0.02</td>
</tr>
</tbody>
</table>

**Table 5.5:** J-V parameters of devices based on SANP, 18NR-Tand 18NR-T/WER2-O sensitized with D149.

<table>
<thead>
<tr>
<th>D149 Devices</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP</td>
<td>16.9 ± 0.3</td>
<td>0.66 ± 0.01</td>
<td>64 ± 1</td>
<td>6.9 ± 0.1</td>
</tr>
<tr>
<td>NR18-T</td>
<td>14.7 ± 0.6</td>
<td>0.66 ± 0.01</td>
<td>58 ± 2</td>
<td>5.6 ± 0.2</td>
</tr>
<tr>
<td>NR18-T/WER2-O</td>
<td>15.7 ± 0.4</td>
<td>0.66 ± 0.02</td>
<td>55 ± 2</td>
<td>5.9 ± 0.3</td>
</tr>
</tbody>
</table>
Table 5.6: The amount of D149 dye loading on SANP, 18NR-Tand films (thickness = 5.0 ± 0.3 µm; Area = 1 cm²) calculated using desorption method. [63]

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>D149 loading (nmol·cm⁻²)</th>
<th>D149 loading (µmol·cm⁻²)</th>
<th>D149 loading (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP</td>
<td>72 ± 1.5</td>
<td>111 ± 2</td>
<td>1.8</td>
</tr>
<tr>
<td>NR18-T</td>
<td>65 ± 0.6</td>
<td>99 ± 1</td>
<td>1.3</td>
</tr>
<tr>
<td>WER2-O</td>
<td>23 ± 0.2</td>
<td>36 ± 1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Figure 5.9: (a) J-V characteristics measured under 1 sun illumination with an area of 0.16 cm²; (b) The incident photon to current conversion efficiency (IPCE); of SANP, NR18-T and NR18/WER2-O based D149 devices.

Figure 5.10: (a) The absorbance spectra of desorbed D149 dye from SANP, NR18-T and WER2-O films using 4 ml of 0.4 M NaOH in methanol, film thickness = 5.0 ± 0.3 µm and film area = 1 cm²; (b) The quantified light harvesting efficiency of D149 desorbed on SANP, NR18-T and WER2-O films.
In addition to examining the phase and crystallinity of the materials, Raman spectroscopy can also provide information about the percentage of specific exposed (001) facets of anatase. This can be quantified from the relative intensity ratios of $E_g^1$ and $A_{1g}$ vibrational modes in Raman spectra, typically from the relative ratio of $E_g^1$ at 144 cm$^{-1}$ and $A_{1g}$ at 513 cm$^{-1}$ vibrational modes ($A_{1g}/E_g^1$). This is of interest as a possible explanation for the significant difference in IEP between SANP and the other TiO$_2$ materials. Figure 5.12 shows Raman spectra of both samples collected in the range of (100-800 cm$^{-1}$). Gaussian fits were applied for the ease of comparison to calculate the Full Width at Half Maximum (FWHM) of all vibration modes. Raman spectra of anatase TiO$_2$ is distinguished by six allowed vibrational

**Figure 5.7:** (a) Isoelectric point (IEP) measurements of SANP, NR18-T and WER2-O in aqueous solutions (0.01 M) using different pH values; (b) Diffuse reflections of SANP, NR18-T and WER2-O films (10.0 ± 0.3 µm thick); (c) The visual image of photoanode films; and (d) The optical band gap ($E_g$) measurements (Tuac plot) of SANP, NR18-T and WER2-O films (10.0±0.3 µm thick)

### 5.3.3 Raman Analysis

In addition to examining the phase and crystallinity of the materials, Raman spectroscopy can also provide information about the percentage of specific exposed (001) facets of anatase. This can be quantified from the relative intensity ratios of $E_g^1$ and $A_{1g}$ vibrational modes in Raman spectra, typically from the relative ratio of $E_g^1$ at 144 cm$^{-1}$ and $A_{1g}$ at 513 cm$^{-1}$ vibrational modes ($A_{1g}/E_g^1$). This is of interest as a possible explanation for the significant difference in IEP between SANP and the other TiO$_2$ materials. Figure 5.12 shows Raman spectra of both samples collected in the range of (100-800 cm$^{-1}$). Gaussian fits were applied for the ease of comparison to calculate the Full Width at Half Maximum (FWHM) of all vibration modes. Raman spectra of anatase TiO$_2$ is distinguished by six allowed vibrational
modes centered at 144 cm$^{-1}$ ($E_g(1)$), 197 cm$^{-1}$ ($E_g(2)$), 399 cm$^{-1}$ ($B_{1g}$), 513 cm$^{-1}$ ($A_{1g}$), 519 cm$^{-1}$ ($B_{1g}$), and 639 cm$^{-1}$ ($E_g(3)$).[65] All active vibrational modes were detected in both SANP and NR18-T, with the good agreement to previously reported values, [66] SANP showed less peak broadening compared to NR18-T which is correlated with smaller particle size, indicating better crystallinity compared to NR18-T.

The percentage of exposed (001) facets of SANP and NR18-T are quantified to be 8% and 7% respectively. While the slightly higher percentage of exposed facets (001) of SANP may slightly affect the IEP (and the number of available binding sites), this is not enough of a difference to explain the ~40% difference in dye packing density.[44]

5.3.4 Fourier transform infrared spectroscopy (FTIR) analysis

Attenuated Total Reflectance-Fourier transform infrared spectroscopy (AT-FTIR) spectroscopy was employed to examine the active surface binding sites on undyed SANP and NR18-T films.

Figure 5.13 a shows the ATR-FTIR spectra of SANP and NR18-T. The band at 3330 cm$^{-1}$ is the broadest in each sample (slightly broader in SANP than NR18-T) and corresponds to the stretching vibration of the hydroxyl group (OH). The band at 1637 cm$^{-1}$ corresponds to bending modes of Ti-OH, while the two peaks at 1550 cm$^{-1}$ and 1417 cm$^{-1}$ observed in SANP originate from the asymmetric and symmetric stretching of carboxylic groups, which are typically seen for TiO$_2$ synthesised using acidic precursor solutions and calcined at only relatively low temperatures (100-250 °C).[67-
The asymmetric carboxylic group coordinated with Ti (1417 cm\(^{-1}\)), as claimed, can be observed even after high sintering temperature.[70] On the other hand, the bands 1637 cm\(^{-1}\) and 1417 cm\(^{-1}\), corresponding to Ti-OH and symmetric COOH were also observed in NR18-T while the asymmetric COOH was significantly smaller.

As acetic acid was involved in SANP synthesis, it is possible that this could remain, adsorbed on TiO\(_2\) surface by a strong bidentate mode, resulting in Ti-COOH bond.[71, 72] During the dye adsorption process, these would presumably be replaced by the carboxylic acid groups on the dye itself, however the specific mechanism and its relation to IEP and charge injection are still not fully understood and will be the subject of further investigation. There also arose a degree of ambiguity from FTIR results, as to whether the observed species are residual groups following synthesis (and a 500°C sintering process) or adsorbed from the atmosphere due to the high IEP providing a favourable substrate for the binding of CO\(_2\)/H\(_2\)O. In order to address this, mass losses in SANP and NR18-T were measured up to 900 °C using thermogravimetric analysis (TGA), as shown in Figure 5.13 b. At lower temperatures (100-400 °C) SANP shows more substantial mass loss than NR18-T, which is ascribed to adsorbed H\(_2\)O. Above this, in the range of 400-600 °C, the mass of SANP was more stable, while a gradual decrease in NR18-T was observed.[69] The notable weight loss observed in SANP above 700 °C, well above the temperatures experienced during device production, indicates the removal of some strongly bound residuals. Unfortunately, we are unable to confirm the identity of this with our present setup, although it seems most likely to be COOH, in line with observations from FTIR analysis. This residual organic component, which exist in SANP after synthesis, but are not observed in NR18-T, appear to play a role in enhancing the SANP surface reactivity and hence the dye packing density. [69]
5.3.5 X-ray photoelectron spectroscopy analysis (XPS)

The surface compositions and the chemical states of SANP and NR18-T were further examined using X-ray photoelectron spectroscopy (XPS) measurements in order to investigate the surface functionality of SANP and NR18-T. XPS spectra were measured in range (260–550 eV). Figure 5.14 shows the spectra of SANP and NR18-T where the peaks of Ti, O and C are observed for both samples. These peaks (Ti, O) are in good agreement with anatase TiO$_2$.[73] Whereas Figures 5.15 a,b show the high-resolution spectra of (Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$) at 458 eV and 464 eV respectively which correspond to Ti 2p representing the Ti$^{4+}$ oxidation state.[74]

The O 1s peaks at 529 and 530.6 eV were assigned to Ti-O and OH respectively.[75] It can be noted that the relative amount of OH to O in SANP (64% vs 36%) is higher than that of NR18-T (52% vs 48%) as shown in Figure 5.15 c,d. These results are consistent with FTIR, however, these differences are not sufficient to explain the dye packing differences.

From FTIR, TGA and XPS analysis SANP have a higher amount of adsorbed OH along with presence asymmetric carboxylic group compared to NR18-T due to probably the use of acetic acid with ethanol as a mixed solvent in the solvothermal reaction. This can increase isoelectric point resulted from the more positive surface charge on SANP; and thus can promote more dye adsorption leading to higher dye packing density.
Figure 5.11: XPS survey of SANP and NR18-T materials.

Figure 5.10: XPS spectra of (a,b) Ti 2p and (c,d) O 1s of; SANP and NR18-T.
5.3.6 Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were carried out on D149 devices under 1 sun illumination, to compare electron transfer rates and lifetimes. The results are shown in Nyquist and Bode plots in Figures 5.16 a,b respectively, with fittings in Figure 5.17). These fits utilised the model proposed by Bisquert and co-workers, [76, 77] with parameters shown in Table 5.7. Here, $R_s$ is the series resistance, $R_{ct1}$ and $R_{ct2}$ are represent the charge transfer resistance at the counter and the working electrode respectively, while $CPE_1$ and $CPE_2$ are the constant phase elements associated with the counter and working electrodes respectively. In all Nyquist plots, two semicircles were observed, with the first, corresponding to high frequencies, representing charge transfer resistance at the counter electrode/electrolyte interface ($R_{ct1}$). As expected these were similar for all devices tested. The second semicircle (mid-range and low frequencies), represents the impedance of the interface between the photoanode material and liquid electrolyte in competition with the transfer of injected electrons through the photoanode material ($R_{ct2}$).[76, 78] Devices based on SANP have a slightly lower electrochemical impedance to charge transport through photoanodes compared to those of NR18-T and NR18-T/WER2-O photoanodes (Table 5.7). Bode plots, in Figure 5.16b, reveal that the local impedance maxima ($f_{max}$, low frequencies) of SANP based devices occurs at a lower frequency (16 Hz) compared to those using either NR18-T and NR18-T/WER2-O, which are at 25 Hz. Subsequently, electron lifetimes calculated as $\tau_n = \frac{1}{2\pi f_{max}}$[79], are seen to be slightly longer indicative of reduced electron recombination, which is in line with higher FF values. Devices based on SANP also have higher chemical capacitance ($C_{µ}$) values compared to NR18-T and NR18-T/WER2-O, indicating higher electron density (i.e. this should be expected due to the higher surface area of SANP).[36] The EIS measurements indicate that SANP devices have better charge collection efficiency ($\Phi_{cc}$) compared to NR18-T and NR18-T/WER2-O devices.
Table 5.7: EIS parameters of devices based on SANP, 18NR-T and 18NR-T/WER2-O sensitized with a D149 dye.

<table>
<thead>
<tr>
<th>D149 Devices</th>
<th>$R_s$ (Ω·cm$^{-2}$)</th>
<th>$R_{ct1}$ (Ω·cm$^{-2}$)</th>
<th>$R_{ct2}$ (Ω·cm$^{-2}$)</th>
<th>$C_µ$ (µF·m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP</td>
<td>4.6 ± 0.1</td>
<td>2.3 ± 0.2</td>
<td>21.1 ± 0.3</td>
<td>1550 ± 100</td>
</tr>
<tr>
<td>NR18-T</td>
<td>4.8 ± 0.1</td>
<td>2.4 ± 0.1</td>
<td>24.9 ± 0.3</td>
<td>1370 ± 100</td>
</tr>
<tr>
<td>NR18-T/WER2-O</td>
<td>4.6 ± 0.1</td>
<td>2.2 ± 0.2</td>
<td>25.3 ± 0.3</td>
<td>1000 ± 80</td>
</tr>
</tbody>
</table>

Figure 5.12: EIS measurements (a) Nyquist and (b) Bode plots of devices based on SANP, 18NR-T and 18NR-T/WER2-O sensitized with a D149 dye.

Figure 5.13: EIS Nyquist plots fitting for devices based on SANP, NR18-T and NR18-T/WER2-O photoanodes sensitized with D149 dye.
As was discussed above, and shown in Figure 5.10, the LHE across a large portion of the spectrum (350 < 620 nm) is near unity for all the films presented here. Additionally, the $\Phi_{cc}$ of SANP devices is only slightly higher, while the peak IPCE values are significantly more for devices with SANP compared to NR18-T or bilayer films, suggesting that $\Phi_{inj}$ is higher on SANP and therefore, the main reasons for the improvement in SANP/D149 performance. [80, 81]

5.3.7 Solar performance for SANP sensitized with N719 dye

Devices based on the three photoanode configurations were also produced and characterised using N719 to investigate the effects of dye packing density, charge injection, charge collection on the DSC performance using such low extinction coefficient dye (Figures 5.18 a,b, and Tables 5.8 and 5.9). Here the SANP again showed slightly higher photocurrents $J_{sc}$ as compared to devices based on transparent NR18-T photoanodes and comparable ones to those of devices based on NR18-T/WER2-O. It was also again observed that the use of SANP results in higher dye loading values, again attributed to higher surface area and packing density (c.f IEP, Figure 5.11 a, and dye loading measurements below in Figures 5.19 a,b and Table 5.10). For consistency with the above section, the same TiO$_2$ film thicknesses (10 $\mu$m) were employed and also the overnight dyeing time was employed to ensure the equilibrium was attained. Figure 5.19 a,b show a lower-bound estimate of the LHE, based on N719 dye loading results. According to this, the LHE of the dyed SANP films is higher than that WER2-O (with more broadening toward 700 nm) which enable it to harvest more light in this range, however, it is similar to that of NR18-T with slightly increase in the range of 700-800 nm. As can be seen from devices based on SANP photoanodes showed average PCEs of 7.7%, higher than for devices based on transparent NR18-T photoanodes (7.2%) and the same (within one standard deviation) as devices employing the scattering layer (NR18-T/WER2-O, 7.9%).

The peak IPCE of SANP based devices is higher than that of NR18-T and the same, within experimental uncertainty, to that of devices based on NR18-T/WER2-O. On the other hand, devices using the latter photoanodes showed a broadening of the response into the range of 600-750 nm, due to the superior scattering effect of large reflector particles (WER2-O, refer back to Figure 5.11 b). All devices show similar $V_{oc}$ while SANP based devices showed slightly lower FF than others. The slightly lower FF of SANP/N719 based devices suggests possible higher charge recombination compared to others. This is investigated in more depth below, with EIS again being employed to
probe charge transport properties.

Figure 5.14: (a,b) J-V characteristics measured under 1 sun illumination with an area of 0.16 cm² and the incident photon to current conversion efficiency (IPCE); (c,d) EIS measurements (c) Nyquist and (d) Bode plots of devices based on SANP, NR18-T and NR18/WER2-O photoanodes sensitized with N719 dye.

Table 5.8: J-V parameters details of devices based on synthesized SANP, NR18-T and NR18-T/WER2-O sensitized with N719 dye.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA·cm⁻²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>**SANP</td>
<td>N719 (10 µm)**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15.5</td>
<td>0.72</td>
<td>70.3</td>
<td>7.88</td>
</tr>
<tr>
<td>2</td>
<td>15.3</td>
<td>0.71</td>
<td>70.1</td>
<td>7.68</td>
</tr>
<tr>
<td>3</td>
<td>15.9</td>
<td>0.69</td>
<td>69.5</td>
<td>7.64</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>15.6 ± 0.3</td>
<td>0.71 ± 0.02</td>
<td>69.9 ± 0.41</td>
<td>7.73 ± 0.13</td>
</tr>
<tr>
<td>**NR18-T</td>
<td>N719 (10 µm)**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>14.8</td>
<td>0.68</td>
<td>73.2</td>
<td>7.35</td>
</tr>
<tr>
<td>2</td>
<td>14.4</td>
<td>0.68</td>
<td>73.5</td>
<td>7.20</td>
</tr>
<tr>
<td>3</td>
<td>14.1</td>
<td>0.70</td>
<td>72.3</td>
<td>7.16</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>14.4 ± 0.4</td>
<td>0.69 ± 0.02</td>
<td>73.0 ± 0.6</td>
<td>7.23 ± 0.10</td>
</tr>
<tr>
<td>**NR18/WER2-O</td>
<td>N719 (15 µm)**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>14.9</td>
<td>0.72</td>
<td>73.0</td>
<td>7.90</td>
</tr>
<tr>
<td>2</td>
<td>16.0</td>
<td>0.71</td>
<td>72.6</td>
<td>8.20</td>
</tr>
<tr>
<td>3</td>
<td>15.2</td>
<td>0.69</td>
<td>73.0</td>
<td>7.65</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>15.37 ± 0.57</td>
<td>0.71 ± 0.02</td>
<td>72.8 ± 0.4</td>
<td>7.91 ± 0.28</td>
</tr>
<tr>
<td><strong>STDEV</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.9: J-V parameters of devices based on SANP, 18NR-T and 18NR-T/WER2-O sensitized with an N719 dye.

<table>
<thead>
<tr>
<th>N719 Devices</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP</td>
<td>15.6±0.3</td>
<td>0.71±0.01</td>
<td>70.0±0.4</td>
<td>7.73±0.13</td>
</tr>
<tr>
<td>NR18-T</td>
<td>14.4±0.3</td>
<td>0.69±0.01</td>
<td>73.0±0.6</td>
<td>7.23±0.10</td>
</tr>
<tr>
<td>NR18-T/WER2-O</td>
<td>15.4±0.6</td>
<td>0.71±0.02</td>
<td>73.0±0.4</td>
<td>7.91±0.28</td>
</tr>
</tbody>
</table>

Table 5.10: N719 dye loading measurements of SANP, 18NR-T and WER2-O films (thickness = 5 ± 0.3 µm; Area =1 cm$^2$).

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>N719 loading (nmol cm$^{-2}$)</th>
<th>N719 loading (µmol cm$^{-3}$)</th>
<th>N719 loading (nm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP</td>
<td>67 ± 2</td>
<td>106 ± 2</td>
<td>1.9</td>
</tr>
<tr>
<td>NR18-T</td>
<td>58 ± 1</td>
<td>93 ± 1</td>
<td>1.4</td>
</tr>
<tr>
<td>WER2-O</td>
<td>20 ± 1</td>
<td>31 ± 1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 5.15: The absorbance spectra of desorbed N719 dye from SANP, NR18-T and WER2-O films (5 ± 0.3 µm thick); dye desorbed spectra from three films for each.

Nyquist plots for N719 sensitised DSCs (Figure 5.20 a,b, Figure 5.21 and Table 5.11) confirm SANP devices to have higher charge transport resistance ($R_{ct2}$) compared to NR18-T and NR18-T/WER2-O based devices. On the other hand, all N719 devices showed the same $f_{max}$ of 25 Hz in Bode plots seen in Figure 5.20 b, indicating that the electron lifetimes ($\tau_n$) are approximately the same. The higher recombination rate, related to lower FF in SANP photoanodes, may be attributable to the higher surface area of SANP nanoparticles [13, 82], although there is no significant difference in the chemical capacitance values ($C_p$) for any of the N719 devices, indicating similar charge
density through photoanodes materials. It is worthy of mentioning that there is a trend off in the recombination rate in N719 and D149 based devices. The lower recombination rate (higher FF) observed in D149 devices may be attributed to the higher charge injection, however, more investigation is required as future work for further understanding. It has been shown that N719 is effective at blocking electron recombination, limiting the access of I$_3^-$ to open space on the TiO$_2$ surface. The same is not necessarily true normally with organic dyes such as D149, and as such, it can be conjectured that the higher dye loading of D149 on SANP may provide a more substantive benefit in terms of blocking possible recombination sites. In addition to this, while high dye loading has also been shown to lead to aggregation, with negative impacts upon device performance, this does not appear to be a major issue here.

Table 5.11: EIS parameters of devices based on SANP, 18NR-T and 18NR-T/WER2-O photoanodes sensitized with N719 dye.

<table>
<thead>
<tr>
<th>N719 Devices</th>
<th>$R_s$ (Ω·cm$^{-2}$)</th>
<th>$R_{ct1}$ (Ω·cm$^{-2}$)</th>
<th>$R_{ct2}$ (Ω·cm$^{-2}$)</th>
<th>$C_µ$ (µF·m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP</td>
<td>5.8 ± 0.1</td>
<td>2.0 ± 0.1</td>
<td>24.1 ± 0.3</td>
<td>800 ± 50</td>
</tr>
<tr>
<td>NR18-T</td>
<td>5.8 ± 0.1</td>
<td>2.0 ± 0.2</td>
<td>19.9 ± 0.3</td>
<td>910 ± 60</td>
</tr>
<tr>
<td>NR18-T/WER2-O</td>
<td>6.0 ± 0.1</td>
<td>2.0 ± 0.2</td>
<td>18.1 ± 0.4</td>
<td>780 ± 90</td>
</tr>
</tbody>
</table>

Figure 5.16: EIS measurements (a) Nyquist and (b) Bode plots of devices based on SANP, NR18-T and NR18/WER2-O photoanodes sensitized with N719 dye.
Devices based on SANP|D149 showed better photovoltaic performance (higher $J_{sc}$ and FF with consistent $V_{oc}$) compared to devices based on NR18-T/D149 and NR18-T/WER2-O/D149 due to higher light harvesting efficiency and lower recombination rate with longer electron lifetime. As for SANP|N719 devices, they showed higher performance compared to NR18-T|N719 while it is slightly lower than NR18-T/WER2-O|N719 due to the higher recombination (charge collection efficiency $\Phi_{cc}$) even with similar $\tau_n$, due to higher charge transfer resistance at SANP/dye/electrolyte interfaces. In spite of the particles interfaces resulted from higher surface area of SANP can increase the charge retransfer resistance, it is also the more dye coverage seen on SANP can reduce the recombination with electrolyte as the dye layer works as a barrier between the semiconductor and the electrolyte.[62] However, the slightly higher performance of NR18-T/WER2-O|N719 is mainly attributed to the lower charge recombination (slightly higher FF).

The comparable device performances of SANP|N719 compared to NR18-T/WER2-O|N719 is attributed to similar (IPCE max, LHE and $\Phi_{cc}$) assuming similar $\Phi_{inj}$.

The enhanced performance of DSCs based SANP|D149 compared to those using commercial TiO$_2$ is mainly attributed to the higher $\Phi_{inj}$, higher IEP and higher surface area which enables efficient dye loading/packing density. The IEP of SANP is probably enhanced as a result of the solvothermal synthesis process using a mixed solvent of
acetic acid and ethanol. This approach can be used to increase the dye packing density and thus enhance the charge injection in DSC. Further investigation is required for more understanding to the reasons why D149 devices are expected to show higher charge injection in term of affecting the residual chemical or adsorbed species observed in FTIR, TGA and XPS on the dye loading/binding and thus $J_{sc}$. This could be investigated for devices based on very thin films as a future application.

5.4 Conclusion

TiO$_2$ nanoparticles were synthesized by a new and facile solvothermal method, with large specific surface area and high IEP, both of which favour dye loading. SANP photoanodes showed reasonable light scattering due to aggregation. From LHE, EIS and IPCE, it appears that SANP devices showed higher charge injection which is led to higher $J_{sc}$ for devices based on only nanoparticles photoanode compared to devices based on a commercial transparent NR18-T nanoparticles photoanode or bilayer photoanode consisted of transparent nanoparticles and large scattering particles NR18-T/WER2-O sensitized with metal-free organic dye (D149). In addition, SANP|D149 devices showed longer electron lifetimes and lower charge transfer resistance through the TiO$_2$ network resulting in slightly enhancement in the charge collection. As the IPCEs of SANP|D149 are higher than those of NR18-T or NR18-T/WER2-O across a fairly broad region, and by a consistent amount, this suggests differences in charge injection efficiency. It is however not clear why this would be the case, and why the same would not be true of N719. This is an area of continued research. Devices based on 10 µm SANP|N719 did show higher $J_{sc}$ and efficiencies, compared to NR18-T|N719, in spite of slightly lower FF values. This was largely attributed to light scattering effects, which are more pronounced when using low extinction co-efficient dyes.

The synthesis procedure using a mixed solvents ethanol and acetic acid (2:1 v/v) used here produced SANP with higher IEP along with higher surface area which enabled higher dye packing density and thereby enhanced the DSC performance. This work sheds light on the role of the IEP of synthesized TiO$_2$ metal oxide on DSC performance which may also be useful for other applications required more reactive surface materials.
5.5 References


Chapter 6

6 A comparative study of TiO₂ paste preparation methods using solvothermally synthesised anatase nanoparticles in Dye-Sensitised Solar Cells

This chapter is based on a published work [K. Al-Attafi, A. Nattestad, S.X. Dou, and J.H. Kim, A Comparative Study of TiO₂ Paste Preparation Methods Using Solvothermally Synthesised Anatase Nanoparticles in Dye-Sensitised Solar Cells. Applied Sciences, 2019. 9(5): p. 979], with contributions of other co-authors as follows: K. Al-Attafi, A. Nattestad, and J. Kim designed experiments. K. Al-Attafi performed synthesis experiments, TEM, SEM, XRD, BET and DSC measurements and wrote the manuscript. K. Al-Attafi, A. Nattestad, and J. Kim analyzed the data and revised the manuscript. A. Nattestad., J. Kim, and S. Dou supervised the work. All authors discussed the results and contributed to revisions.

DSCs continue to be a promising photovoltaic technology for indoor and outdoor applications, with increased interest in power window applications integrated into buildings. This results from properties not seen in other, more established solar technologies, such as the range of available colours, partial transparency and good performance under low light intensities or in partial shade. In spite of the attractiveness of this application and the commercial availability of suitable non-scattering TiO₂ materials, the vast majority of new TiO₂ materials being developed and reported in the literature are dried prior to being made into a paste and subsequently into photoanode films. In this Chapter, a detailed side-by-side comparison of different paste-forming techniques, with one yielding scattering films, and the other yielding non-scattering films was presented. The effects of these two paste preparation approaches on the performance of DSCs based on TiO₂ nanoparticles sensitised with organic or organometallic dyes have been compared to understand the differences in the performances of the devices using these two typical dyes. Devices utilising the organic dye D149 showed comparable performance using both approaches (6.9% photovoltaic conversion efficiency (PCE) with drying versus 6.4% PCE without drying), while the difference was slightly more marked with the dye N719 (7.7% PCE versus 6.8% PCE), suggesting that the trade-off in light harvesting required for power windows may be
acceptably small. We also discuss ways by which these differences may be further decreased.

6.1 Introduction

In spite of recent developments in new photovoltaic technologies and decreases in the cost of mature ones,[1-4] DSCs are still of interest to both researchers and industry. This is at least in part due to their application in large-scale built-in photovoltaics (BIPV) as power windows, due to features such as transparency and the range of dye colours which may be employed. Additionally, DSCs are expected to find significant use in indoor applications in the near future, for which efficiencies over 28% using artificial lighting have already been reported [5], where the DSC absorption spectra was tuned to better match the light source used. DSCs also have a benefit in that they are not significantly affected by partial shading, changes in temperature or the light incident angle, as silicon solar cells tend to be.[5-8]

TiO₂ photoanodes can be fabricated with different degrees of transparency, depending on the particle size and the paste preparation process.[9, 10] Well-dispersed, small particles can result in a high transmission photoanode (>80%) across the visible range.[11] On the other hand, light scattering is a widely employed technique to increase the mean pathlength of photons through the photoanode, leading to an increased likelihood of said photons being absorbed by bound dyes.[11-13] This is particularly pertinent when the extinction co-efficient of the dye is low, and simply making the photoanode film thicker leads to increased charge recombination. Indeed, many researchers have intentionally tuned the light scattering properties of their particles to enhance the light-harvesting efficiency (LHE). [10, 14-16] However, this is less necessary because of recent developments in sensitiser design and is not desirable for most BIPV applications.

A large portion of work published on DSC development (~40%, which equates to more than 1200 publications) has been on the synthesis and/or modification of metal oxides, mostly TiO₂, as efficient photoanode materials.[17] The vast majority of synthesised TiO₂ nanoparticles in these reports were dried, calcined and then re-dispersed to make a printable paste [14, 18, 19]. While a handful of exceptions exists where the nanoparticles were kept in suspension after their synthesis [7, 10, 11], producing a transparent film due to the high nanoparticle dispersion.

In 2008 Ito et al. reported high-efficiency DSC based on TiO₂ nanoparticles, with
solvent transfer from the synthetic medium to the screen-printing paste matrix, where the TiO$_2$ was sensitized with the ruthenium complex N719. In this case, both small particle (transparent) and a second layer of larger, scattering particles were employed, as well as an anti-reflective film. The optimum thickness of a bi-layer photoanode including a transparent layer and a large scattering layer was 12–14 μm, and photovoltaic conversion efficiencies (PCEs) of 9.1% and 10% were reported for the transparent photoanode- and bi-layer (scattering) photoanode-based devices, respectively.[10] A few years later, Yoon et al. investigated the effect of photoanode transparency and thickness on DSC performance for BIPV application. Using a protocol without drying their nanoparticles, they were able to obtain a printable paste and then deposit a transparent photoanode, which was subsequently sensitised with N719. Their best PCEs were 5.13% and 6.64% for photoanode thicknesses 8.13 μm and 32.2 μm, respectively.[7] More recently, Sanchez et al. provided further insight as they studied the effect of autoclave pressure in hydrothermal synthesis on the pore and particle sizes of non-scattering TiO$_2$ photoanodes, again sensitised with the N719 dye, with an optimized PCE of 5.63%.[20]

Until recently, the organometallic dye N719 has been a staple of DSC research, in spite of high production costs and the low extinction coefficient.[21] Metal-free organic dyes have attracted attention, including application in record PCE devices. [21-23] The indole-based metal-free dye D149 is one of the most widely reported organic dyes and is commercially available.[24, 25]

There is, to our knowledge, only one report comparing the two paste-making approaches, and while this article makes direct comparisons regarding the photoanode transparency, it does not look at the solar cell performance of the devices with photoanodes made with the same material but through different processes.[11] In 2017, Zama et al. used a wet-acid method and rotary evaporation to obtain the paste directly from a nanoparticle suspension after thermal treatment by adding organic binders and solvents in suitable ratios. They produced another paste in a similar way but included a drying step. They discussed the effect of using two paste preparation approaches on the transparency and surface morphology of TiO$_2$ photoanode; however, there was no direct comparison of the performance of DSCs using these two approaches. They did, however, report a PCE of 5.2%, compared to that of 4.63% obtained when using NR18-T.[11]

In this work, we make a direct comparison between these two paste-making approaches,
in terms of both optical properties and subsequent photovoltaic properties. We do this with solvothermally-synthesised anatase nanoparticles, labelled SANP-S and SANP-T depending on the presence or absence of a drying step, respectively. We also compare the use of N719 and D149 as dyes in this study, as the higher extinction co-efficient of the organic dye is expected to mitigate the importance of the scattering effects. We recently reported on this TiO₂ material (SANP) and its performance in efficient DSCs, showing that it benefited from a high isoelectric point (IEP) which led to increased dye loading.[26]

6.2 Experimental

6.2.1 DSC Device Assembly

Using the prepared pastes, 10 µm films of SANP-S or SANP-T were screen-printed using (Keywell Screen Printer KY-500FH, Taiwan) onto cleaned FTO glass (Hartford, U.S.A) for use as photoanodes (two layers using a 43T mesh, with a 125 °C drying step). Before depositing this porous film, a dense layer was formed through the spray pyrolysis of titanium (IV) diisopropoxide-bis-acetylacetonate (75 wt.% in isopropanol, Sigma, U.S.A) solution (1:9 v/v in ethanol) at 450 °C). After that, the printed photoanodes were sintered using a multi-step program up to 500 °C. Finally, the photoanodes were surface-treated by soaking in an aqueous solution (20 mM) of TiCl₄ (Sigma, U.S.A) for 30 min at 70 °C, then washed and re-sintered at 500 °C for 30 min. The photoanodes were immersed in either a 0.5 mM N719 (Solaronix, Switzerland) dye solution of a mixture of tert-butanol (LR, Ajax Chemicals, Australia) and acetonitrile (HPLC, Lab scan, Chem Supply, Australia) [1:1 v/v], or a 0.5 mM D149 (1-material, Canada) solution in a 1:1 (v/v) mixture of acetonitrile and tert-butanol. The photoanodes were taken out from the dye solution after 24 h, washed with acetonitrile and then dried. Counter electrodes were prepared by first drilling holes in a separate piece of FTO glass, to be used as a filling port for the electrolyte solution. One drop of H₂PtCl₆ (Sigma, U.S.A) solution (10 mM in ethanol) was smeared on the cleaned pre-FTO counter electrode and heated to 400 °C for 20 min. The counter electrodes were cooled before being sandwiched together with the photoanode, using a 25 µm Surlyn (Solaronix, Switzerland) spacer and a home-made hot press. Electrolyte solutions [acetonitrile/valeronitrile (Sigma, U.S.A) (85:15 vol %), 0.03 M iodine (I₂, Merck, U.S.A), 0.5 M 4-tertbutyl pyridine (4-tBP, Sigma, U.S.A), 0.6 M 1-butyl-3-methylimidazolium iodide (BMII, Sigma, U.S.A)), and 0.1 M guanidinium thiocyanate (GuSCN, Sigma, U.S.A) for N719 or [0.05 M iodine (Sigma, U.S.A), 0.6 M 1,2-
dimethyl-3-propylimidazinium iodide (Solaronix, Switzerland), 0.1 M lithium iodide (Acros Organics, U.S.A) in methoxypropionitrile (Sigma, U.S.A) for D149 were introduced into the filling port by the vacuum back-filling technique, and the filling port was then closed with a piece of Surlyn laminated to aluminium foil.

6.2.2 Materials and Devices Characterizations

The crystalline structures of SANP-S and SANP-T were examined using X-ray diffractometer (MMA, GBC Scientific Equipment LLC, Hampshire, IL, USA) (40 kV, 30 mA, Cu Kα radiation, λ = 1.5406 Å) in the range of 2θ = 20–80°, with a scan rate of 1°/min. The morphologies were examined by field emission scanning electron microscopy, FE-SEM (JEOL JSM 7500FA, Japan). A Tristar-3020 nitrogen adsorption–desorption equipment (Micrometrics, U.S.A) was used to obtain the specific surface area and pore volume values. A Dektak 150 Surface Profiler (Veeco, U.S.A) was used to determine the film thicknesses. The amounts of N719 and D149 dyes on the different films were calculated by measuring the absorbance of dyes desorbed from the films (thickness = 5 µm, area = 1 cm²) in 4 mL of a 0.1 M NaOH (Sigma, U.S.A) solution (distilled water/ethanol 1:1 v/v) for N719 or in 4 mL of 0.4 M NaOH in methanol (Chem Supply, Australia) for D149[15, 27], using a Shimadzu UV-3600 spectrophotometer (Japan). Diffuse reflectance measurements were conducted using an integrating sphere attachment (ISR-3100) (Japan) and the above spectrophotometer. A Horiba Jobin Yvon HR800 confocal Raman (Japan) with a 632.8 nm laser was used to measure the Raman shift of films (also 3 µm). The Raman spectra were recorded in the wavenumber range between 100 and 800 cm⁻¹. Photocurrent density–voltage (J–V) measurements were measured using a solar simulator with an AM1.5 filter set to 1 sun (100 mW/cm², PV Measurements, Colorado, U.S.A.). A QEX10 system from (PV Measurements, U.S.A) was used for the incident to photocurrent conversion efficiency (IPCE) measurements in 5 nm steps. A Reference 600 Potentiostat (GAMRY Instrument, U.S.A) was used for electrochemical impedance spectroscopy measurements (EIS) which were carried out for DSCs based on different photoanodes under 1 sun illumination with Voc in a frequency range of 0.1–10⁶ Hz and AC voltage of 10 mV.
6.3 Results and discussion

6.3.1 Structural analysis

SANP-S was synthesised by a new and facile one-step solvothermal process, as reported elsewhere. [26] Briefly, titanium isopropoxide (TTIP, Sigma, U.S.A) (1.5 mL) was added dropwise to an acetic acid (Sigma, U.S.A)–ethanol (Chem-Supply, Australia) mixed solvent (1:2 v/v) under vigorous stirring for (1 h) at room temperature. A transparent solution was formed, which was then transferred into a 45 mL Teflon-lined stainless steel autoclave (Parr Instrument Company, U.S.A) and heated to 200 °C (ramp time of 1 °C /min) for 9 h. After cooling down to room temperature, the resulting white precipitate was collected and washed with distilled water and ethanol three times. The material for SANP-S was then dried overnight at 90 °C and calcined at 500 °C (ramp time of 1 °C /min) in the air for three hours. This was then redispersed in ethanol, while SANP-T was maintained in ethanol. The dispersions were combined with terpineol (Alfa Aesar, U.S.A) and ethyl cellulose (Sigma, U.S.A) to create pastes similar to those in our previous reports. [15, 18, 28]. These pastes were then screen-printed onto substrates and calcined following a multi-step program up to 500 °C.

The X-ray diffraction (XRD) patterns in Figure 6.1 a show that the samples collected from printed films of SANP-S and SANP-T were both phase-pure and well-crystallised anatase TiO₂ (JSPD.21-1272), with crystalite sizes of around 25 nm. The SANP-S sample showed slightly narrower peaks, implying slightly higher crystallinity due to the additional sintering time. Previously, we demonstrated the role amorphous content plays on DSC performance, as a result of decreased charge injection efficiency.[18] Preliminary measurements showed the amorphous content to be quite low in these materials (only a few percent at most; data to be published elsewhere[26]), indicating that this would not be a major factor affecting the charge injection efficiency. Raman spectra of SANP-S and SANP-T (Figure 6.1 b) also showed both materials to be anatase TiO₂, confirmed by six characteristic Raman vibrational modes centered at 144 cm⁻¹ (E₉ (1)), 197 cm⁻¹ (E₉ (2)), 399 cm⁻¹ (B₁g), 513 cm⁻¹ (A₁g), 519 cm⁻¹ (B₁g), and 639 cm⁻¹ (E₉ (3)), respectively. [29] The slightly higher intensity (less broadening) of peaks in SANP-S again indicates better crystallinity compared to SANP-T.
The low- and high-magnification scanning electron microscope (SEM) images (Figure 6.2 a-d) show the morphologies of SANP-S and SANP-T films. It can be observed that SANP-S (Figure 6.2 a,b) had a more aggregated structure and non-uniform surface topography compared to SANP-T (Figure 6.2 c,d), in line with our expectations. SANP-S films also showed significant cracking at this scale, which is attributed to aggregation. Both had similar particle size about 25 ± 3 nm, in line with the above XRD results.

Figure 6.2: Microstructural characterisations of SANP-S and SANP-T photoanode films: (a,b) Low- and high-magnification SEM images of SANP-S; (c,d) Low- and high-magnification SEM images of SANP-T.
6.3.2 Surface area and pore size distribution analysis

Figure 6.3 a,b show the specific surface area and the pore size distributions in the two structures. The type (IV) nitrogen adsorption/desorption isotherm branches indicate that both materials have mesoporous structure [30, 31] with similar porosities of ~64% (Figure 6.3 a).[28] On the other hand, SANP-T has a more uniform pore size distribution, with a broader range of pores in the 2-30 nm range. SANP-S also revealed some larger pores, as shown in Figure 6.3 b, which were attributed to the cracked structure seen in SEM images above and in (Figure 6.4). The SANP-S also has a slightly lower surface area (113 m²·g⁻¹) compared to SANP-T (119 m²·g⁻¹), which could be attributed to aggregation, and is in line with our previous experimental results for similar systems.[15]

Figure 6.3: (a) Nitrogen adsorption–desorption isotherms obtained using the Brunauer–Emmett–Teller (BET) method; the inset is the pore size distribution obtained by the Barrett–Joyner–Halenda (BJH) method for powders collected form SANP-S and SANP-T films; (b) Pore volume/pore size distribution for SANP-S and SANP-T.
6.3.3 Optical Properties of Printed SANP-S and SANP-T Films

Since both dye loading and light scattering affect the LHE, these properties were quantified for SANP-S and SANP-T films, including dye loading after sensitisation with either D149 or N719. [32] Figure 6.5 a,b (and Table 6.1) show the results of the dye desorption experiments, with SANP-T films hosting slightly more dye compared to SANP-S films of the same thickness. This is roughly in line with the differences in surface area reported above. Meanwhile, undyed SANP-S films (10 μm) showed a considerably higher diffuse reflection (35–55%) (with lower direct transmittance) than undyed SANP-T (5–10%), as shown in Figure 6.6 a,b; and in the visual images of photoanode films (Figure 6.7).

Figure 6.4: Low magnification SEM images of (a) SANP-S; (b) SANP-T; and (c) photographs of undyed films demonstrating the difference in scattering properties.
Table 6.1: The amount of D149 dye loading on SANP-S and SANP-T films (thickness = 5.0 ± 0.3 µm; area = 1 cm²) calculated using the desorption method. [32]

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>D149 Loading (nmol·cm⁻²)</th>
<th>D149 loading (µmol·cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP-S</td>
<td>D149</td>
<td>72 ± 2</td>
</tr>
<tr>
<td>SANP-T</td>
<td>D149</td>
<td>81 ± 2</td>
</tr>
<tr>
<td>SANP-S</td>
<td>N719</td>
<td>68 ± 2</td>
</tr>
<tr>
<td>SANP-T</td>
<td>N719</td>
<td>74 ± 2</td>
</tr>
</tbody>
</table>

Figure 6.5: (a) and (b) Absorbance spectra of dye (D149 or N719) desorbed from either SANP-S or SANP-T films (5.0 ± 0.3 µm thick).

Figure 6.6: (a) Diffuse reflections of SANP-S and SANP-T films (10.0 ± 0.5 µm thick); (b) The transmittances of undyed SANP-S and undyed SANP-T photoanode films with an average thickness of (10.0±0.5 µm). The inset is their corresponding visual images.
The photovoltaic performances of DSCs based on SANP photoanodes (10.0 ± 0.5 µm) were compared, with the current–voltage responses (J-V) and incident photon to charge carrier efficiency (IPCE) results shown in Figure 6.8a,b and (Figure 6.9, highlighted scattering effects on IPCE responses, supplementary materials) and; Table 6.2 and Table 6.3. In brief, devices based on SANP-S were more efficient than those using SANP-T films. The differences were more significant with the lower absorbing N719 (peak $\varepsilon \sim 14700$ $\text{M}^{-1}\cdot\text{cm}^{-1}$) than with D149 ($\varepsilon \sim 68700$ $\text{M}^{-1}\cdot\text{cm}^{-1}$). Differences in short-circuit current densities ($J_{sc}$) were the primary reason for these discrepancies and occurred in spite of SANP-T having a slightly higher dye loading compared to SANP-S, while the lower $J_{sc}$ seen in SANP-S|N719 was reflected as differences in both magnitude and breadth of IPCE (Figure 6.8 b). The differences in dye loading shown above can be used to estimate a lower limit of light harvesting (negating the scattering effects). When accounting for fluorine doped tin oxide (FTO) coated glass absorption, all devices will have an LHE very close to unity at the peak wavelength, and as such, this is not ascribed to be the cause of the discrepancy in the IPCE peak. It should also be

6.3.4 Solar Performance of SANP-S and SANP-T Devices

The photovoltaic performances of DSCs based on SANP photoanodes (10.0 ± 0.5 µm) were compared, with the current–voltage responses (J-V) and incident photon to charge carrier efficiency (IPCE) results shown in Figure 6.8a,b and (Figure 6.9, highlighted scattering effects on IPCE responses, supplementary materials) and; Table 6.2 and Table 6.3. In brief, devices based on SANP-S were more efficient than those using SANP-T films. The differences were more significant with the lower absorbing N719 (peak $\varepsilon \sim 14700$ $\text{M}^{-1}\cdot\text{cm}^{-1}$) than with D149 ($\varepsilon \sim 68700$ $\text{M}^{-1}\cdot\text{cm}^{-1}$). Differences in short-circuit current densities ($J_{sc}$) were the primary reason for these discrepancies and occurred in spite of SANP-T having a slightly higher dye loading compared to SANP-S, while the lower $J_{sc}$ seen in SANP-S|N719 was reflected as differences in both magnitude and breadth of IPCE (Figure 6.8 b). The differences in dye loading shown above can be used to estimate a lower limit of light harvesting (negating the scattering effects). When accounting for fluorine doped tin oxide (FTO) coated glass absorption, all devices will have an LHE very close to unity at the peak wavelength, and as such, this is not ascribed to be the cause of the discrepancy in the IPCE peak. It should also be
noted that the fill factors (FF) of the devices using SANP-T|D149 were also lower than those of the devices made with SANP-S|D149, while for N719-sensitised devices, the difference in FF was within experimental uncertainty.

**Figure 6.8:** (a) Current–voltage (J–V) characteristics of SANP-S and SANP-T based devices using D149 or N719, measured under 1 sun illumination with an active area of 0.16 cm²; (b) incident photon to charge carrier efficiency (IPCE) of the devices in (a).

**Figure 6.9:** Normalised IPCEs of SANP-S and SANP-T devices sensitized with N719 and D149 highlighting scattering effects on IPCE responses.
Table 6.2: J-V parameters details of devices based on synthesized SANP-S and SANP-T sensitised either with D149 or N719.

<table>
<thead>
<tr>
<th>Devices (10 µm)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D149 devices</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SANP-S1</td>
<td>17.1</td>
<td>0.67</td>
<td>64.7</td>
<td>7.02</td>
</tr>
<tr>
<td>SANP-S2</td>
<td>16.5</td>
<td>0.68</td>
<td>63.3</td>
<td>6.85</td>
</tr>
<tr>
<td>SANP-S3</td>
<td>17.2</td>
<td>0.65</td>
<td>64.8</td>
<td>6.72</td>
</tr>
<tr>
<td>SANP-S4</td>
<td>16.7</td>
<td>0.66</td>
<td>63.4</td>
<td>6.80</td>
</tr>
<tr>
<td>Average</td>
<td>16.9±0.3</td>
<td>0.66±0.01</td>
<td>64±1</td>
<td>6.91±0.12</td>
</tr>
<tr>
<td>SANP-T1</td>
<td>16.5</td>
<td>0.635</td>
<td>60.7</td>
<td>6.5</td>
</tr>
<tr>
<td>SANP-T2</td>
<td>16.3</td>
<td>0.655</td>
<td>61.3</td>
<td>6.5</td>
</tr>
<tr>
<td>SANP-T3</td>
<td>15.4</td>
<td>0.635</td>
<td>62.7</td>
<td>6.3</td>
</tr>
<tr>
<td>Average</td>
<td>16.1±0.6</td>
<td>0.64±0.01</td>
<td>61±1</td>
<td>6.4±0.1</td>
</tr>
<tr>
<td>N719 devices</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SANP-S1</td>
<td>15.5</td>
<td>0.72</td>
<td>70.6</td>
<td>7.88</td>
</tr>
<tr>
<td>SANP-S2</td>
<td>15.3</td>
<td>0.71</td>
<td>70.1</td>
<td>7.68</td>
</tr>
<tr>
<td>SANP-S3</td>
<td>15.9</td>
<td>0.69</td>
<td>69.5</td>
<td>7.64</td>
</tr>
<tr>
<td>Average</td>
<td>15.6±0.3</td>
<td>0.71±0.01</td>
<td>70±1</td>
<td>7.73±0.13</td>
</tr>
<tr>
<td>SANP-T1</td>
<td>12.7</td>
<td>0.710</td>
<td>71.2</td>
<td>6.9</td>
</tr>
<tr>
<td>SANP-T2</td>
<td>12.9</td>
<td>0.690</td>
<td>70.6</td>
<td>6.5</td>
</tr>
<tr>
<td>SANP-T3</td>
<td>13.4</td>
<td>0.690</td>
<td>71.8</td>
<td>7.0</td>
</tr>
<tr>
<td>Average</td>
<td>13.0±0.4</td>
<td>0.70±0.01</td>
<td>71±1</td>
<td>6.8±0.3</td>
</tr>
</tbody>
</table>

Table 6.3: J–V parameters of devices based on either SANP-S or SANP-T sensitised with D149 or N719, including short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF) and photovoltaic conversion efficiency (PCE).

<table>
<thead>
<tr>
<th>Devices</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP-S</td>
<td>D149</td>
<td>16.9 ± 0.3</td>
<td>0.66 ± 0.01</td>
<td>64 ± 1</td>
</tr>
<tr>
<td>SANP-T</td>
<td>D149</td>
<td>16.1 ± 0.6</td>
<td>0.64 ± 0.01</td>
<td>61 ± 1</td>
</tr>
<tr>
<td>SANP-S</td>
<td>N719</td>
<td>15.6 ± 0.3</td>
<td>0.71 ± 0.01</td>
<td>70 ± 1</td>
</tr>
<tr>
<td>SANP-T</td>
<td>N719</td>
<td>13.0 ± 0.4</td>
<td>0.70 ± 0.01</td>
<td>71 ± 1</td>
</tr>
</tbody>
</table>
6.3.5 Electrochemical Impedance Spectroscopy (EIS)

The charge collection efficiencies ($\Phi_{cc}$) were investigated through impedance spectroscopy, carried out under 1 sun illumination, with Nyquist and Bode plots shown in Figure 6.10 a,b respectively, and summarised in Table 6.4, on the basis of the Bisquert model. [33, 34] The charge transfer resistance $R_{ct1}$ was similar for all devices tested, which was expected, as this is known to originate from the counter electrode–electrolyte interface, which was common to all devices. Meanwhile, the SANP-S|D149 devices showed slightly lower $R_{ct2}$ values, related to charge transport through photoanodes, compared to the SANP-T|D149 devices. Although this correlates with differences seen in the FF values, it is debatable if this difference in $R_{ct2}$ is enough to fully explain the differences in FF. On the other hand, SANP-S|N719 and SANP-T|N719 were approximately the same.

As shown in the Bode plots in Figure 6.10 b, the maximum values of local impedance ($f_{max}$, low frequencies), were governed by the dye, with both D149-sensitised devices showing a peak at 16 Hz, while the two N719-containing architectures displayed a peak at 25 Hz. Electron lifetimes, obtained using $\tau_n=1/2\pi f_{max}$ [35], in the D149-based devices therefore appeared longer than those in the N719-based devices. Higher chemical capacitance ($C_\mu$) values were also calculated for the D149-sensitised devices compared to the N719 ones, suggesting higher electron density resulting from more injected electrons from the photoexcited dye molecules.[27]
Table 6.4: EIS parameters of the devices based on SANP-S and SANP-T sensitised with D149 or N719, where $R_s$ is the series resistance, $R_{ct1}$ and $R_{ct2}$ are the charge transfer resistance of the mediator at the counter and in the working electrode respectively, $CPE_1$ and $CPE_2$ are the constant phase elements associated with the counter and working electrodes, respectively.[33, 36]

<table>
<thead>
<tr>
<th>Devices</th>
<th>$R_s$ (Ω·cm$^{-2}$)</th>
<th>$R_{ct1}$ (Ω·cm$^{-2}$)</th>
<th>$R_{ct2}$ (Ω·cm$^{-2}$)</th>
<th>$C_{µ}$ (µF·m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANP-S</td>
<td>D149</td>
<td>4.6 ± 0.1</td>
<td>2.3 ± 0.2</td>
<td>21 ± 0.3</td>
</tr>
<tr>
<td>SANP-T</td>
<td>D149</td>
<td>4.8 ± 0.1</td>
<td>2.4 ± 0.2</td>
<td>24 ± 0.4</td>
</tr>
<tr>
<td>SANP-S</td>
<td>N719</td>
<td>5.8 ± 0.1</td>
<td>2.0 ± 0.1</td>
<td>24 ± 0.3</td>
</tr>
<tr>
<td>SANP-T</td>
<td>N719</td>
<td>5.2 ± 0.1</td>
<td>2.0 ± 0.2</td>
<td>25 ± 0.5</td>
</tr>
</tbody>
</table>

Although these results show slightly better electronic properties for the SANP-S devices, this is most likely due to longer annealing times. It is conjectured that increasing the time the SANP-T electrodes are exposed to 500 °C should have a similar effect without increasing aggregation, as is the case with the SANP-S approach.

6.4 Conclusion

We investigated two approaches of preparing TiO$_2$ films, using pastes made from the same solvothermally-synthesised anatase nanoparticles, which were in turn incorporated into solar cells. Both methods resulted in high-crystallinity anatase TiO$_2$ nanoparticle films. The approach which eliminated the drying step led to highly transparent photoanodes (SANP-T) along with slightly higher surface area and uniform pore size distribution, resulting in increased dye loading compared to that obtained with the more conventional drying step (SANP-S). The differences in PCE between SANP-T|D149 (6.4%) and SANP-S|D149 (6.9%) were modest, with slightly lower $J_{sc}$ and FF attributed to a lower LHE and $\Phi_{cc}$, respectively. On the other hand, the differences in N719 devices resulted solely from lower $J_{sc}$, which was due to lower light scattering and a low extinction co-efficient. This indicates that D149, or other dyes with high extinction coefficients, is more promising for BIPV applications than N719. Unfortunately, from the perspective of BIPV applications, much of the development of DSCs has been strongly focused on increasing the performance of devices with N719, meaning that highly scattering structures were desirable (as can be seen from the differences in performance between the two N719-based architectures). This work suggests that many of the reported TiO$_2$ nanoparticles materials may be suitable for such an application if they were to be incorporated into a paste without a drying step.
6.5 References


30. Anovitz, L.M. and D.R. Cole, *Characterization and analysis of porosity and


Chapter 7

7 Cubic aggregates of Zn$_2$SnO$_4$ nanoparticles and their application in dye-sensitized solar cells

This chapter is based on a published work [K. Al-Attafi, F.H. Jawdat, H. Qutaish, P. Hayes, A. Al-Keisy, K. Shim, Y. Yamauchi, S.X. Dou, A. Nattestad, and J.H. Kim, Cubic aggregates of Zn$_2$SnO$_4$ nanoparticles and their application in dye-sensitized solar cells. Nano Energy, 2019. 57: p. 202-213], with contributions of other co-authors as follows: K. Al-attafi, A. Nattestad and J. Kim designed the study and research plan. K. Al-Attafi synthesized the materials, prepared devices and characterized, analyzed the results (J-V, EIS, SEM, TEM, XRD, BET, FTIR, Mott-Schottky, Zeta potential, optical measurements) and wrote the manuscript. K. Al-Attafi and F. Jawdat measured and analyzed the photoactivity measurements. K. Al-Attafi and Amar Al-Kasay measured and analyzed Mott-Schottky measurements. K. Al-Attafi, P. Hayes and H. Qutaish measured and analyzed the FTIR measurements. K. Al-Attafi and K. Shim contacted and analyzed TEM images. K. Al-Attafi and Y. Yamauchi measured and analyzed BET measurements. K. Al-Attafi, A. Nattestad and J. Kim revised the manuscript. S. Dou, J. Kim and A. Nattestad supervised the study.

Recently, Zn$_2$SnO$_4$ (ZTO) has emerged as an alternate photoanode material for DSCs, as it offers some advantages as compared to TiO$_2$ including photostability. In this Chapter, a solvothermal approach resulting in the formation of ZTO cubic aggregates, comprised of nanoparticles was presented. ZTO cubic aggregates nanoparticles were then employed in photoanodes of DSCs, with either a high extinction coefficient organic (D149) or an organometallic (N719) dye. The performance of DSC devices based on cubic aggregated ZTO nanoparticles sensitised with organometallic and organic dyes were compared to those of TiO$_2$ devices in terms of the dye binding mechanism, and the charge injection and collection efficiencies. In spite of recent record PCEs being achieved with other sensitizers, the application N719 persists as a de facto standard, especially in report of novel metal oxides (non-TiO$_2$) in DSCs, where a well understood control is usually desired. While the performance of ZTO DSCs with an organic dye, D149, showing promising photovoltaic conversion efficiencies (PCE) of 4.9%, close to those of TiO$_2$D149, the same was not true for N719. The investigations show that this is due to low injection yields in the non-TiO$_2$ system, which appears to be tied to a
different binding mechanism. These findings have substantial importance with respect to overs who are attempting to develop new metal oxides for DSCs, such as ZTO. Furthermore, this highlights the interconnectedness of DSC components and the need for researchers to approach development in a holistic manner.

7.1 Introduction

Since 1991, binary semiconducting metal oxides such as ZnO, TiO₂, and SnO₂, have been utilised as photoanode materials for DSCs.[1-5] Meanwhile, ternary metal oxide semiconductors such as Zinc Tin Oxide (ZTO) have attracted a modest amount of attention more recently, as a promising alternative photoanode material. [6-10] ZTO photoanode-based DSCs have achieved efficiencies over 6% to date, as reported by Hwang et. al. [11] ZTO has also recently been applied as an electron transparent layer (ETL) for high-efficiency perovskite solar cells (PSCs). [12-14] The DSCs as the PSCs can be integrated with other energy storage systems for efficient energy harvesting-storage systems.[15] DSCs based on metal oxide photoanodes are still the subject of interest by researchers as clean energy resource due to their promising performance in indoor and outdoor applications.[16, 17]

Among the properties making ZTO of interest are the high electron mobility (10-15 cm² V⁻¹ s⁻¹), compared to TiO₂ (0.1-1 cm² V⁻¹ s⁻¹) and low absorption in the visible light range. [7, 18] ZTO is also seen to be less response to UV irradiation than TiO₂ suggesting its use can extend DSC service life. [19-21] Furthermore, ZTO does not suffer the same chemical stability issues which ZnO or SnO₂ photoanodes do in acidic local environments, such as can result from attachment by dyes. [6, 10, 19, 22] Furthermore, ZTO has a significantly higher isoelectric point compared to TiO₂ which is expected to lead to better light-harvesting efficiency through higher dye loading. [23-25] ZTO photoanodes have been reported using nanoparticles [6, 9, 18], as well as hierarchical structures. [22, 26, 27]

In spite of record solar-to-electric conversion efficiencies being set recently using other dyes, [28-30] and the large number of sensitizers being developed [31], N719 is still a common benchmark dye, for DSC researchers. N719 has a high electrostatic binding on TiO₂ with low electrostatic repulsion among the dye molecules leading to high dye loading, and good shielding against recombination. [32-34] TD-DFT modelling performed by De Angelis et al. of N719 bound to TiO₂ through different mechanism revealed significant differences in charge injection rates based on this binding. [35]
These calculations showed electron density of the excited state frontier orbital (approximated by the LUMO) physically overlaps significantly with the TiO$_2$ when the dye is bound in its protonated state. This work also showed (from a theoretical approach) the impact that different binding mechanisms has upon the absorption properties of N719.

The role of N719 as a benchmark dye has largely continued with ZTO, where reports of comparatively low current densities (and subsequently efficiencies), are mainly attributed to high charge recombination and/or low light harvesting efficiencies (LHE).[6, 9, 18] Improvements in $V_{oc}$ values, attributed to decreased recombination, were achieved by using core-shell structured (ZTO-ZnO) thin film photoanodes, resulting in a PCE of 6%.[36] Wang et. al employed a bi-layer structure with microporous ZTO as a scattering layer over ZTO nanoparticles to enhance the LHE through increasing the light scattering ability. This resulted in a higher efficiency of 6.1% compared to 4.7% for nanoparticle-only photoanode. [18]

As mentioned, the majority of the work in ZTO development has been done using N719; however, the low quantum efficiencies seen motivated some authors to investigate organic dyes, with more success. Recently the highest ZTO based DSCs efficiency has been achieved of 6.3% using hierarchically structured mesoporous ZTO microspheres assembled, from nanobeads with an organic dye and the iodide-triiodide redox mediator, [11] higher than any reported ZTO|N719 system. The high efficiency resulting from these ZTO aggregated nanobead microspheres was attributed to the high LHE, resulting from the high surface area, high light scattering resulting from the microsize as scattering centres, efficient electrolyte penetration, which was claimed to be an issue with I/I$_3$ in an organic solvent. [11, 37] Meanwhile, Wang reported 4.28% for ZTO nanoparticles sensitized with another organic dye [24], with it being observed that higher dye packing densities can be achieved on ZTO, due to its higher isoelectric point (IEP) compared to TiO$_2$ [24]. One of the advantages of organic dyes is the higher extinction coefficient, therefore near unity LHE can be achieved for films of either ZTO and TiO$_2$ with even modest surface areas.

Most of micro and nano size ZTO morphologies were synthesised either using a surfactant to control the morphology or using long synthesis procedures or obtained as a mixed crystalline phase (presence of other phases, mostly SnO$_2$).[38-40]

There are many advantages to use ZTO aggregated nanoparticles morphologies compared to other counterparts-nanoparticles, nanoplates, nanowires, nanoflower, etc.
Cubic ZTO aggregated nanoparticles can ensure high dye loading through maintaining high surface area, the packing density of cubic ZTO aggregated nanoparticles also can enhance the light scattering ability and also the planar contact among these aggregates particles can form a uniform connected porous structure which is important for better electron transportation and better electrolyte diffusion.[12, 41] The cubic ZTO aggregated nanoparticles was observed as an initial shape during some synthesis[8, 42], however, there are only two reports to date of cubic ZTO aggregated nanoparticles for DSCs, both with efficiencies of about 2% when sensitized with N719.[21, 43] Therefore, the appropriate particle size and the phase purity need to be obtained for efficient photoanode material based on DSCs (as shown in this work).

In ZTO synthesis, crystalline phases formed and their morphologies are strongly affected by the Zn/Sn metal ion ratio and mineralizer concentration. [12, 38] Zinc Tin hydroxide ZnSn(OH)$_6$ is generally formed as an intermediate phase due to the reaction of Zn(OH)$_4$ and Sn(OH)$_6$, which themselves result from the reaction of Zn$^{2+}$ and Sn$^{4+}$ ions respectively with OH$^-$, released from the mineralizer in the alkali solution.[12, 21, 38, 43, 44] At temperatures over 200 °C ZnSn(OH)$_6$ can be thermally decomposed to Zn$_2$SnO$_4$ and either SnO$_2$ or ZnO depending on the Zn/Sn ratio in the precursor.[12, 38] High sintering temperatures, in the range of 600-800 °C, normally result in thermal decomposition of ZTO and forms ZTO comspited with other phases such as SnO$_2$ or ZnO.[12, 13, 21, 25, 43, 45-48]

It is expected that the presence of other secondary crystalline phases, such as ZnO or SnO$_2$ among the cubic ZTO aggregates nanoparticles, could negatively impact DSC efficiencies, as previously reported by some authors.[21, 43] As such, and in the interest of completeness, the performances of mixed oxide (ZTO+SnO$_2$ and ZTO+ZnO) based DSCs were also investigated in this work. Typically either large particle sizes (low surface area) or excess SnO$_2$ result when synthesised using a Zn: Sn ratio of 1:1, and/or using mineralizers.[12, 38, 43, 46, 47] Although Zn$_2$SnO$_4$ stoichiometry assumes Zn: Sn=2:1, using this ratio of precursors has been shown to produce ZTO with a secondary ZnO phase [13, 25, 48]. Therefore, in order to synthesise a pure phase of ZTO cubes aggregated nanoparticles, sintering temperature, Zn: Sn of ratio (1:1) and the amount of mineralizer should be carefully adjusted.

In spite of the number of reports on ZTO to date, the band gap value is still controversial, with values from 3.2-3.9 eV reported.[21, 38, 46, 49] The sintering temperature and presence of SnO$_2$ as a secondary phase are likely to be factors affecting
the measurement of the optical band gap of ZTO, as well as multiple trap states, located near to the conduction band edge. [43, 46] One of the larger estimates of the band gap (around 3.8 eV) was reported using a photo-electrochemical method, indicating that trap states are localised close to the conduction band, resulting in smaller optical band gap values.[38] Also, it has been reported that the presence of a secondary phase of SnO$_2$ in ZTO resulted in stronger UV absorption.[46]

In this work, cubic aggregates of ZTO nanoparticles, along with some non-aggregated particles, have been synthesised using a mixed solvent approach (ethanol: water) and control of the sintering temperature. Zinc acetate Zn(CH$_3$COO)$_2$·2H$_2$O and sodium stannate Na$_2$SnO$_3$·3H$_2$O were used as precursor materials (1:1 Zn: Sn atomic ratio) in a mixture of ethanol and water without any additional mineralizer. This procedure gave a phase pure, polycrystalline ZTO material, with morphology as mentioned above. DSC performance was investigated using the synthesised ZTO, formed into porous films, deposited on top of a ZTO blocking layer and sensitized with either the organic dye D149 or N719. Previously there has only been one study using a ZTO blocking layer to limit charge recombination from the FTO. Shin et al. deposited ZTO using a pulsed laser deposition method.[36] While others have also tried to use TiO$_2$ blocking layers (from TiCl$_4$), the higher conduction band edge of TiO$_2$ (compared to ZTO) introduced a barrier and led to a decreased efficiency compared to the devices without a blocking layer.

In this work, DSCs using ZTO sensitized with D149 is shown to lead to a PCE of about 4.9%, higher than that of ZTO sensitized with N719 (4%). The value of 4.9% achieved here is among the highest reported for ZTO based DSCs. As mentioned above, N719 is commonly used in DSCs (as it has been a benchmark dye for many years now), however low quantum efficiencies have regularly been observed when using ZTO, especially compared to on TiO$_2$, while both semiconductors had similar responses with organic dyes. We examine this discrepancy, which may allow for even higher ZTO conversion efficiencies in the future.

### 7.2 Experimental

#### 7.2.1 Synthesis of ZTO material

1 mmol of zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O, ≥ 99%, Sigma-Aldrich) and 1 mmol of sodium stannate trihydrate (Na$_2$SnO$_3$·3H$_2$O, 95%, Aldrich) were dissolved separately in mixtures of ethanol (100% Chem-Supply) and distilled water (1:1 v/v). After stirring for 20 minutes, the sodium stannate solution was added dropwise to the
zinc acetate solution (Zn: Sn=1:1) and again stirred for 20 min. The solution was then transferred into a Teflon-lined stainless steel autoclave bomb, (45 mL Parr Instrument Company) and heated up to 180 °C for 12 h (ramp rate 1 °C/min starting from room temperature). After cooling down to room temperature, the obtained white precipitate was thoroughly centrifuged with a mixed solution (again 1:1 water: ethanol) to remove any unreacted material. After that, the powder was dried overnight at 90 °C and calcined at 400 °C for 6 h (ramp rate of 5 °C/min). Alternately, 2 mmol zinc acetate dihydrate and 1 mmol sodium stannate trihydrate (Zn: Sn=2:1) were used following the above protocol.

A ZTO precursor solution, prepared using a modified solvothermal method[50] was employed to deposit a ZTO blocking layer. Here, 0.66 g of zinc acetate dihydrate (0.150 M) and 0.53 g of (tin (IV) chloride pentahydrate, 98%, Sigma-Aldrich) (0.075 M) were dissolved in 20 ml of absolute ethanol and stirred for 2 h. (NaOH, ≥97% Sigma) (0.5 M) was added dropwise stirred for more 1 h. The solution was solvothermal treated at 180 °C for 12 h (ramp time 1 °C/min). After cooling down to room temperature, the precursor was used to deposit a dense ZTO blocking layer by spray pyrolysis (details below).

7.2.2 DSC device assembly

ZTO and TiO₂ photoanodes were prepared as follows: FTO glass (Hartford) was cleaned using soapy water, acetone (100% Chem-Supply) and then ethanol in three successive sonication steps. Following this, it was heated to 450 °C where a blocking layer was deposited by spray pyrolysis. The ZTO precursor is described above, while a 1:9 v/v in ethanol dilution of titanium diisopropoxy bis (acetylacetonate) solution (75 wt% in IPA, Sigma) in ethanol was used for TiO₂. After cooling down to room temperature, porous layers were deposited using commercially available TiO₂ pastes (NR18-T, WER0-2) or a ZTO paste prepared by a method analogous to one reported previously.[51] While TiO₂ was screen printed, ZTO was cast by a doctor blade method.

After that, the printed photoanodes were sintered using a multi-step program (up to 500 °C). Finally, TiO₂ photoanodes were treated by soaking the photoanodes in (20 mM) aqueous solution of (TiCl₄, ≥99% Fluka) for 30 min at 70 °C, then washed and re-sintered at (500 °C for 30 min), the photoanodes were immersed in an 0.5 mM N719 (Solaronix) dye solution of a mixture of tert-butanol (≥99% Sigma-Aldrich) and acetonitrile (99.8% Sigma-Aldrich) [1:1 v/v], or 0.5 mM D149 (1-material, Canada) also in a 1:1 (v/v) mixture of acetonitrile and tert-butanol. The photoanodes were taken
out from the dye solution after 24 h and washed with acetonitrile and then dried. Counter electrodes were prepared by first drilling holes in a separate piece of FTO glass, to be used as a filling port for the electrolyte solution. One drop of 10 mM (H₂PtCl₆·6H₂O, ≥37.5 wt.% Pt Sigma-Aldrich) solution (in ethanol) was smeared on the cleaned pre-FTO counter electrode and heated to 400 °C for 20 min. The counter electrodes are cooled before being sandwiched together with the photoanode, using a 25 μm Surlyn (Solaronix) spacer, by a hot press. The electrolyte solutions [acetonitrile/valeronitrile (99.5% Aldrich) (85:15 vol %), 0.03 M iodine (I₂) (99.999% Merck), 0.5M 4-tertbutyl pyridine (4-tBP) (96% Aldrich), 0.6 M 1-butyl-3-methylimidazolium iodide (BMII) (99% Sigma-Aldrich), and 0.1 M guanidinium thiocyanate (GuSCN) (≥99% Sigma-Aldrich)] for N719 or [50 mM iodine (Sigma), 0.6 M 1,2-dimethyl-3-propylimidazelium iodide (Solaronix), 0.1 M lithium iodide (99% Acros Organics) in 3-methoxypropionitrile (≥98% Sigma-Aldrich)] for D149 were introduced into the filling port by a vacuum back-filling technique, and the filling port was then closed with a piece of Surlyn laminated to aluminium foil.

7.2.3 Materials characterizations
The crystalline diffraction peaks of ZTO were examined using X-ray diffractometer (MMA, GBC Scientific Equipment, 40 kV, 30 mA) (Cu Ka radiation, λ = 1.5406 Å) in the range of (2θ = 20-80°) with scan rate (1°/min). The morphology and internal structure of ZTO were examined by field-emission scanning electron microscopy (FE-SEM) (JEOL JSM-7500) and transmittance electron microscopy TEM (JEOL JEM-2010). Microtrac Belsorp-mini nitrogen adsorption-desorption equipment was used to obtain specific surface area, and pore size distributions using the Brauner-Emmett-Tell (BET) and Brauner-Joyner-Halenda (BJH) approaches. The amount of N719 and D149 dyes on the different films was calculated by measuring the absorbance of dyes desorbed from the films (thickness = 5 ± 0.3 μm, area = 1 cm²) in (4 ml) of (0.1 M) NaOH solution (distilled water: ethanol 1:1 v/v) for N719 or in (4 ml) of (0.4 M) NaOH in methanol (100% Chem-Supply) for D149 using a Shimadzu UV-3600 spectrophotometer. The diffuse reflectance and optical band gap measurements were conducted using an integrating sphere (ISR-3100) and the above spectrophotometer. A Veeco Dektak 150 Surface Profiler was used for the film thickness measurements. Zetasizer Nano-ZS was used to measure zeta potentials of TiO₂ and ZTO in order to determine the isoelectric points. TiO₂ and ZTO aqueous solution with different pH values (2-12) were prepared using 0.25 M NaOH and 35 vol% HCl to increase and
decrease the pH values respectively. VSP-300 potentiostat workstation (Biologic science instruments) was used to carry out Mott-Schottky measurements (conducted at 1 kHz) to determine the flat band potential of TiO$_2$ and ZTO films (3 µm) deposited on FTO glass. 0.1 M (Na$_2$SO$_4$, ≥99% Sigma-Aldrich) was used as an electrolyte, Saturated Calomel Electrode (SCE) as a reference electrode and platinum counter electrode. Simulated solar illumination (Oriel LCS-100, 100 mW/cm$^2$) was used to measure the photocatalytic activity of ZTO and TiO$_2$ materials dispersed in an aqueous solution of (Rhodamine B dye, 95% Sigma) (catalyst loading ~20 mg per 20 mL of 25 µM dye solution). Shimadzu IR prestige -21 was used to measure FTIR spectra of dyed/undyed TiO$_2$ and ZTO films (3 µm thicknesses) and for N719 and D149 dyes powders. The transmittance spectra of materials in FTIR measurements were normalized to make a reasonable comparison. Keithley 2400 used to measure the J-V response for ZTO blocking layer test.

7.2.4 Software

- ChemDraw Professional V17.1 and Chem3D V17.1 were used to draw the dyes structure and calculate the spacing between the functional groups.
- Vesta software was utilized to draw the crystalline structure of TiO$_2$ and ZTO.

7.2.5 Device characterizations

Photocurrent density-voltage (J-V) measurements were measured using a solar simulator with an AM1.5 filter; set to 1 sun (100 mW·cm$^{-2}$, PV Measurements, Colorado). A QEX10 system (PV Measurements) was used for the incident to photocurrent conversion efficiency (IPCE) measurements in 5 nm steps. A Reference 600 Potentiostat (GAMRY instrument) was used for electrochemical impedance spectroscopy measurements (EIS) which were carried out for DSCs based on different photoanodes under 1 sun illumination at $V_{oc}$ in a frequency range (0.1–10$^6$ Hz) and AC voltage of 10 mV.

7.3 Results & discussion

7.3.1 Nanostructure analysis

X-ray diffraction patterns (Figure 7.1 a), and Selected Area Electron Diffraction (SAED) (Figure 7.1 b) confirmed that both individual (non-aggregated) particles and those in the secondary cubic aggregates are both cubic spinel-type ZTO (JCPDS no. 00-24-1470). From this trace, the crystal size was estimated by the Scherrer equation to be about 13 nm. The crystallinity of the ZTO phase was controlled by adjusting the precursor concentration and sintering temperature, with pure, ZTO obtained by using a
1:1 Zn:Sn ratio and 400 °C. Crystalline SnO$_2$ appeared when using higher calcination temperatures (600-800 °C) and leads to a distortion in the shape of the cubic aggregated structures. It is believed that SnO$_2$ is present the whole time, however, does not crystallise until higher temperatures are reached, which is investigated below with quantitative XRD analysis. Mixed-phase products, including either ZTO: ZnO or ZTO: SnO$_2$: ZnO, were obtained when using a precursor ratio of 2:1 Zn: Sn (atomic) with either 400 °C or 800 °C calcination temperatures respectively (Figure 7.2 a-d).

Scanning Electron Microscopy (SEM), (Figure 7.1 c) and Transmission Electron Microscopy (TEM), (Figure 7.1 d) shows the morphology and particle size of the synthesised ZTO sample. A secondary cubic structure of aggregated nanoparticles, with average size 75 nm, along with some unbound nanoparticles, both with an average size (13 nm), were observed. The majority of the ZTO nanoparticles were assembled to form these aggregate cubes during the solvothermal reaction (Figure 7.3 a).

High-resolution TEM images (HRTEM) (Figure 7.1 e and 7.1 f) show the interplanar distances and the corresponding miller indices that again confirm the crystalline structure of the primary ZTO nanoparticles which form the secondary cubic structures. It can be noted that some ZTO nanoparticles and cubic aggregated nanoparticles showed no fringes, indicating partially crystallisation, which suggests the presence of amorphous ZTO or SnO$_2$.

Na$_2$SnO$_3$.3H$_2$O is used here as a source of Sn$^{4+}$ ions and as a mineralizer at the same time, reducing the formation of an excess of Sn(OH)$_6$ which in turn, could be thermally decomposed or reacted with the initial phase of ZnSn(OH)$_6$ during the solvothermal reaction and eventually produce SnO$_2$ as a separate phase. [12, 38] A 1:1 Zn:Sn ratio was found to be the optimum ratio, to prevent formation an undesirable excess of Zn(OH)$_4$ which can be thermally decomposed to ZnO resulting in a mixed phase ZTO+ZnO.[25] As for the calcination process, 400 °C is the optimum calcination temperature to form a pure polycrystalline ZTO, while at 800 °C, SnO$_2$ is also seen in other phases (Figure 7.2 a-d). Of those trialled, 400 °C was the highest that did not lead to decomposition of ZTO into other materials, but was high enough to give good crystallinity.

Using Zn:Sn =1:1, the resultant intermediate phase was ZnSn(OH)$_6$ with residual (unreacted) Zn(OH)$_6$ and Sn(OH)$_4$, as seen in Figure 7.2 a. Since the ZnSn (OH)$_6$ is a metastable phase which can easily react with Zn(OH)$_6$ at 400 °C to form Zn$_2$SnO$_4$, Sn(OH)$_4$ can also easily thermally decomposed at this temperature to SnO$_2$ and OH$^-$. 

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however, it is not high enough to crystallise SnO\textsubscript{2}, leaving amorphous SnO\textsubscript{2}. At calcination temperature between (600-800 °C), this amorphous SnO\textsubscript{2} phase was seen to crystallise.

![Figure 7.1: Structural characterizations of solvothermally synthesised (180 °C for 12 h) Zn\textsubscript{2}SnO\textsubscript{4} (ZTO) (1:1 at. Zn: Sn), sintered at 400 °C for 6 h (a) X-ray diffraction patterns; (b) Selected Area Electron Diffraction (SEAD); (c) SEM, (d) TEM and (e,f) HRTEM of crystalline ZTO aggregated nanocubes and ZTO nanoparticles (from d).]
When a 2:1 Zn:Sn ratio, nominally giving the correct stoichiometry, was used, both ZnSn(OH)$_6$ and ZnO were seen after synthesis. It is speculated that some Sn$^{4+}$ remains in the supernatant in the reaction vessel. Calcination at 400 °C (see Figure 7.2 b) produced a Zn$_2$SnO$_4$+ZnO composite, while higher temperature (800 °C) treatments resulted in Zn$_2$SnO$_4$+SnO$_2$. After the solvothermal reaction, the resulting intermediate phase (Figure 7.2b) is also ZnSn(OH)$_6$ and Sn(OH)$_4$, however, with a higher amount of unreacted Zn(OH)$_6$, some Zn(OH)$_6$ will decompose to ZnO + OH$^-$. ZnSn(OH)$_6$ can react with Zn(OH)$_6$ at 400 °C calcination temperature to form Zn$_2$SnO$_4$ while Sn(OH)$_4$ and the excess of Zn(OH)$_6$ can easily decompose to SnO$_2$ + OH$^-$ and ZnO + OH$^-$ respectively. This temperature is high enough to crystallise ZnO but not SnO$_2$, resulting in an amorphous SnO$_2$ with crystallised ZnO and low crystalline degree.
of ZTO. At higher calcination temperatures between (600-800 °C), the amorphous SnO$_2$ converted to a crystalline phase in addition to well-crystallised ZnO and ZTO.

As mentioned, the ZTO sample used for making devices (1:1 Zn: Sn) was suspected of containing amorphous SnO$_2$.[46] Accordingly, the reference intensity method (RIR) of XRD analysis for quantification analysis was used to assess the degree of crystallinity and quantify the amorphous content.[52] ZTO was mixed with about 10% silicon to act as an internal standard to assess the degree of crystallinity. The measured ratios of ZTO and Silicon from this trace were 91:9 (Wt.%). However, the calculated weight ratios obtained from the integrated intensities (after subtracting the background) of ZTO and Silicon are 90% and 10% respectively (Figure 7.3 b). The lower than expected amount of ZTO is due to the amorphous content, (i.e. the reduced intensity of ZTO phase will change the relative phase fractions in a spiked sample) which can be calculated as:

$$\text{Amorphous ZTO (Wt%) = 100 (Wt%) - \left[ \frac{\text{Si mass (Wt%)}}{\text{Si XRD (Wt%)}} \right] \times \text{crystalline ZTO XRD (Wt%)}}$$

The amorphous content in ZTO is approximately 10% which may be partially attributed to a non-crystalline SnO$_2$.

In spite of the XRD patterns in Figure 7.1 a showing only a crystalline phase of ZTO (i.e. no other crystalline phases such as SnO$_2$ or ZnO), the lower peak intensity and the broadening hump observed in the diffraction patterns of ZTO compared to those of silicon confirmed the presence of some amorphous content after treatment at 400 °C which could be a non-crystalized SnO$_2$ (Figure 7.3 b). This amount of amorphous content was only about 10% which may belong to SnO$_2$ or/and ZTO. This may affect the performance of DSCs,[53] however, a protocol for its removal has not yet been developed and is the subject of further investigation.

**Figure 7.3:** (a) TEM images of crystalline ZTO aggregated nanocubes/ZTO nanoparticles synthesised using Zn: Sn=1 molar ratio and calcined at 400 °C; (b) Quantifying of crystallinity degree in XRD traces of synthesised ZTO using the reference intensity method (RIR) using silicon as an internal reference.
The proposed chemical reaction mechanism during the synthesis of ZTO is described by Figure 7.4.

Figure 7.4: Proposed mechanism of synthesis polycrystalline cubic aggregates of ZTO nanoparticles from Zn(CH₃COO)₂·2H₂O and Na₂SnO₄·6H₂O as first materials by solvothermal reaction method.

Figure 7.5 a,b show the nitrogen adsorption/desorption isotherm, and the pore size distributions, calculated by the Barrett-Joyner-Halenda (BJH) technique of the phase pure ZTO sample, along with those of commercial TiO₂ nanoparticles (NR18-T) and TiO₂ scattering particles (WER2-O). The ZTO synthesised here, has a lower specific surface area (58 m²·g⁻¹) than that of NR18-T (79 m²·g⁻¹) but higher than that of WER2-O (15 m²·g⁻¹), as shown in Table 7.1. BJH analysis showed the mean pore diameter in the ZTO to be about 7.5 nm, which is smaller than both those of the transparent nanoparticles at 27 nm and the large scattering particles, which were 39-120 nm (not shown here due to equipment limitations). The small pores seen with ZTO are due to the high packing density. This tight packing of the nanoparticles in the aggregate also results in a lower porosity of 41% as compared to NR18-T at 66% (Table 1).
Figure 7.5: N$_2$ adsorption/desorption isotherm; (b) The pore size distribution measurements of ZTO, NR18-T and WER2-O materials.

**Table 7.1:** Porosity, surface area of ZTO, 18NR-T, and WER2-O.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Porosity (%)$^a$</th>
<th>Specific surface area (m$^2$·g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTO</td>
<td>41</td>
<td>58</td>
</tr>
<tr>
<td>NR18-T</td>
<td>66</td>
<td>79</td>
</tr>
<tr>
<td>WER2-O</td>
<td>35</td>
<td>15</td>
</tr>
</tbody>
</table>

$^a$The porosity calculated as $P = P_V / (\rho^{-1} + P_V)$, where $P_V$ is the pore volume (cm$^3$·g$^{-1}$), and $\rho^{-1}$ is the inverse of the density of anatase TiO$_2$ or ZTO ($\rho^{-1} = 0.257$ and $0.155$ cm$^3$·g$^{-1}$) respectively.[23, 54]

In spite of having a slightly lower surface area than the TiO$_2$ nanoparticles, dye desorption measurements confirmed that ZTO could host a larger number of dyes per unit volume and higher dye packing density (dye molecules/nm$^2$) for both N719 and D149 dyes as shown in Table 2 and Figure 7.6. This may be attributed (at least in part) to the higher isoelectric point (IEP) of ZTO, as shown in Figure 7.7 a. The measured isoelectric point (IEP)s of ZTO and TiO$_2$, were (pH = 8.3) (pH = 4.6) respectively, this phenomenon of increased dye loading has previously been reported [23-25] (Table 7.3).

**Table 7.2:** Dye loadings of D149 and N719 on TiO$_2$ and ZTO films (thickness 5.0±0.3 µm).

<table>
<thead>
<tr>
<th>Dye</th>
<th>Photoanode</th>
<th>Dye loading (nmol·cm$^{-2}$)</th>
<th>Dye loading (µmol·cm$^{-3}$)</th>
<th>Dye packing$^a$ (nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D149</td>
<td>ZTO</td>
<td>69.7 ± 0.3</td>
<td>107.3 ± 0.5</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ (NR18-T)</td>
<td>64.1 ± 0.6</td>
<td>98.6 ± 0.9</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ (WER2-O)</td>
<td>20.2 ± 0.2</td>
<td>29.0 ± 0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>N719</td>
<td>ZTO</td>
<td>80.4 ± 0.2</td>
<td>123.7 ± 0.3</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ (NR18-T)</td>
<td>69.8 ± 0.6</td>
<td>107.4 ± 0.9</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ (WER2-O)</td>
<td>23.3 ± 0.6</td>
<td>35.8 ± 0.9</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Dye packing density on ZTO and TiO$_2$ calculated using the porosity, surface area and dye loading per film area. [55]

**Table 7.3:** Zeta potential measurements of TiO$_2$ and ZTO with different pH values.

<table>
<thead>
<tr>
<th>pH-ZTO</th>
<th>RUN1</th>
<th>RUN2</th>
<th>RUN3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>22</td>
<td>23</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>17</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>18</td>
<td>17</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>8</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>11.5</td>
<td>-41</td>
<td>-43</td>
<td>-44</td>
<td>-42</td>
</tr>
<tr>
<td>12</td>
<td>-41</td>
<td>-38</td>
<td>-41</td>
<td>-41</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH-TiO$_2$</th>
<th>RUN1</th>
<th>RUN2</th>
<th>RUN3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>37</td>
<td>38</td>
<td>39</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>16</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>-31</td>
<td>-33</td>
<td>-33</td>
<td>-32</td>
</tr>
<tr>
<td>8</td>
<td>-43</td>
<td>-44</td>
<td>-44</td>
<td>-43</td>
</tr>
<tr>
<td>10</td>
<td>-45</td>
<td>-45</td>
<td>-45</td>
<td>-45</td>
</tr>
<tr>
<td>11.5</td>
<td>-42</td>
<td>-45</td>
<td>-46</td>
<td>-44</td>
</tr>
<tr>
<td>12</td>
<td>-41</td>
<td>-46</td>
<td>-50</td>
<td>-45</td>
</tr>
</tbody>
</table>

Figure 7.6: Absorption spectra of solutions of (a) D149 and (b) N719 after desorption from films of TiO$_2$ nanoparticles (NR18-T), TiO$_2$ scattering particles (WER2-O) or ZTO.

Figure 7.7 b shows the diffuse reflectance of films of 18NR-T, WER2-O and ZTO at the same thickness as used in the devices for each configuration. ZTO showed better scattering in the whole wavelength range (>400 nm) compared to NR18-T but less than WER2-O. The scattering of ZTO could further contribute to enhancing the LHE.
7.3.2 Photovoltaic tests (J-V &IPCE)

Device performances were investigated under simulated sunlight with either ZTO, or TiO$_2$ sensitized with either N719 or D149. As can be seen from Table 7.4 and Figure 7.7 c, TiO$_2$ and ZTO devices sensitized with D149 show similar $J_{sc}$ values, however, the obtained $V_{oc}$ using ZTO is ~80 mV lower. Similar deference in $V_{oc}$ is seen with N719, however here the $J_{sc}$s are markedly different, with that of ZTO being about half that of N719|TiO$_2$. Interestingly, the ZTO|N719 devices have higher FF values than TiO$_2$|N719 ones, suggesting that recombination may not be as much of an issue, as other authors have previously claimed. [6, 9, 10, 21, 24, 43] This is investigated in depth later in this manuscript.

The peak quantum efficiencies of devices based on ZTO sensitized with D149 are comparable to those of TiO$_2$ sensitized with D149 and N719 while ZTO sensitized with N719 showed low quantum efficiency (Figure 7.7 d); with these results matching well with the $J_{sc}$ values of the devices measured under 1 sun.

![Figure 7.7](image)

**Figure 7.7:** (a) Isoelectric point measurements of TiO$_2$ and ZTO in aqueous solutions with different pH values; (b) Diffuse reflection measurements (film thickness 18 μm, 12 μm and 5 μm for ZTO, NR18-T and WER2-O respectively); (c) J-V characterizations; (d) IPCE measurements, of devices based on TiO$_2$ and ZTO.
Table 7.4: Key parameters from J-V measurements DSCs with photoanodes consisting of ZTO or TiO₂ sensitized with N719 or D149.

<table>
<thead>
<tr>
<th>Device</th>
<th>( J_{sc} ) (mA·cm(^{-2}))</th>
<th>( V_{oc} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTO</td>
<td>D149</td>
<td>13.3 ± 0.4</td>
<td>0.56 ± 0.02</td>
<td>65 ± 1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>D149</td>
<td>13.8 ± 0.2</td>
<td>0.64 ± 0.02</td>
<td>62 ± 1</td>
</tr>
<tr>
<td>ZTO</td>
<td>N719</td>
<td>8.2 ± 0.5</td>
<td>0.68 ± 0.01</td>
<td>73 ± 1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>N719</td>
<td>14.3 ± 0.2</td>
<td>0.76 ± 0.01</td>
<td>68 ± 3</td>
</tr>
</tbody>
</table>

The thickness of ZTO photoanodes sensitized with N719 and D149 dyes were optimized to give the highest PCE (see Table 7.5 and Table 7.6).

The effect of using spray pyrolysis deposited ZTO blocking layer on the performance of ZTO|D149 based devices was also investigated, with the sprayed ZTO layer shown to acts as a blocking layer, in Figure 7.8 a,b. The performances of devices made using ZTO prepared either with 2:1 Zn: Sn ratio (i.e. resulting in the formation of a secondary phase of ZnO) or with 1:1 Zn: Sn ratio with high-temperature treatment (including SnO₂) were measured, using D149 and are shown in Figure 7.9 a,b and Table 7.7. These devices showed substantially lower solar performance compared to devices based on a pure ZTO crystalline material.

Figure 7.8: ZTO blocking layer investigation (a) J-V response for sandwich devices with either two FTO electrodes or two FTO|ZTO electrodes filled with 0.1 M Ferrocene electrolyte, showing much lower dark current across the operating voltage range (b) ZTO|D149 device performance with and without ZTO blocking layer (dark curves in inset).
Table 7.5: Photoanode thickness optimisation for ZTO|D149 based DSCs.

| ZTO|D149 Thickness (µm) | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|----------------------|----------------------|----------------|---------|---------|
| 14                   | 12.6 ± 0.8           | 0.51 ± 0.01    | 58 ± 2  | 3.7 ± 0.3 |
| 16                   | 12.6 ± 0.8           | 0.59 ± 0.02    | 59 ± 2  | 4.4 ± 0.3 |
| 18                   | 13.3 ± 0.4           | 0.56 ± 0.02    | 65 ± 2  | 4.9 ± 0.2 |
| 20                   | 13.4 ± 0.3           | 0.56 ± 0.02    | 61 ± 1  | 4.6 ± 0.3 |
| 22                   | 13.7 ± 1.0           | 0.57 ± 0.01    | 60 ± 2  | 4.4 ± 0.2 |

Table 7.6: Photoanode thickness optimisation for ZTO|N719 based DSCs.

| ZTO|N719 Thickness (µm) | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|----------------------|----------------------|----------------|---------|---------|
| 4                    | 4.4 ± 0.1            | 0.65 ± 0.02    | 67 ± 5  | 2.0 ± 0.2 |
| 8                    | 6.4 ± 0.5            | 0.68 ± 0.01    | 72 ± 1  | 3.1 ± 0.2 |
| 12                   | 8.2 ± 0.6            | 0.68 ± 0.01    | 73 ± 1  | 4.0 ± 0.2 |
| 16                   | 7.8 ± 0.3            | 0.67 ± 0.01    | 71 ± 1  | 3.7 ± 0.1 |
| 20                   | 6.5 ± 0.6            | 0.63 ± 0.01    | 67 ± 1  | 2.7 ± 0.2 |

Figure 7.9: Photovoltaic performance of devices based on ZTO composited with other secondary phases sensitized with D149 dye ZTO: SnO$_2$ synthesised using Zn: Sn= 1:1 and a 800 °C calcination temperature; ZTO: ZnO synthesised using Zn: Sn=2:1 and a 400 °C calcination temperature, with the pure phase material for comparison. (a) J-V responses and (b) IPCE.
Table 7.7: Photovoltaic parameters of ZTO+SnO$_2$ and ZTO+ZnO devices sensitized with D149 dye.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTO+SnO$_2$-1</td>
<td>7.4</td>
<td>0.62</td>
<td>63</td>
<td>2.9</td>
</tr>
<tr>
<td>ZTO+SnO$_2$-2</td>
<td>7.7</td>
<td>0.60</td>
<td>64</td>
<td>3.0</td>
</tr>
<tr>
<td>ZTO+SnO$_2$-3</td>
<td>7.3</td>
<td>0.59</td>
<td>65</td>
<td>2.8</td>
</tr>
<tr>
<td>Average</td>
<td>7.5 ± 0.2</td>
<td>0.61 ± 0.02</td>
<td>64 ± 1</td>
<td>2.9 ± 0.1</td>
</tr>
<tr>
<td>ZTO+ZnO-1</td>
<td>5.7</td>
<td>0.49</td>
<td>62</td>
<td>1.8</td>
</tr>
<tr>
<td>ZTO+ZnO-2</td>
<td>5.5</td>
<td>0.48</td>
<td>60</td>
<td>1.6</td>
</tr>
<tr>
<td>ZTO+ZnO-3</td>
<td>5.6</td>
<td>0.49</td>
<td>62</td>
<td>1.6</td>
</tr>
<tr>
<td>Average</td>
<td>5.6 ± 0.1</td>
<td>0.49 ± 0.01</td>
<td>61 ± 1</td>
<td>1.6 ± 0.1</td>
</tr>
</tbody>
</table>

7.3.3 Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were carried out under open circuit conditions and simulated solar illumination (1 sun), to compare charge transfer rates and lifetimes under operational conditions, with Nyquist and Bode plots shown in Figure 7.10 a,b respectively. This is particularly of interest in the context of literature claims about recombination issues in ZTO DSCs and concerns about trap states. Nyquist plots, which were fitted in Figure 7.11 using an equivalent circuit shown in the inset and Table 7.8, show that devices based on TiO$_2$ sensitized with either D149 or N719 have a slightly lower resistance to charge transport ($R_{ct2}$) compared to their ZTO counterparts. The $R_{ct2}$ of devices based ZTO sensitized with D149 is also slightly lower than that of ZTO|N719. This is however not enough of a difference to explain the variation in J-V responses. Indeed, the differences in EIS responses here can themselves be explained by the lower $J_{sc}$ seen in devices based on ZTO|N719 (lower charge injection leading to lower charge density in the films during testing).

As shown in Figure 7.10 b, the frequencies of the local impedance maxima ($f_{max}$, low frequencies) in the devices based on TiO$_2$ and ZTO sensitized with D149 were 31 Hz and 50 Hz respectively. The electron lifetime was calculated using $\tau_n = 1/2\pi f_{max}$. In TiO$_2$ based devices these values are seen to be longer than in their ZTO counterparts, consistent with observed $R_{ct2}$ values. While frequencies of the local impedance maxima in the devices based on TiO$_2$ and ZTO sensitized with N719 were 25 Hz and 79 Hz respectively, indicating there is the more substantial difference between their electron lifetimes. In addition, the electron transit diffusion time (the electron transit time) calculated using $\tau_t = 1/f'_{max}$, where $f'_{max}$ is the maximum frequency of the second semicircle, which is 80 μs for ZTO|D149 devices 40 μs for TiO$_2$|D149 60 μs for
TiO$_2$|N719 devices, and 100 μs for ZTO|N719. This final value indicates slower charge transfer, in line with expectation for a device with low charge density. The shorter electron lifetimes ($\tau_n$) and longer electron transit diffusion times ($\tau_d$) along with lower charge density of devices based on ZTO|N719 and ZTO|D149 could affect the charge collection efficiency.

Furthermore, devices based on TiO$_2$ sensitized with either D149 or N719 showed higher chemical capacitance ($C_\mu$) compared to ZTO, in line with higher carrier density.[56]

Figure 7.10: EIS measurements (a) Nyquist plots; (b) Bode plots of DSCs using TiO$_2$ or ZTO, sensitized with either D149 or N719 dyes.

Table 7.8: Electrochemical impedance spectroscopy measurements of TiO$_2$ and ZTO sensitized with D149 and N719 dyes.

<table>
<thead>
<tr>
<th>Device</th>
<th>$R_S$ (Ω·cm$^{-2}$)</th>
<th>$R_{ct1}$ (Ω·cm$^{-2}$)</th>
<th>$R_{ct2}$ (Ω·cm$^{-2}$)</th>
<th>$C_\mu$ (μF·m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTO</td>
<td>D149</td>
<td>4.9 ± 0.1</td>
<td>4.6 ± 0.1</td>
<td>28.6 ± 0.4</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>D149</td>
<td>4.9 ± 0.1</td>
<td>4.1 ± 0.1</td>
<td>24.8 ± 0.3</td>
</tr>
<tr>
<td>ZTO</td>
<td>N719</td>
<td>4.9 ± 0.1</td>
<td>5.0 ± 0.4</td>
<td>32.5 ± 0.5</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>N719</td>
<td>4.9 ± 0.1</td>
<td>4.3 ± 0.3</td>
<td>20.0 ± 0.4</td>
</tr>
</tbody>
</table>
Using the above lifetime values, a lower bound estimation of the collection efficiency can be calculated as $\Phi_{cc} = 1 - (\tau_d / \tau_n)$.\cite{57, 58} Both TiO$_2$|N719 and TiO$_2$|D149 based devices show similar charge collection efficiencies of ~99%, while ZTO|D149 has 97.5% and ZTO|N719 ~95%. In other words, the charge collections efficiencies in all the devices here are close to 100%, and the lower $J_{sc}$ observed in ZTO|N719 devices is shown to not originate from charge recombination losses. Based on these observations of high light harvesting and charge collection efficiencies, the poor performance of ZTO|N719 is concluded to be related to charge injection issues.

**Figure 7.11:** Nyquist plots fitting of TiO$_2$ and ZTO sensitized with D149 and N719 based DSCs.
At present, the highest efficiency TiO$_2$|N719 based devices in the literature use a Li$^+$ free electrolyte, in contrast to DSCs made with TiO$_2$ and most other dyes, where it (or similar small cations) are understood to be essential for good charge injection and electron transport.[59, 60] To probe whether the absence of Li$^+$ is the leads to low charge injection efficiency ($\Phi_{inj}$) in ZTO|N719, devices were prepared using the same Li$^+$ containing electrolyte as for the D149 based devices (Figure 7.12 and Table 7.9). While there is an enhanced $J_{sc}$ (~15%) compared to the standard Li$^+$ free electrolyte, there is also a lower FF and $V_{oc}$. Even though the maximum IPCE values of ZTO|N719 devices with different electrolyte compositions were roughly the same (~40%), the Li$^+$ containing one resulted in a broader shape, leading to higher $J_{sc}$, although still well below those of the ZTO|D149 devices.

![Figure 7.12: Investigation of the electrolyte effect on the performance of ZTO|N719 devices.](image)

**Table 7.9:** Photovoltaic parameters of ZTO|N719 devices using different electrolytes.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTO</td>
<td>N719 (D149 electrolyte)</td>
<td>9.4 ± 0.4</td>
<td>0.66 ± 0.01</td>
<td>59 ± 1</td>
</tr>
<tr>
<td>ZTO</td>
<td>N719 (N719 electrolyte)</td>
<td>8.2 ± 0.5</td>
<td>0.68 ± 0.01</td>
<td>73 ± 1</td>
</tr>
</tbody>
</table>

Figure 7.13 a shows Mott-Schottky measurements for undyed TiO$_2$ and ZTO films. The E$_{fb}$ value can be determined from the extrapolation of $1/C^2$. [61] The E$_{fb}$ of ZTO (~0.68 V vs. SCE) is lower than that of TiO$_2$ (~0.78 V vs. SCE) suggesting the conduction band edge of ZTO should also be slightly lower than that of TiO$_2$. Since the conduction band edges (ECB) of n-type semiconductors are typically reported to be approximately 0.1
eV more negative than their flat band potential value ($E_{fb}$), depending on the electron effective mass and the carriers concentration [62]. The approximated conduction band edges of ZTO and TiO$_2$, in the vacuum level scale, are -4.1 eV and -4.0 eV respectively [E (eV) = -4.5 +[-SCE +0.244]. [62-64] This lower $E_{fb}$ potential, measured for ZTO compared to TiO$_2$, is consistent with values reported previously [14, 36, 42, 58, 65] and should favour charge injection, ruling out lower chemical driving forces ($\Delta G_{inj}$) as a reason for low $\Phi_{inj}$. Furthermore, these differences in CB edge are similar to the ~80 mV differences seen in the device in $V_{oc}$ values.

ZTO has a lower charge density than TiO$_2$, which can be estimated from the slope in the fitted Mott-Schottky plots $N_d=(2/e_0\varepsilon\varepsilon_0)(d(1/C^2)/dV)-1$ where $N_d$ the electron donor density, $e_0$ the electron charge, $\varepsilon$ the dielectric constant, $\varepsilon_0$ the permittivity of vacuum, $C$ the capacitance and $V$ the applied voltage. [66] The lower charge density of ZTO is confirmed by Mott-Schottky and the electrochemical capacitance ($C_{\mu}$). Thus the lower charge density of ZTO along with lower extinction coefficient of N719 may slightly affect $\Phi_{cc}$.

Figure 7.13 b shows the measured optical band gap of TiO$_2$ and ZTO and a complete energy level diagram is shown in Figure 7.13 c, with oxidation potentials of the dyes (measured attached to these semiconductors respectively, see Figure 7.14 a-c) [67], while the I$_3$ potential was obtained from the literature [68]. The optical bandgaps of TiO$_2$ and ZTO are seen to be 3.2 eV and 3.1 eV respectively; a factor further explored later in this manuscript with respect to photoactivity under AM1.5 illumination.
Figure 7.13: (a) Mott-Schottky measurements of TiO$_2$ and ZTO; (b) Tauc plot measurements of TiO$_2$ (inset) and ZTO, and (c) The relevant energy levels of the different components of the four DSC configurations.
Figure 7.14: (a) Square wave voltammograms showing the oxidation potentials of N719 and D149 dyes bound to ZTO or TiO$_2$ (b) and (c) The absorption onsets of N719 and D149, bound to ZTO or TiO$_2$. 
As dye aggregation has previously been seen to be an impediment to charge injection efficiency,[69] and N719 packing on ZTO was shown to be higher than on TiO₂. Films were examined after short (15 min) and long (24 hours) dying times, with only a slight shift in the ZTO|N719 absorbance peak position observed suggesting aggregation not significant. This was followed by with devices produced using with thin film ZTO|N719 DSCs, either with or without chenodeoxycholic acid as a co-adsorbant,[69] to prevent aggregate formation. The Absorbed Photon to Charge carrier Efficiencies (APCE) for these devices were quite similar, discounting dye aggregation as a major contributing factor to the low $J_{sc}$ in ZTO|N719 devices (Figure 7.15). It was however noted during this that the dye absorption profiles of N719 on ZTO were markedly different to those on TiO₂, while ZTO|D149 and TiO₂|D149 films showed similar absorbance profiles (Figure 7.16, below). The causes for these observed differences are explored further below.

![Figure 7.15](image)

**Figure 7.15:** Dye aggregation investigations for ZTO sensitized with N719 or N719: Chenodeoxycholic acid (1:10 molar ratio). (a) Absorbance of ZTO|N719 and ZTO (N719:CDCA) films (b) Incident photon conversion efficiency (IPCE); (c) absorbed photon conversion efficiency (APCE) and (d) J-V responses of devices.
Fourier-transform infrared (FTIR) spectroscopy

FTIR spectroscopy was employed to examine the bindings of both D149 and N719 on the two semiconductors (Figure 7.17 a,b). As shown in Figure 7.17 a, little difference was observed comparing ZTO|D149 and TiO$_2$|D149, in line with expectations given that there is only one carboxylic acid binding group as shown in Figure 7.18 a, limiting the ways in which the dye can bind to the surface (also corresponding well with the absorption properties in Figure 7.16).

Meanwhile, the FTIR response of N719 is strongly dependant on the semiconductor. It has previously been reported that N719 can bind to TiO$_2$ through a number of different mechanisms [70], including through two COOH groups on different bipyridyl ligands (bpy) (Figure 7.18 b), or COOH and COO$^-$ on the same one. This second configuration may explain the presence of some residual COOH in the FTIR spectra of (at ~1700 cm$^{-1}$). The presence of dyes bound through a combination of these mechanisms can also explain the split in the NCS vibration (2102 and 2079 cm$^{-1}$) for N719|TiO$_2$, as the different configurations of N719 will either result in the ligand being pointed away from the surface (where it will not interact). In the case of binding through -COOHs of the two bpys it will be far from the surface, while it will point slightly towards the surface if bound through COOH and COO$^-$ groups on the same bpy.

The differing FTIR results for N719 bound to surfaces can be explained by looking inter-atomic spacing of the metals in the two oxides. In TiO$_2$ Ti are ~3.78Å apart, which corresponds reasonably well with both the 7.1 Å separation of the COOH and COO$^-$ (measured from the carbon) and the 8.46 Å between COOH on neighbouring bpys (two
across one down, similar to the way a knight moves in chess) as shown in Figure 7.19 and Figure 7.18 c-e. This suggests that both binding mechanisms should be favourable, with minimal strain. Meanwhile, the spacing of neighbouring metals in ZTO is ~8.65 Å, which can accommodate binding from two COOH groups, albeit with more strain than the dye experiences on TiO₂. The alternate is of course that the dye only binds through one COOH, however the absence of COOH group vibration in the FTIR for N719|ZTO suggests this may not be so common. The single, symmetric binding mechanism of N719 to ZTO would be more likely to lead to the sharp optical absorption peak, whereas the combination of mechanisms on TiO₂ gives rise to a broader, convoluted absorption peak. This symmetry would also explain the presence of only one NCS peak (at 2102 cm⁻¹). It has also been claimed recently that the interaction between the NCS ligand and TiO₂ plays a major role in the effectiveness of this dye.[71, 72]

![FTIR spectroscopy measurements](image)

**Figure 7.17**: FTIR spectroscopy measurements (a) D149 dye; and (b) N719 dye as films and on TiO₂ and ZTO films.

The binding between D149 and ZTO is similar to TiO₂ resulting from similar interaction with D149. There are multiple modes of binding between N719 and TiO₂, but more simple for N719 on ZTO, which correlates with less broadening in the optical absorption, as well as lower charge injection yields.

As N719 remains a common benchmark dye, especially for new (non-TiO₂) metal oxide semiconductors (MOS), the understanding developed here may be useful to other researchers and motivation to revisit previous materials.
Figure 7.19: The chemical structures of (a) D149 and (b) N719; The crystalline structure of (c) ZTO and (d and e) TiO$_2$.

Figure 7.18: The spacing between the two carboxylic groups or between the carbonyl group and carboxylic group of N719 using Chem3D V17.1.
7.4 Photo-degradation measurements

One of the key arguments in favour of using materials such as ZTO is their decreased response to UV light, which is anticipated to translate to better photostability. It is expected that ZTO is more likely to show lower photodegradation toward organic dyes (less dye bleaching), in part due to a lower absorption coefficient (Figure 7.20). On the other hand, the thicknesses of optimal working electrodes in DSCs means the differences in extinction coefficient have limited effect on the total number of UV photons absorbed and the absorption onset of ZTO is slightly red shifted. In spite of this, the photodegradation of organic D149 dye on ZTO is expected to be less than that of TiO\textsubscript{2}, in line with expectation based on previous reports.[19-21]

![Graph](image.png)

**Figure 7.20:** Absorption coefficients of ZTO and TiO\textsubscript{2} (films thickness 18 \( \mu \)m and 12 \( \mu \)m respectively).

Dye bleaching or dye photodegradation is one factor that affects DSC operation lifetime. The response of wide bandgap semiconductors (photoanode material) to UV light can cause the dye degradation including due to generating reactive species (\( \text{O}_2^{-} \), H\textsuperscript{+} and OH\textsuperscript{-}) as a result of electron-hole charge separation or directly through oxidative strength of holes in the valence band.[73]

TiO\textsubscript{2} or ZTO can response to UV light because their band gaps are located within UV region. Therefore, the photocatalytic activities of TiO\textsubscript{2} and ZTO were investigated. The experiments were performed using ZTO and TiO\textsubscript{2} powders in aqueous dispersions to degrade Rhodamine B. The absorption traces and rate constant can be seen in Figure 7.21 a,b. Under the same conditions (same solid loading, initial dye concentration and irradiation), ZTO exhibited very low photo-dye degradation rate compared to TiO\textsubscript{2}.
indicating that ZTO is inactive photocatalytically material compared to TiO₂. This means ZTO is less likely to cause dye bleaching. Figure 7.21 b is a pseudo-first order reaction representing the reaction rate constants of TiO₂ and ZTO, obtained from the slope values, which are 1.4 h⁻¹ and 0.05 h⁻¹ respectively suggesting the poor photocatalytic efficiency of ZTO which is further verifying the dramatic difference in photodegradation compared to TiO₂.

The differences in morphologies (reactivity of sites on the surface), surface area, porosity, crystal structure, band edge potentials (driving forces) and light harvesting between the TiO₂ and ZTO are also, responsible for the high variations in their photocatalytic activates.[73] Moreover, the lower dark charge carriers’ density in ZTO may affect the electron-hole charge separation resulting in producing fewer radical species and hence reducing the photocatalytic activity.

As mentioned in the optical band gap measurements part, the optical band gap was smaller than nominally expected. This is probably attributed to the expected higher trap states localised close to ZTO conduction band resulting in narrowing the band gap value due to affecting the absorption properties.[38]

**Figure 7.21:** Photocatalytic activity measurements for ZTO and TiO₂ materials using Rhodamine B dye under simulator AM1.5 illumination.
7.5 Conclusion
Cubic aggregates of ZTO nanoparticles were synthesized using a simple solvothermal approach. The primary nanoparticles (13 nm) self-assembled to form cubic aggregated structures using 1:1 Zn: Sn precursor ratio, in spite of the product having 2:1 ratio. The optimum compositional ratio Zn: Sn 1:1 and optimum sintering temperature were used to control the crystallinity.

ZTO was applied and compared against a benchmark TiO$_2$ material as a photoanode for DSCs with film thicknesses of photoanodes optimized with either N719 or D149 dyes. The ZTO material led to 4.9% PCE devices when sensitized with D149, higher than ZTO|N719 (4.0%).

Although having a slightly lower surface area, ZTO afforded higher dye loading (both for D149 and N719) which was attributed to its higher isoelectric point. In spite of this, ZTO|N719, however, showed a low $J_{sc}$. The FF of the devices and EIS investigation suggest that recombination issues are not to blame for this issue. Equally, chemical driving forces for charge injection were shown to be similar for ZTO|N719 as for TiO$_2$|N719, with the different performance revealed to be related to the binding configuration, seen with both dye absorption and FTIR spectroscopy. Whereas the FTIR indicates multiple modes of binding between N719 and TiO$_2$, only one is seen for N719 on ZTO. This also correlates with less broadening in the optical absorption, as well as lower charge injection yields.

Furthermore, ZTO|D149 showed higher photostability under exposure to broad-spectrum light (300-350 nm) indicated that dyes are less likely to degrade on ZTO than on TiO$_2$. One of the persisting challenges is to get well-crystalized ZTO without presence other phases due to the thermal decomposition. As such, we see that ZTO is a promising photoanode material for organic dye based DSCs. Even though the performance of ZTO based devices is still lower than TiO$_2$ based devices.
7.6 References


31. Shimogawa, H., M. Endo, T. Taniguchi, Y. Nakaie, M. Kawaraya, H. Segawa, Y. Murata, and A. Wakamiya, *D–π–A Dyes with an Intramolecular B–N Coordination Bond as a Key Scaffold for Electronic Structural Tuning and Their Application in Dye-Sensitized Solar Cells*. Bulletin of the Chemical Society of


8 Conclusions and Future works

8.1 Conclusions
This thesis has discussed some issues for photoanode materials (TiO$_2$ or Zn$_2$SnO$_4$) that have been overlooked and were not investigated by most DSC researchers. The effects of amorphous material, aggregated mesoporous structure, the dye packing density, paste preparation approaches, and the dye binding mechanism on the light harvesting efficiency, including the dye loading and the light scattering, charge injection, and collection efficiencies, were investigated for DSCs based on photoanode materials fabricated from either TiO$_2$ or Zn$_2$SnO$_4$, and sensitized with organometallic ruthenium dye or organic dye. Typically, to fabricate an efficient DSC, photoanode materials should meet a number of requirements, such as high surface area with suitable dye binding sites to ensure high dye loading, high light scattering in the visible wavelength region, an optimum pore size distribution with uniform mesoporous structure to ensure efficient dye adsorption and electrolyte diffusion, suitable energy levels to match the sensitizer energy levels for efficient charge injection efficiency, and a highly connected mesoporous network with appropriate particle size to ensure efficient charge transport with lower recombination losses. Meeting all these requirements in a DSC system is still a challenge and depends on the photoanode material properties and other components.

In Chapter 3, the effect of amorphous TiO$_2$ in P25 on DSC performance was investigated, as commercial P25 (mixed phase anatase and rutile TiO$_2$) is widely used as a control in DSCs. It has been proven recently, however, that the low performance of DSC based P25 is not due to the rutile phase, as claimed previously. Therefore, removing and recrystallizing the amorphous TiO$_2$ by selective hydrothermal treatment resulted in enhancement of the PCE of hydrothermally treated P25 (H-P25) to 5.3% compared to untreated P25 (3.2%) without further optimization. This enhancement is mainly attributed to enhancement of the dye binding/loading, even with the lower surface area of H-P25, thereby increasing the $J_{sc}$. This study can be useful, as it stresses the importance of eliminating the negative effects of amorphous TiO$_2$ in other samples and other applications.

In Chapter 4: Two morphologies of sub-micron sized aggregated mesoporous anatase TiO$_2$ nanoparticles (TiO$_2$-700 and TiO$_2$-300) were synthesized by a new and facile solvothermal approach and applied as scattering layers for DSCs based on commercial anatase nanoparticles (NR18-T) sensitized with N719 dye. The DSC devices containing
these scattering layers showed higher performances (PCE of 9.1% and 8.2%) compared to devices based on commercial scattering layers (WER2-O) (PCE of 7.2%). This enhancement of DSC performance resulted from the higher dye loading and scattering of light, along with the more mesoporous structures of TiO$_2$-700 and TiO$_2$-300.

In Chapter 5: Solvothermally synthesized anatase TiO$_2$ nanoparticles (SANP) were obtained by a new and facile solvothermal reaction. The SANP photoanode (10 μm) sensitized with organic D149 dye showed higher PCE of 6.9% compared to only commercial nanoparticles (NR18-T) (5.6%) or a bi-layer with commercial large scattering particles (NR18-T/WER2-O) (5.9%). The SANP sensitized with N719 dye showed higher PCE of 7.7% compared to only commercial nanoparticles (NR18-T) (7.2%), however, but this is slightly lower than or comparable to the PCE value (7.9%) for commercial nanoparticles with commercial scattering layer (NR18-T/WER2-O). The enhancement of the SANP performance is mainly attributed to the enhancement of the light harvesting efficiency (dye loading and light scattering). Higher surface area and higher dye packing (higher isoelectric point) along with the scattering from aggregated nanoparticles resulted in higher SANP performance. SANP sensitized with organic D149 dye could potentially be used to make an efficient and low-cost DSC based on metal-free organic dye with further future optimization.

In Chapter 6, it was known that the preparation method for TiO$_2$ paste can significantly affect the transparency and the light scattering properties of photoanode materials. There has been no direct comparison, however, of the effects of using two different TiO$_2$ paste preparation approaches on DSC performance using N719 or D149 dyes. The performance of DSCs using dried or non-dried solvothermally synthesized anatase TiO$_2$ nanoparticles, labeled SANP-S and SANP-T, respectively, were compared. SANP-S/N719 and SANP-S/D149 devices showed higher performance (7.7% and 6.9%) compared to SANP-T/N719 (6.8%) and SANP-T/D149 (6.4%), respectively. The enhanced performance of SANP photoanode resulted from its higher light scattering ability (more aggregated nanoparticles), while the lower performance of SANP-T photoanodes is due to poor light scattering with higher transparency. SANP-T showed higher surface area (higher dye loading) and a more uniform pore size distribution with uniform surface morphology compared to SANP-S. The performance of SANP-T/D149 was only slightly lower compared to SANP/D149, which can enable us to make low-cost and efficient transparent DSCs with further future optimization.

In Chapter 7, cubic aggregates of Zn$_2$SnO$_4$ nanoparticles were synthesized using a
solvothermal approach for DSC application. The performance of ZTO DSCs with D149 is reflected by promising PCEs (4.9%), close to those of TiO₂|D149. The same was not true for N719. This is due to low injection yields in the non-TiO₂ system, tied to a different dye-binding mechanism.

ZTO is a promising photoanode material for DSCs; however, but its full potential depends on researchers’ consideration of the device as a whole, not simply swapping one component. As such, we believe that this chapter can provide significant insights in the following areas: (1) the mechanism for the synthesis of cubic aggregated ZTO; (2) the mechanism of dye binding (N719 and D149) on TiO₂ and ZTO, and its impact on charge injection; and (3) the performance of ZTO sensitized with organic dye. The device engineering strategies outlined here provide guidelines for the future development of DSCs based on ZTO material.

Finally, it can be concluded that many studies on designing optimum metal oxides nanostructures photoanode for efficient DSCs have been reported since 1991. However, there are some important aspects still unlooked and not deeply investigated in terms of light-harvesting efficiency. Many researchers have underestimated the challenges on DSCs and the future applications of this technology as the research trend has turned to develop other photovoltaic systems such as organic or perovskite solar cells to be more competitive in term of cost-effective compared to low-cost silicon solar cells. This thesis addressed and deeply investigated a number of effects such as amorphous content, optimum aggregated particle size, isoelectric point, paste preparation approach on TiO₂ or Zn₂SnO₄ photoanode materials sensitized with organometallic (N719) or organic (D149) dyes that affect the dye loading, light scattering, dye packing density, and dye-binding mechanism.

### 8.2 Future works

- As the role of amorphous material has not been considered for most novel metal oxide semiconductors used in DSCs, it is suggested that some of these materials should be revisited. By selective removal, charge injection yields may be substantially increased.
- By controlling the solvent ratio, particle and aggregate sizes may be fine-tuned and further optimized. These conditions can be tuned to optimize for different dye and electrolyte combinations.
- SANP-T devices can be further developed for BIPV applications. This includes the application of low absorbing redox mediators, such as Cu (I/II) complexes,
which also have been shown to deliver high efficiencies. Other sensitizers should also be considered here as these can provide a range of colours which may be desirable.

- Other metal oxide semiconductors may also be re-visited, if they suffer the same mis-match as exists between N719 and ZTO. As mentioned, N719 has been the de facto standard, and as such low efficiencies realized using this dye may not rule out the possibility of attaining high efficiencies with a better suited dye.