Synthesis and Characterization of Nanostructured Catalysts for Photovoltaic Applications

by

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Abstract

The objective of this project was to investigate the effect of the morphology of titanium dioxide (TiO₂) nanoparticles on the electron transport properties and light harvesting potential in a dye sensitized solar cell (DSSC). Particular attention was given to develop synthetic methods to produce metal oxide photocatalysts with similar crystallite size, with different morphologies (spheres, fibers, hierarchical spheres, and globular structures) with the aim of studying the relationship between morphology and photocatalytic activity. The addition of CNTs to the synthesis showed that they acted as nucleation sites and altered the morphology. Materials were fully characterized using Raman, SEM, XRD, BET, and FTIR.

The photocatalytic activity of the as-synthesized materials was tested in a DSSC configuration and characterized using electrochemical impedance spectroscopy. It was found that the different morphologies had different light scattering properties which influenced the efficiencies. Based on these preliminary results, the nanofibres prepared in heptane performed the best, with good dye loading, electron lifetime and diffusion coefficient. The addition of a scattering layer using hierarchical spheres showed promising results in decreased transparency and increased efficiency. The addition of CNTs had an adverse effect, this could be due to light blocking by the black CNTs and increased recombination with the electrolyte.

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Abbreviations and Physical Constants

<u> </u>		
h	Planck's constant	$6.620 \times 10^{-34} \text{ m}^2 \cdot \text{kg/s}$
e	Electron charge	$1.602 \times 10^{-19} C_{22}$
K _B	Boltzmann constant	$1.381 \times 10^{-23} \text{ m}^2 \cdot \text{kg/s} \cdot \text{K}$
С	Speed of light	2.998x10° m/s
А	Photoelectrode area	
AC	Alternating current	
AcOH	Acetic acid	
$B_{1/2}$	Full width half maximum	of the XRD peaks
BET	Brunauer-Emmett-Teller	
BSE	Backscatter electron micro	oscopy
CB	Conduction band	
C_{dl}	Double layer capacitance	
C_{DL}	Double layer capacitance	at working electrode/electrolyte interface
CNT/MWCNT	Carbon nanotubes/multiwa	alled carbon nanotubes
C _{pt}	Double layer capacitance	at counter electrode/electrolyte interface
CV	Valence band	
C_{μ}	Chemical capacitance	
d	TiO_2 film thickness	
D	TiO ₂ average crystallite si	ze
DC	Direct current	
DSC	Scanning differential calor	rimetry
DSSC	Dye sensitized solar cells	
Ef	Fermi level	
FF	Fill factor	
FTIR	Fourier transform infrared	spectroscopy
FTO	Fluorine doped tin oxide g	lass
η_c	Charge collection efficient	cy
η_{inj}	Injection efficiency of the	electron from the dye into the TiO_2
η_{LHE}	Light harvesting efficiency	У
I _{MP}	Current at the maximum p	ower point
IPCE	Incident photon-to-current	t conversion efficiency
I_{ph}	Photocurrent	
IS(EIS)	Impedance Spectroscopy ((Electrochemical impedance spectroscopy)
I _{SC}	Short circuit current	
I-V	Current-voltage	
jd	Dark reverse current densi	ity
Jsc	Short circuit current densi	ty
k_1, k_2	Raman-XRD correlation f	itting parameters
L	Electron diffusion length	
NIST	National Institute of Stand	lards and Technology
m	Ideality factor	
P _{in}	Total incident solar power	to the cell
Q	Raman wavevector	

R _{cell}	Total resistance of a DSSC cell
R _{ct}	Charge transfer resistance
R _D	Resistance associated with electrolyte diffusion
R _{pt}	Counter-electrode resistance
r _r	Recombination resistance
R _r	Recombination resistance of the film
R _s	Series resistance
R _{sh}	Shunt resistance
r _t	Transport resistance
R _t	Transport resistance of the film
R _{TiO2}	Total resistance of the TiO ₂ photoelectrode
SEM	Scanning electron microscopy
TGA	Thermal gravimetric analysis
TTIP	titanium tetraisopropoxide
V_{MP}	Voltage at the maximum power point
V _{oc}	Open circuit voltage
XRD	X-Ray diffraction
Z	Impedance
θ	Diffraction angle
Γ	Raman 141 cm ⁻¹ FWHM
Го	Intrinsic Raman 141 cm ⁻¹ FWHM
ωο	Intrinsic Raman 141 cm ⁻¹ peak position
Δω	Raman 141 cm ⁻¹ peak position

1 Chapter 1: Introduction

It is well known that in order to meet the world's energy requirements, and maintain a healthy ecosystem on earth we must find alternatives to conventional fossil fuel energy resources. There is a growing need to produce alternative forms of fuel and fuel production technologies that are pollution free, storable, and economical. Solar energy is one of the most viable solutions, and the development of inexpensive and efficient solar technologies is one of the primary goals of current research around the world.

The sun continuously irradiates the earth with 120,000 terawatts of energy which dramatically dwarfs the 13 terawatts of energy we currently consume per day[1,2]. Harnessing a small fraction of this energy to produce heat or electricity would be enough to meet the world's growing energy demands. Sunlight can be converted into energy in numerous ways: concentrated sunlight can produce heat for use or conversion into electricity; it can produce fuels synthetically and naturally for the storage of energy, using a photochemical process as in photosynthesis; and it can be directly converted into electricity by exciting electrons in a photovoltaic device. Since Einstein's discovery of the photovoltaic effect, there has been significant progress in the field. The word photovoltaic pertains to a type of material able to convert solar energy into useful electrical energy. They exploit the capability of semiconductors to excite electrons into a higher energy state within the material, creating a potential difference when exposed to light. The excited electrons are delocalized with greater mobility and can be collected by an external circuit and used for work. Different materials and solar cell configurations have been proposed to increase the efficiency and reduce their cost. These systems can be divided into three main groups (as shown in Figure 1-1):

(I) First generation solar cells: composed of mono-crystalline, poly-crystalline silicon or other homojunction semiconductors. They depend on a p-n junction to create a depletion region and separate the electron-hole pairs. The disadvantages of the silicon based photovoltaic are that they cannot absorb radiation with energy below that of the band gap (1.12 eV for crystalline silicon) [3] and they lose the thermal energy of photons exceeding the bandgap. Furthermore, there is a theoretical limit for photovoltaic conversion, known as the Shockley-Queisser limit, at 33.7% [4]. These solar cells have been commercially manufactured since the 1950's and have proven reliable. They are currently the most efficient generation of solar cells and make up most of the market. To compete with the fossil fuel industry a production cost of \$0.5/W would need to be achieved. Currently crystalline silicon cells are very energy intensive to produce and have an energy cost of about \$3/W[5,6].

- (II) Second generation photovoltaic cells: comprised of thin film solar cells made of CdTe, CIGS, and amorphous silicon (a-Si). They are lighter, more flexible, easier to manufacture and can be used in multiple junction solar cells. They are less expensive than silicon based solar cells but are less efficient, ~10%, and in some cases use more toxic materials [5]. Currently their energy cost is around \$1/W[6].
- (III) Third generation photovoltaic cells: this group includes a collection of unconventional systems created with the goal of surpassing the Shockley-Queisser efficiency limit and lowering production cost. Within this group are tandem and multi-junction solar cells; nano-crystalline solar cells which use the principle of quantum dots; organic solar cells or hetero-junction solar cells, which use photoreactive polymers as electron donors and fullerenes as acceptors; and finally dye sensitized solar cells (DSSC)[2,5].



Figure 1-1: Projections of cost and efficiency for the three solar cell generations. The single bandgap limit pertains to the Shockley-Queisser limit for unconcentrated (31.0%) and concentrated (40.8%) light. The thermodynamic limit is given by the theoretical efficiencies without energy lost for multi-junction solar cells. (Reproduced from ref [2]).

1.1 Dye Sensitized Solar Cells

The framework for DSSCs was set up by Fujishima and Honda in 1972 [7], when they demonstrated that one could photo-decompose water using a TiO₂ electrode. Since then, much research has gone into understanding the fundamental physical and chemical processes of TiO₂ photocatalysts. This lead Brian O'Regan and Michael Grätzel [8], to create a new photo-electrochemical cell termed the dye sensitized solar cell that used a TiO₂ electrode in conjunction with a dye to harvest visible light and near infrared radiation [8]. In 2010, Michael Grätzel's work was recognized with the prestigious Millennium Technology Grand Prize for his contributions to the field [9].

Dye sensitized solar cells rely on an interpenetration network of chemical junctions instead of the conventional solid-state homo junction devices. They separate the functions of the

absorption of light and the separation of the charge carriers unlike conventional cells that do this in a single step. As shown in Figure 1-2, DSSCs are comprised of five main components: (i) a dye, commonly a ruthenium complex (Figure 1-3), adsorbed on a (ii) mesoporous nanocrystalline semiconducting oxide, commonly TiO₂, deposited on to; (iii) a transparent conductive oxide on a glass substrate, most often fluorinated tin oxide (FTO) which makes up the photoanode; (iv) a counter electrode, commonly platinum on FTO; and (v) a redox mediator, conventionally an iodide/tri-iodide couple when using a ruthenium dye [10].



Figure 1-2: Schematic of a DSSC showing the main components: the photoanode $(FTO/TiO_2/Dye)$, the electrolyte, and the platinum counter-electrode.

Suitable dyes for this application are ones that have a broad absorption spectrum in the visible region, the dominant irradiation region on earth (Figure 1-4), as well as a reduction potential higher than that of TiO₂ and an oxidation potential lower than I_3/I_2 redox potential (Table 1-1). Moreover these dyes need to have a high photochemical stability in both the ground and excited states to allow for millions of turnovers and a long lifetime [11]. The sensitizer dyes most commonly used are ruthenium based complexes such as N-3 (C₂₆H₁₆N₆O₈RuS₂) and N-719 (C₅₈H₈₆N₈O₈RuS₂) because they possess the above mentioned properties.

	Energy	evel vs NHE (eV)
TiO ₂	2.70 (valence band)	-0.58 (conduction band)
N-3	1.10 (HOMO)	-0.70 (LUMO)
N -719	1.15 (HOMO)	-0.96 (LUMO)
I_{3}/I_{2}	0.3 (reduction redox potential)	

Table 1-1: Energy levels of TiO₂, N-3 and N-719 dyes and I_2/I_3 vs NHE[6,12].



Figure 1-3: Structure of common ruthenium bipyridine complexes, used as sensitizers in DSSCs.



Figure 1-4: Absorption spectrum of N719 in 0.1 M NaOH (1:1 ethanol-water) overlapping in the visible region with the solar irradiation on earth. The solar spectrum corresponds to AM 1.5 (solar irradiation at an angle of 48°). From American Society for Testing Materials (ASTM) http://rredc.nrel.gov/solar/spectra/am1.5/.

In a DSSC, the photocurrent depends on the number of electrons that can be promoted from the HOMO to the LUMO of the ruthenium complex sensitizer, The percentage transfered to the conduction band of the TiO₂ substrate, and finally to the FTO. As illustrated in Figure 1-5, the photoelectrons pass through the external circuit to the counterelectrode where the reduction of iodine (triiodide) to iodide takes place, then iodine will reduce the dye to sustain the cycle [6]. The maximum voltage depends on the potential difference between the Fermi level of TiO₂ and the redox potential of the iodide/triiodide couple [13]. The highest efficiency for a lab size cell (0.16 cm^2) stands at 12.3% under AM 1.5 G irradiation [14]; while for larger modules, 25-100 cm², value of about 8.5% is reported [2]. An air mass of 1.5 (AM1.5) is used as a representative spectrum at Earth's surface and corresponds to a light path length through the atmosphere at 48° angle.

Since O'Regan's and Grätzel's paper in 1991 [8] DSSC technology has gained a great deal of attention. The amount of research in the field has grown exponentially, reaching around 2000 publications in 2012. Because of the low fabrication cost, light weight, diversity of colours, and transparency options, industries such as Dyesol[®] and Solaronix[®] have started to produce modules and cater to research and development in this field. Clearly, the optimization of such complex system will require the work of chemists, physicists and engineers.



Figure 1-5: Schematic diagram of the electron transfer processes in a DSSC: a) Electron transfer band diagram; red arrows show the desired pathway for electron collection and green are the deleterious processes. The redox levels and band positions relative to vacuum level.

1.2 The TiO₂ Film: A Key Element in the Photoanode

Titanium dioxide (TiO₂) is the most widely used material in dye sensitized solar cells, mainly due to its photo- and thermal stability, chemical inertness, low cost, and low toxicity. The TiO₂ nanoparticles function as an electron/hole charge separator. Furthermore they form a mesoporous structure providing a scaffold for the dye, channels for the electrolyte, and a pathway for electron conduction.

 TiO_2 has three crystalline phases: brookite, anatase and rutile, with a Ti coordination of 6. The crystal structures are shown in Figure 1-6 and some physical properties of these phases are given in Table 1-2.



Figure 1-6: Crystal structures of different polymorphs of TiO₂. (Reproduced from ref [15]) **Table 1-2:** Physical properties of TiO₂ polymorphs [16].

			Rutile	Anatase	Brookite
Crystal system			Tetragonal	Tetragonal	Rhombohedral
Space group			P4 ₂ /mmm I4 ₁ /amd		Pbca
0	ſ	a	4.594	3.784	9.166
Lattice constants (Å)	4	b	4.594	3.784	5.436
		c	2.958	9.515	5.130
Density (kg/m ³)			4240	3830	4170
Band gap (eV)			3.0	3.2	-

Brookite is the least common form of TiO₂ with a rhombohedral crystal structure and a dark brown colour. Rutile is the most common and the most stable at high temperature and large crystal sizes [17]. It is tetragonal, with a band gap of 3.0 eV, and is a translucent reddish brown solid [16]. Anatase stems from the Greek word 'anatasis' meaning extension because it resembles the rutile tetragonal structure only elongated in the "c" direction (Figure 1-6). The physical properties of these three polymorphs are given in Table 1-2. Anatase is stable at small particle sizes ~14 nm [18], and has a large band gap of 3.2 eV, that limits the absorbance to the ultraviolet region, $\lambda < 385$ nm, which represents approximately 5-8% of the solar spectrum on earth. Despite the larger band gap, anatase is the more photocatalytically active, because of its higher redox potential, high absorbance onto TiO₂, better electron mobility, and fewer occurrences of recombination [19,20]. For this reason it has become a promising photocatalyst for a wide range of applications; it is also used in thin films and self-cleaning devices and as UV-shielding in paints, textiles and sunscreens [16].

Representative Raman spectra of anatase is shown in Figure 1-7 Anatase has six characteristic vibration fundamental modes: a very intense peak at 141cm^{-1} (E_g mode) and bands at 195, 395, 514, and 635 cm⁻¹ corresponding to E_g, B_{1g}, A_{1g}+B_{1g}, and E_g Raman modes respectively (the 514 peak comprises of two peaks which can only be identified under 74K)(Figure 3-17) [21].



Figure 1-7: Raman spectrum of TiO₂ anatase from Sigma Aldrich.

A representative X-ray diffraction spectrum of anatase is shown in Figure 1-8. The planes in the crystal (Bravais) lattice are given by the Miller indices. The (101) plane is the most stable. Other peaks correspond to the (103), (004), (112), (200), (105) and (211) surfaces.[18]



Figure 1-8: Powder X-ray diffraction spectrum of TiO₂ antase from Sigma-Aldrich.

Anatase TiO_2 can absorb ultraviolet radiation, and work as a photocatalyst by itself. Upon absorption of light an electron is excited from the valence band (highest electron energies at absolute zero) to the conduction band (minimum electron energy required to free the electron from its binding atom). The promotion of the electron into the conduction band allows the electron to move freely and conduct electricity, but it leaves behind a positively charge atom or "hole". The oppositely charged electron-hole pair will recombine if the charge carriers are not removed by other processes, like in a DSSC[16].

The electron-hole pair has a lifetime usually in the nanosecond regime, but if the charge carriers can migrate to the surface (the holes by diffusion) they can undergo charge transfer to

adsorbed species on the TiO_2 [20]. As expected, recombination in the semiconductor, or back transfer from the adsorbed species, lowers the quantum efficiency (IPCE).

Ideal TiO₂ crystal lattices are seldom possible in nanoparticles, instead the surface and bulk are filled with defects occurring from the synthesis. Although anatase is 6-fold coordinated, it is almost always oxygen-deficient, TiO_{2-x} ($x\approx0.01$) [2]. These deficiencies act as an n-type dopant (an excess of electrons) [20]. The n-type characteristic causes an accumulation of electrons at the surface forming a depletion layer and the bands to bend upwards at the interface between the particle and a metal forming a Schottky barrier [16]. These irregularities also have a different energy state than the bands and act as trapping sites on the surface helping to suppress recombination [20]. The smaller the particle the more reactive it is. A small particle size (~20 nm) is desired not only to increase the surface area, but also to increase surface/volume ratio and the distance charged carriers need to travel, thus reducing recombination[16,22]. Particle sizes less than 12 nm introduce quantum size effects and increase the band gap [20].

In the nanoporous network of TiO₂, an excited electron is subjected to hundreds of thousands of trapping events caused by isolated nanoparticles, surface states, and defects [23]. Trapping events slow the electron percolation towards the electrode and increase the probability of recombination. To guarantee that particles are electronically interconnected, a high temperature sintering step is applied to the TiO₂ film before adsorbing the dye [11]. Liao *et al.* [24] found that the morphology of the particles can be as important as crystallinity and size due to light scattering. They showed that TiO₂ hierarchical spheres had greater efficiency in the photoanode of a DSSC due to greater dye loading and light scattering even though the electron lifetime was greater than in highly crystalline and smaller particle photoanodes. Other methods of increasing the efficiency include placing a 200-400 nm nanoparticle scattering layer on top of the smaller particles; this increases the absorbance of light in the red or near-infrared region and scatters the light back through the photoanode.

The mixture of anatase and rutile has proven to be a better catalyst than any pure phase. It was proposed that rutile acts as an electron sink because of its lower band energy, thus leading to greater electron-hole separation and reducing the recombination [25]. However, Hurum *et al.* [19] showed that rutile can act as a sensitizer and pass electrons to lower energy anatase lattice

trapping sites. This stabilizes the charge separation allowing the charge carriers to move to the surface for catalysis and reduces recombination. Commercially available Degussa P25[®] is often used as a reference because of its excellent photocatalytic activity. It is produced through the pyrolysis of TiCl₄ at high-temperatures, and is a mixture of 80% anatase, 15% rutile, and 5% amorphous titania [26,27].

1.2.1 Summary of Synthetic Approaches

The number of experimental methods used to prepare TiO_2 nanostructures is extremely large and a detailed description of these methods is out of the scope of this thesis. However, a list of some of these methods, the experimental conditions and main reaction products are summarized in Table 1-3, for a better evaluation of the methods used in this thesis. The information presented in this table was taken from a Chemical Review paper published by Chen and Mao in 2007 [28].

Method	Experimental details and reaction products.				
Sol-gel	It is an extremely versatile method for producing metal oxide materials, from dense ceramics and films using spin-coating and dip-coating to highly porous and extremely low density materials (aerogels) when combined with other methods (spray pyrolysis, supercritical drying, solvothermal, metal and organic templates, etc). The sol-gel approach has been used to produce nanomaterials with variable size, morphology, and crystal structure				
Miscelle/ inverse miscelle	Commonly used to produce TiO_2 nanoparticles. The as-synthesized material is amorphous; nanoparticles of ~ 10 to 20 nm in diameter can be produced, but the particle size increases as a consequence of the heat treatment required for crystallization.				

Table 1-3: Description of TiO₂ synthetic methods

Sol	Usually it involves the reaction of TiCl ₄ with an oxygen donor molecule
	(titanium alcoxide or organic ether). The condensation reaction between
	Ti-Cl and Ti-OR results in the formation of Ti-O-Ti bridges and the
	formation of extremely small nanoparticles (1-5 nm). The method can also
	be combined with other approaches.
Hydrothermal	It is also highly versatile, but it requires a high pressure vessel (or
	autoclave) and controlled pressure and temperature conditions.
	Temperatures can be well above the normal boiling point of water, usually
	in the 150 to 250 °C range, and pressures between 5 - 20 MPa.
	Nanocrystalline materials can be obtained at extremely high temperature,
	under supercritical water conditions. Nanoparticles (rods and particles)
	between 7-25 nm in diameter were prepared by adjusting the concentration
	of the titanium precursor, the composition of the solution, temperature and
	reaction time.
Solvothermal	Almost identical to the hydrothermal method except that a non-aqueous
	solvent is used instead of water. It provides a better control of the size,
	shape distribution, and crystallinity at lower temperatures. Common
	solvents are ethanol, methanol, etc.
Direct Oxidation	The method involves the oxidation of a titanium substrate (anode). For
	instance, TiO ₂ nanotubes (15-120 nm diameter and 20 nm to 10 μ m in
	length) have been prepared by anodic oxidation of a titanium foil in a
	0.5 wt% HF solution under 10-20 V for 10 to 20 min using Pt as the
	counter electrode. The product has to be annealed at high temperature
	(~ 500 °C for 6 h in oxygen) to obtain crystalline anatase
Chemical Vapour	In this approach, TiO ₂ nanoparticles (and films) are produced by pyrolysis
Deposition (CVD)	of a titanium precursor (i.e. titanium tetraisopropoxide, TTIP). It requires a
	vacuum chamber.

Physical Vapour	Similar to CVD, but a chemical reaction such pyrolysis is not required.			
Deposition (PVD)				
Electrodeposition	TiO ₂ nanowires have been prepared by electrodeposition of a titanium			
	metal from a 0.2 M TiCl ₃ solution at pH=2 using an anodized alum			
	template as cathode and a pulse electrodeposition method. After deposition,			
	the deposited metal/template is heated and kept at 500 °C for a few hours			
	in oxygen to oxidize the metal and promote the formation of anatase. T template is removed using a H ₃ PO ₄ aqueous solution			
Sonochemical	Ultrasound can be used to synthesize crystalline nanomaterials taking			
	advantage of the high temperatures and pressures (up to \sim 5000 K and			
100 MPa) that can be achieved by acoustic cavitation (formation, and implosive collapse of bubbles in a liquid). TiO ₂ nanoparticle				
Microwave	Microwave radiation has been used to prepare different TiO ₂			
	nanomaterials. One of the best advantages of this approach is the time			
	required for the syntheses. Colloidal titanium nanoparticles have been			
	prepared in 5 to 60 min. The method can be used to produce anatase and			
	rutile nanoparticles, nanotubes, and nanorods.			

Synthesis of TiO₂ Aerogels using Supercritical Carbon Dioxide.

The use of supercritical fluids for the synthesis of nanomaterials is an attractive alternative to vacuum techniques or other solution based methods because nanoparticles with highly controlled size and morphology can be prepared by changing the metal precursor, the temperature and/or the pressure of the fluid. In addition, the method is ideal for *in-situ* surface modification when used in combination with capping agents, surfactants, or self-assembly methods.[29]

It is particularly useful for preparing composite materials d ue to the excellent conformity that can be obtained over highly complex topographies because of the low viscosity, high diffusivity, and zero surface tension of fluids in the supercritical region. The microscopic precision of TiO_2 replicas of materials such cotton and pollen, obtained using a sol-gel method in supercritical carbon dioxide (SC-CO₂) was better than the one obtained by a conventional sol-gel method, because the titanium precursor, aided by the SCF, can reach the surface of the sample and react with the -OH groups and H_2O adsorbed on the substrate surface. In addition, the low viscosity of SC-CO₂ prevents the collapse of the structure.[29]

TiO₂ /CNTs Composites for DSSC Photoanodes

Recently multi-walled carbon nanotubes (MWCNTs) have been added to the TiO_2 nanoporous network in order to improve the photodecomposition of organic compounds [30] and the efficiency of DSSCs [22,31]. Conductive carbon nanotubes act as 1-dimensional nanowires and have excellent electron mobility along their length [32].

Carbon Nanotubes (CNTs) were first identified by Sumio Iijima's group in 1991[33]; since then there has been an explosion of research into carbon nanotubes applications because of their fascinating electronic, mechanical and optical characteristics. Some proposed applications involve molecular containers for hydrogen and biological substances, nanowires, chemical and biological sensors, tips in scanning probe microscopy, utilization in flat-panel displays, photovoltaic devices, etc.

Carbon nanotubes can be described as a sheet of graphene rolled into a tube, where each carbon atom is connected to three others through strong σ bonds at 120° (sp² orbitals). The remaining π electrons are delocalized over the plane allowing it to be electrically and thermally conductive [34]. Single walled carbon nanotubes (SWCNT) are classified by length, diameter and chirality (the orientation of bonds around the circumference). The length of nanotubes ranges from hundreds of micrometers and even centimetres [35].

Multi-walled nanotubes (MWCNTs) are coaxial layers of single walled nanotubes held together through van der Waal interactions with an interlayer spacing of about 0.34 nm [34]. They tend to be metallic or semi metallic due to intertube coupling causing electron-hole pairing and the decrease in band gap with increase in diameter. The electrical properties are determined by the outer most layer of the MWCNT, because the π electrons are more delocalized outside the tube [34].

Three main proposed mechanisms have been proposed by which CNTs attached to TiO_2 nanoparticles can increase the efficiency of DSSCs: *i*) act as an electron sink by forming a Schottky barrier at the interface between TiO_2 and the CNT, trapping the electron and increasing its mobility (Figure 1-9); *ii*) act as a sensitizer absorbing light and exciting electrons to the TiO_2 (this method is only possible with single walled nanotubes of semiconducting type); and *iii*) act as a general carbonaceous impurity and induce defects into the TiO_2 band gap from local lattice reordering (this adds interstitial points in the band gap and makes it easier to promote an excited electron) [22,31]. This work is only interested in the first mechanism, using the MWCNT to decreasing the distance electrons need to percolate through the mesoporous network to enter the circuit.



Figure 1-9: Band diagram of the TiO_2 /CNT junction showing the bending of the bands of the n-type TiO_2 semiconductor and the formation of a Schottky barrier at the junction with the CNT.

It is worth noting that the black MWCNTs absorb in a wide spectrum range and undoubtedly lead to blockage of photons, but there are other deleterious processes. The Schottky barrier height at the interface between TiO_2 and MWCNT limits the charge collection efficiency by the MWCNTs [31], and in DSSC a naked spot on a MWCNT provides a place for recombination of the photogenerated electrons with the electrolyte, as carbon is a catalyst for the reduction of the electrolyte [36].

1.3 Thesis Objectives

The main objective of this thesis was to investigate the photocatalytic activity of TiO_2 and $TiO_2/MWCNTs$ photoanodes prepared with TiO_2 nanoparticles of different size and shape. Special attention was given to the methods used for the synthesis, with the aims of obtaining well uniform products and enough amount of material for a complete characterization and the preparation of dye sensitized solar cells.

To achieve this objective the following steps were taken:

- A high pressure and high temperature system was designed and constructed for synthesis involving supercritical carbon dioxide. A view-cell (autoclave) with sapphire windows was used to confirm the presence of more than one phase, and the evolution of the reactions. The system is described in Chapter 2.
- 2) Different synthetic approaches were investigated and tested in the laboratory, until a method able to produce enough amount of material for the preparation of dye sensitized solar cells could be identified and implemented. The sol-gel approaches used for the synthesis and the characterization methods (XRD, Raman, FTIR, SEM, etc) are presented in Chapter 3.
- 3) A method for screen printing TiO₂ films on FTO was implemented to prepare the photoanodes used in the DSSCs for studying the photoelectrical properties of the cells. The methods used for the fabrication of DSSCs and the photoelectric properties of the cells are summarized in Chapter 4.

2 Chapter 2: High Pressure System Design

2.1 Supercritical Fluids and High-Pressure System for Supercritical Drying and Synthesis

For a first-order phase transition, discontinuous changes in the density, enthalpy, and entropy of a substance are observed as the transition takes place. As shown in Figure 2-1, the vapour pressure lines divide the (p,T) plane into different regions, each point on a line represents the equilibrium between two phases, above and below the vapour pressure curve, only one phase is stable. In the case of liquid-gas equilibrium, the vapour pressure line ends at the critical point, at this temperature and pressure, the density of the liquid and gas phases are equal.



Figure 2-1: Pressure vs temperature phase diagram for CO₂ (REFPROP Database, NIST).

At temperatures and pressures above the critical point, it is possible to pass from the liquid to the gaseous state without undergoing any discontinuous change of state, being an ideal medium for the synthesis of nanomaterials because it shows vapour and liquid-like properties

depending on the temperature and pressure. A list of commonly used solvents and there critical parameters is given in Table 2-1.

Fluid	Critical Temperature (°C)	Critical Pressure (MPa)	Critical Density (kg/m ³)
CO_2	30.98	7.377	467.6
Water	373.9	22.10	322.0
Heptane	267.0	2.736	232.0
Ethanol	240.8	6.148	276.0

Table 2-1: Critical parameters for commonly used solvents for the synthesis of nanomaterials

Despite carbon dioxide being a greenhouse gas and a by-product of most industrial processes, CO_2 as solvent is environmentally benign. It can be recycled, the energy costs associated with thermal control, mixing, separation, purification, and drying are very low, and the solvent can be easily removed by depressurization. It is also non-flammable, non-toxic, and inexpensive; and it is an excellent alternative to non-polar organic solvents due to its low dielectric constant. Supercritical carbon dioxide has been extensively used for the synthesis of nanostructured materials with controlled size, particle distribution, and morphology [37])

2.2 Design and Construction of a High Pressure Injection System

In this work, the syntheses were carried out using the high pressure cell and a highpressure flow injection system shown in Figure 2-2 and Figure 2-4. A high pressure Teledyne ISCO pump with a cooled jacket was used to inject the solvent into the cell. The pump piston was kept at approximately 1 °C using a MGW Lauda Brinkmann cooling bath. A check valve at the pump outlet prevented the reactants or the reaction products from reaching the pump. Downstream several high pressure ON-OFF valves and filters were used to fill the cell with the solvent (CO_2), and the co-solvents or modifiers (H_2O_2 , acetic acid, or ethanol). A rupture disk rated at 35 MPa was connected to the cell for safety purposes. At the end of the high pressure line and after the cell, the pressure of the system was controlled by a high-pressure ON-OFF conditions) Swagelok valve (static or а Swagelok back-pressure regulator (KPB1S0A412P20000) for experiments carried out under flow conditions. A Swagelok nipple (20 cm³ in volume) was used as a trap to prevent any solid material to reach the pressure

regulator or the ON-OFF Swagelok valve. A schematic of the cell and the heating cradle, along with a picture of the custom made view-cell (50 mL) used for the syntheses are shown in Figure 2-3.



Figure 2-2: Picture of the high-pressure injection system used for the syntheses in supercritical carbon dioxide.



Figure 2-3: Schematic of cell and high-pressure view-cell with sapphire windows.



Figure 2-4: Schematic of the high-pressure injection system and oven used for the synthesis in supercritical carbon dioxide.

Pressure and Temperature Sensors Calibration

The thermocouple and the Pt-RTD 100 sensors used to control and measure the temperature of the cell were calibrated using the normal freezing and boiling points of water, 0 °C and 100 °C, respectively.

The pressure transducer was calibrated using the vapour pressure of liquid CO_2 at five different temperatures in the range 13.3 to 28.9 °C. The recommended vapour pressures values for liquid CO_2 were taken from REFPROP (REFerence fluid PROPerties), a database developed by the National Institute of Standards and Technology (NIST). For the pressure transducer calibration, the cell was filled with liquid CO_2 , and after equilibration the change in pressure at constant temperature was recorded as the fluid was allowed to leave the cell. A typical pressure

vs. time plot at 24.7 °C is presented in Figure 2-5. As shown, a pressure drop is observed until the liquid-gas coexistence line is reached; at this point the vapour pressure of the fluid remains constant until there is no more liquid into the cell. After vaporization of the liquid, the pressure of CO_2 gas decreases until there is no more gas in the cell.

The plateau pressure at each temperature corresponds to the equilibrium vapour pressure given by the Clapeyron-Claussius equation. The values were taken from REFPROP. The atmospheric pressure required for the calculations of absolute pressures was obtained from the Oshawa Municipal Airport.



Figure 2-5: Pressure transducer calibration (24.7 °C). Left axis: temperature of the cell vs time; right axis: pressure of the cell vs time (from left to right: liquid CO₂, vapour pressure of CO₂ gas/liquid equilibrium, CO₂ gas)



Figure 2-6: Calibration of Omega DYNE pressure transducer; blue point at atmospheric pressure from Oshawa municipal airport. (y_{int} =- 0.471; slope =3.533; R² = 0.99996)

3 Chapter 3: Synthesis and Characterization of TiO₂ and TiO₂/CNTs Composites

3.1 Introduction to Sol-Gel Synthesis of Metal Oxide Nanomaterials

Ebelmen [38], in 1846, synthesized the first metal alkoxide compound by reaction of silicon tetrachloride (SiCl₄) with isoamylalcohol (3-methyl-1-butanol); in subsequent years analogous products were obtained using a similar approach and different metal chloride precursors. It was in some of these pioneering studies that researchers observed the hydrolysis of tetraethyl orthosilicate, Si(OC₂H₅)₄, which under acidic conditions resulted in the formation of SiO₂ [39]. In 1930, the sol-gel method was used for the preparation of metal oxide films by the Schott glass company in Germany, and soon after, a first attempt to produce a silica aerogel using ethyl alcohol, and supercritical drying was made [39]. Since then, the sol-gel method has

been used to produce radioactive oxide ceramics for use in fuel rods in an effort to avoid harmful dust, multicomponent glasses, aerogel and dense ceramic materials, and coatings [40].

The Sol-Gel Process

The sol-gel reaction is a solution based synthesis method, which is an easy and versatile way to make a metal oxide ceramic. It allows for control over stoichiometry, and morphology, and offers the capability of producing composite materials. The main steps are: hydrolysis and polycondensation of an alkoxide precursor followed by aging and drying. In general, a metal precursor reacts with a catalyst to form a colloidal solution termed the *sol*, which polymerizes with time forming a *gel* that matures and hardens upon aging and drying. Metal-alkoxides are commonly used for these reactions; they belong to the family of metal-organics and are defined as a metal atom attached to organic ligands through metal-oxygen-carbon linkages [40]. In the hydrolysis reaction the metal-alkoxide reacts with water to produce a sol:

$$M(OR)_{n}+H_{2}O\rightarrow HO-M(OR)_{n-1}+ROH$$
(3-1)

where M represents the metal atom and OR the ligand. The extent of the hydrolysis reaction depends on the amount of water present in the reaction media. Condensation reactions between two hydrolysed or partially hydrolysed molecules:

$$(OR)_n M-OH + HO-M(OR)_n \rightarrow (OR)_n M-O-M(OR)_n + H_2O$$
 (3-2)

or

$$(OR)_n M-OR + OH-M(OR)_n \rightarrow (OR)_n M-O-M(OR)_n + ROH$$
 (3-3)

can also result in the formation of water (3-2).

The extent of the hydrolysis reaction will depend on the amount of water and it will determine the gelation time, structure and crystallization temperature. Hydrolysis and condensation reactions will result in the formation of a gel, a continuous interconnected network of a porous solid phase, and a liquid dispersed phase. Depending on the method used for

removing the liquid from the gel, supercritical drying or drying in ambient conditions, an aerogel or a xerogel can be obtained, respectively. A schematic of the overall process is shown in Figure 3-1.



Figure 3-1: Schematic of the sol-gel process for the synthesis of aerogels, xerogels and dense ceramic materials.

The sol-gel method offers good control over the chemical and physical properties of a material and it is an ideal approach for synthesizing nanomaterials tailored towards specific applications like DSSCs.

3.1.1 Synthesis of TiO₂ Nanomaterials using the Sol-Gel Reactions

Titanium tetraisopropoxide, Ti $\{OCH(CH_3)_2\}_4$ titanium butoxide, Ti $\{OC_4H_9\}_4$, and titanium tetrachloride, TiCl₄, are the most popular precursors for the synthesis of TiO₂ nanoparticles. Compared to silicon alkoxide, titanium alkoxides are orders of magnitude more reactive [40], and chemical additives need to be incorporated to the reaction media to control their reactivity. The reaction of Ti(O^{*i*}Pr)₄ or Ti(O^{*n*}Bu)₄ with water is also very fast and results in the formation of ill-defined metal oxide products. Acetic acid is commonly used to moderate the reactivity of titanium alkoxides through a ligand substitution reaction:
$$Ti(OR)_4 + 2 CH_3 COOH \rightarrow Ti(OR)_2 (CH_3 COO)_2 + 2 ROH$$
(3-4)

The reaction is exothermic and results in the Ti coordination number increasing from 4 to 6, with the acetates acting as bidentate and/or bridging ligands through a substitution reaction (Figure 3-2 b) [41-43]. The bridging ligands are the result of two or more monomers condensing to form dimers and trimmers [41].



Figure 3-2: a) Molecular structure of titanium tetraisopropoxide; b) Titanium dimer with acetate bridging ligands in blue.

In addition to the previous mechanism, direct linkages through transesterfication reactions can also occur [5],

$$Ti(OR)_4 + Ti(OR)_3 (OAc) \rightarrow (OR)_3 Ti - Ti(OR)_3 + AcOR$$
 (3-5)

In the case of titanium tetraisopropoxide (TTIP), when the acetic acid-to-titanium isopropoxide ratio is 1:2 or less, most of the acid is consumed in the ligand substitution reaction and any free acid can react with the isopropanol to form isopropyl acetate (an ester) and water (reaction (3-6)).

$$CH_3COOH + (CH_3)_2CHOH \rightarrow CH_3COOCH(CH_3)_2 + H_2O$$
 (3-6)

This reaction is inherently slow, but the titanium species formed in the first stages of the sol-gel reaction act as a Lewis acid catalyst, increasing the rate of the reaction [29,41]. Through this reaction water is gradually released and allows better control of the reaction rate. Previous studies have also shown that water reacts more rapidly with the less electronegative isopropyl groups than the acetate ligands and it is one of the reasons for the different TiO₂ morphologies observed when changing the acetate-to-titanium precursor ratio [42]. These studies have shown that in the initial stages of the sol-gel process dimers and trimmers form and arrange into the stable configuration of a hexamer ring cluster $Ti_6O_4(OPr)_8(OAc)_8$ [41,42,44]. As shown in the hexaprismane clusters (Figure 3-3), the isopropyl groups are oriented in the axial direction, while the acetate groups are bridging two titanium atoms. Over time the hexamer rings link together through condensation reactions and ultimately precipitate out of solution.



Figure 3-3: Hexaprismane shape $Ti_6O_4(OPr)_8(OAc)_8$ cluster. Isopropyl groups in the axial direction (red circles) and acetate ligands in the radial direction (blue circles). Figures reproduced from [45].

Recently, Sui *et al.* [45] used this approach for producing fibers and nanoparticles in heptane and supercritical carbon dioxide. In these studies, the different reactivity of the isopropoxide and acetic acid ligands in the clusters was used to control the morphology of the final products as shown in Figure 3-4. At acetic acid-to-titanium tetraisopropoxide ratios greater than 4, the excess of water resulted in a complete hydrolysis of the isopropoxide ligands and

condensation reactions in a preferred linear orientation takes place and a 1-D and 2-D structures were obtained. At lower ratios, incomplete hydrolysis of the isopropyl groups will interfere with how the hexamer rings come together, resulting in condensation reactions in random orientations depending on the ratio, nanoparticles (3-D) or nanosheets (2-D) were synthesized.



Figure 3-4: Reaction condensation pathways depending on amount of acetic acid added (from ref [45]).

The approach of Sui *et al.* [45] is particularly attractive for the synthesis of TiO_2 nanomaterials for dye sensitized solar cell applications since a change in the morphology of the TiO_2 solid used to prepare the films could improve the electron percolation toward the electrode and reduce the probability of recombination either with the oxidized dye or with the tri-iodide (I₃⁻) as it was discussed in section 1.2.

Summarizing, the replacement of a metal alcoxide by a mono- or bidentate ligand such as acetic acid has several consequences: (i) the degree of crosslinking is reduced because of the

reduction in the number of hydrolysable groups per titanium, (ii) the connectivity between titanium building blocks is lowered and avoids the formation of crystalline materials, (iii) the complexing ligands can make the hydrolysis and condensation reactions more favourable in one particular position resulting in the formation of materials with very distinct morphology (fibers or particles).

Synthesis of TiO₂ –MWCNTs Composites

The chemical inertness of CNTs provides a challenge in processing them; they have a tendency to agglomerate due to van der Waal forces between them and are difficult to keep in solution. Oxidation, also known as functionalization, is commonly used to increase the reactivity of the CNTs by adding –COOH and –OH groups at the ends and the outer walls of the tubes. The process can dramatically change the properties of the material and it should be carefully monitored [46]. Sinterization of TiO₂/CNT composites can strengthen the chemical linkage between TiO₂ and CNTs if functional groups are present [22].

3.2 Experimental

3.2.1 Chemicals and Materials

All starting materials were of analytical reagent grade and used without further purification. TiO₂ and TiO₂-MWCNTs composites were synthesized from titanium(IV) tetraisopropoxide (97%, Sigma-Aldrich) using glacial acetic acid (>99.5%, Sigma-Aldrich) as chemical additive with/without carbon nanotubes in two alternative reaction media, heptane (HPLC grade, Fisher Chemical) and supercritical carbon dioxide (CO₂, 99.99%, PRAXAIR). Multiwalled carbon nanotubes were purchased from Bucky USA (BU-200, 95 wt%, 5-15 nm diameter, 1-10 μ m length). The as-purchased carbon nanotubes were purified with a nitric acid/sulfuric acid mixture (1:3 vol/vol ratio) mixture. Approximately 8 ml of the nitric /sulfuric acid solution was used to purify 200 mg CNTs. The mixture was sonicated for 30 min and then refluxed for another 30 min at 120 °C with stirring as described by Fogden *et al.* [47]. The

nitric/sulfuric acid mixture is stronger than its component parts because of the formation of the strongly oxidizing nitronium ion (NO_2^+) .

$$H_2SO_4 + HNO_3 \rightleftharpoons HSO_4^- + NO_2^+ + H_2O$$
(3-7)

After that, the mixture is dispersed in 500 ml water and vacuum filtered using a 0.2 μ m Teflon membrane (Millipore) until neutral pH. The CNTs were then re-suspended in 500 ml 0.01 M sodium hydroxide aqueous solution (50%, Sigma Aldrich), filtered, and then washed with deionized water (16 M Ω ·cm) until neutral pH was achieved. They were collected and dried in a vacuum oven at 120 °C for 12 hours. Raman and FTIR spectroscopy, along with thermal gravimetric analysis were used to evaluate the success of the purification procedure.

3.2.2 Synthesis of TiO₂ Nanomaterials in Heptane and SC-CO₂

Two different synthetic methods were used to produce TiO_2 nanomaterials with welldefined morphology, particle size, and surface area: a sol-gel method in supercritical CO₂ to produce TiO_2 aerogels; and a sol-gel method in heptane, also a non-polar solvent, to produce xerogels. The properties of both solvents are summarized in Table 3-1.

In both cases, the experimental conditions were taken from previous studies. The synthesis in SC-CO₂ was proposed by Charpentier's group at Western University [48], while the synthesis in heptane was developed by Sui *et al.* [45] at the University of Calgary. To the best of our knowledge, this is the first time that any of these materials, with or without CNTs, were used for a DSSC application.

	Heptane	Carbon dioxide
Molar Mass (g·mol ⁻¹)	100.21	44.01
Normal sublimation temperature (°C)	N/A	-78.4
Normal boiling point (°C)	98.4	
Critical temperature (°C)	266.98	30.98
Critical pressure (MPa)	2.73	7.37

Table 3-1: Properties of heptane and carbon dioxide

Critical density (kg/m ³)	232.0	467.6
Density (kg/m ³ at 60°C)	649.41 ^a	764.73 ^b
Viscosity (μ Pa·s at 60°C)	272 ^a	66.0 ^b
Surface tension (mN/m at 20°C and 0.1 MPa)	20.14 ^a	

^a values at 0.1 MPa (synthesis conditions in heptane) ^b values at 23 MPa (synthesis conditions in SC-CO₂).

The syntheses in heptane were carried out at 60 °C under a nitrogen atmosphere using a three-neck round-bottom flask, connected to a condenser, in an oil bath. The temperature of the flask was controlled by a hot plate. The flask was purged with nitrogen for 10 min and then a nitrogen filled balloon was attached to the condenser to prevent air/moisture to get in contact with the titanium precursor. Acetic acid and titanium tetraisopropoxide were injected into the flask through a silicon septum and the stirrer was turned on and kept running until gelation. A summary of the synthesis conditions is given in Table 3-2.

	AcOH /TTIP: 3.5	AcOH /TTIP: 5.5	AcOH /TTIP: 7
Heptane	8 mL	8 mL	8 mL
Acetic acid (AcOH)	4.5 mL	7.2 mL	9 mL
Titanium tetraisopropoxide (TTIP)	6.7 mL	6.7 mL	6.7 mL
Temperature	60 °C	60 °C	60 °C
Time	5 d	5 d	5 d
Pressure (heptane)	0.1 MPa	0.1 MPa	0.1 MPa

Table 3-2: Synthesis conditions for different AcOH/TTIP ratios in heptane.

In all cases, the initial amber colour solution became white and opaque after a few hours, indicating the formation of colloids, with lower ratios taking much longer. The gelation time of the reaction also depended upon the AcOH/TTIP mole ratio: 16 h, 1 d, and 2 d, for the 7, 5.5, and 3.5 molar ratios, respectively. In all cases, the gel was collected after a five day period to allow for adequate aging time and comparison between runs. The solid samples were placed in a vacuum oven at 80 °C for 12 h to remove heptane and other volatile reaction products. Subsequently, the material was annealed at 500 °C for 90 min to remove acetate surface groups

and to undergo the desired phase transition from amorphous to anatase. XRD and Raman spectroscopy were used to confirm that the transition was completed after 90 min.

The syntheses in SC-CO₂ (Figure 3-3) were carried out under conditions similar to those for heptane (60 °C for 5 days) except that they were done at high pressure, around 22.5 \pm 1.5 MPa using the high pressure system described in Chapter 2.

	AcOH/TTIP	AcOH /TTIP	AcOH /TTIP	AcOH /TTIP
	3.5	4 0	5 5	7 0
Acetic acid	7.5 mL	8.7 mL	11.8 mL	9.0 mL
Titanium tetraisopropoxide	11.1 mL	11.1 mL	11.1 mL	11.1 mL
Temperature	60 °C	60 °C	60 °C	60 °C
Pressure (SC-CO ₂)	~22.5 MPa	~21 MPa	~22 MPa	~23 MPa
Time	5 d	5 d	5 d	5 d

Table 3-3: Synthesis condition for different AcOH/TTIP ratios in SC-CO₂.

For the syntheses, the reactants were introduced into the stainless steel autoclave in a glove bag under a nitrogen atmosphere to minimize any possible contact with water. The high pressure system was purged with CO_2 at 3 ml/min for 5 min to remove any moisture, and then brought to the final pressure at a temperature of 60 °C. As shown in Figure 3-5, the solution started off the same amber colour as the one in heptane. With time, emulsions started to form and become thicker until the windows became opaque, about 12 h for the 5.5 ratio, but longer for lower AcOH/TTIP ratios. In all cases, the reaction mixture was stirred for a day and a half and left to age for three and a half more days. The system was purged with 500 mL of CO_2 at around 5 ml/min at 60 °C and 20 MPa to remove reaction by-products and unreacted acetic acid. When the autoclave was opened the TiO₂ material was a light, airy, white powder encompassing the entire volume of the cell; very different in texture from the thick gel obtained in heptane. The TiO₂ solid products were collected and annealed at 500 °C in air for 90 min. The syntheses were repeated several time and the results were reproducible.



Figure 3-5: Progression of TiO_2 synthesis in SC-CO₂ a) two phase system before pressurizing; b) liquid phase after pressurizing, but before heating; c) supercritical phase, 60 °C and 23 MPa; d-g) emulsion formation until the window becomes opaque.

3.2.3 Synthesis of TiO₂/CNT Composites in Heptane and SC-CO₂

 TiO_2/CNT composites were prepared in two different ways: mechanically mixing the pretreated CNTs and the TiO_2 solids with a mortar and pestle; or adding to the titanium precursor and acetic acid mixture. Numerous groups have reported beneficial results by mixing CNTs with TiO_2 [31], or adding them to a conventional sol-gel synthesis [36], but a literature review revealed TiO_2/CNT composites were not synthesized, using the method described above, in heptane or SC-CO₂ without a co-solvent.

For the synthesis in heptane, ~ 3 mg of acid treated CNTs were added to each of the AcOH/TTIP mixtures, as summarized in Table 3-2, to get a solid with ~ 0.2 wt% CNTs; the mixtures were sonicated for about 30 min and then transferred to the three neck round flask. The initial dark grey mixtures underwent gelation faster than in the absence of CNTs. The gelation time for the 5.5 ratio decreased form 1 d to about 18 h and a similar decrease was observed for the 3.5 ratio. A similar approach was adopted for the syntheses in SC-CO₂.

For the syntheses in SC-CO₂, 5mg of acid treated CNTs (\sim 0.2 wt%) were sonicated for 30 min in acetic acid before being added to the autoclave in the glove bag where the titanium precursor was previously loaded. The conditions were identical to those in Table 3-3.

3.2.4 Materials Characterization

Powder X-ray diffraction (XRD) analysis was used to characterize the crystal phase and crystallite size. The experiments were performed with a Philips XRD system with PW 1830 HT generator, a PW 1050 goniometer, PW3710 control electronics and X-Pert system software. A Cu K-Alpha 0.154 nm X-ray source was used, scanning from 20° to 60° 20 with a step size of 0.02° . The average crystallite size was estimated using the Scherrer equation:

$$D = \frac{k\lambda}{B_{1/2} \times COS\theta}$$
(3-8)

where λ is the wavelength of incident X-ray, B_{1/2} is the full width half maximum of the peak in radians, θ is the diffraction angle in radians, and k is the Scherrer constant dependent on instrumental broadening, for the 101 peak which was found to be k = 1.114 for the 101 peak using 25 nm anatase from Sigma Aldrich. The crystallite size is inversely dependent on the full width half maximum (FWHM).

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed on the samples to identify the elemental mass composition, decomposition temperatures and phase changes of the materials. Thermal decomposition studies were performed with an SDT Q600 Thermal Gravimetric Analyzer from TA Instruments under argon (Praxair, AR5DVH-T, Airgas AR UHP200) and under dry air (Praxair, A10.0 XD-T, Airgas AI UZ200). Mass and temperature calibrations were conducted periodically, to ensure a reliable comparison between runs.

Raman measurements were used as the primary characterization method; it provided a quick and easy way of identifying impurities, crystallinity and particle size. A confocal Renishaw Raman Imaging Microscope System 2000 was used in this study. Stokes scattering was collected in the range 4000-100 cm⁻¹ with an argon ion laser at 514 nm at 25 mW output power. Repeated acquisitions (20 scans) with an acquisition time of 10 s at the highest magnification (50x), were accumulated to improve the signal-to-noise ratio. The spectrum was collected for no less than 3 sample locations to ensure uniformity. The Raman peaks become

broader and a blue shift can be seen in the 141 cm⁻¹⁻ (E_g) peak when crystallite size becomes smaller.

The samples were also analysed with a JOEL JSM6610-Lv Scanning Electron Microscope (SEM); with an Oxford/SDD EDS detector, X-Ray Microanalysis; digital imaging via SE, BSE and X-ray signals. The samples were mounted using carbon tape sputter coated with a gold film and examined at 20 kV.

Fourier transform infrared spectroscopy (FTIR) was used to examine the effectiveness of the purification method used. A Perkin Elmer spectrum 100 attenuated total reflectance (ATR) was used with powder samples, covering a spectrum from 600 - 4000 cm⁻¹.

The surface area of the TiO₂ samples was determined by nitrogen sorption measurements. The determination of the specific area of the sample using the Brunauer, Emmett and Teller (BET) theory is based on the phenomenon of the physical adsorption of nitrogen. Even though several assumptions involved in this model do not necessarily apply for all materials, the BET model constitutes the standard technique for surface area determinations. The gas adsorption measurements were made using a Micromeritics 2390a with nitrogen as the adsorbent. The typical sample mass used was 50 mg. The samples were degassed under nitrogen flow at 50 °C, for a minimum of 2 h prior to gas adsorption measurements.

3.3 **Results and Discussion**

As described, the materials were synthesized over a wide range of different conditions: synthesis medium (liquid vs supercritical fluid), temperature, AcOH/TTIP ratios; and with and without the addition of carbon nanotubes. This section discusses the results of the different syntheses and compares the findings with the work of others.

3.3.1 Effect of Temperature on Synthesis in SC-CO₂

Most syntheses in SC-CO₂ (60 $^{\circ}$ C, ~22.5 MPa) involved three different acetic acid (AcOH) to titanium tetraisopropoxide (TTIP) molar ratios (Table 3-3). An additional run at a 4.0 ratio was also carried out in the initial stages of this thesis for BET studies, but it was not used to prepare any DSSC film.

We have used the view-cell described in Chapter 2 to approximately determine the time required for the colloidal suspension to become thick enough to block the light coming through the windows (Figure 3-5). As expected, as the AcOH/TTIP ratio increased, more water was released by the condensation and esterification reactions and the overall sol-gel process became faster. For the 3.5 AcOH/TTIP ratio the windows became opaque after about 18 h, 16 h for the 4.0 ratio, while it took only 12 h for the 5.5 ratio to become opaque, in good agreement with previous studies [41,42].

The effect of temperature on the kinetic of reaction was also investigated with the aim of speeding up the synthesis time and reducing the particle size. Figure 3-6 shows the reaction products obtained in three different runs at 60, 100, and 150 °C at 23 MPa and an AcOH/TTIP ratio equal to 4. In the case of the synthesis at 100 °C, it took only 60 min to completely block the window; 15 hours less than at 60 °C. The products formed at different temperatures are shown in Figure 3-6.



Figure 3-6: SEM images of TiO_2 samples synthesized in supercritical CO₂: a,b) 60 °C, c) 100 °C, d,e) 150 °C at 22 MPa. All syntheses involved a AcOH/TTIP ratio of 4:1 and an aging time of five days. The images indicate increased nucleation and the formation of smaller particles with increasing temperature.

The SC-CO₂ synthesis at a AcOH/TTIP ratio of 4, resulted in the formation of spheres a few micrometers in diameter (<4 μ m) coated with small fibers that gradually decreased in length and eventually disappear at 150 °C. We attribute these changes in morphology to an increasing number of nucleation sites due to the pronounced decrease in the density of SC-CO₂ as the temperature is increased from 60 to 150 °C at constant pressure, as illustrated in Figure 3-7. The greater number of nucleation sites formed at high temperatures is the result of the increase in the supersaturation degree and precipitation of the product [49]. It can be seen that the large microparticles (Figure 3-6e) are made up of many smaller particles; this is not as evident in the other samples.



Figure 3-7: Dielectric constant and density of CO_2 as a function of temperature at 23 MPa (data obtained from REFPROP).

The crystallinity of TiO_2 was analysed as the synthesis temperature increased. Figure 3-8 shows the normalized Raman spectrum of TiO_2 solid products obtained at three different temperatures (60, 100, and 150 °C); the spectrum of a commercial anatase (25 nm) sample was included for comparison. As the temperature increased, there is a significant decrease in the

anatase peaks bandwidths, which is consistent with the formation of more crystalline materials. Moreover, the significant reduction in the intensity of the CH₃ band at 2935 cm⁻¹ associated to acetate or isopropanol is an indication that more pure materials can be obtained at higher temperatures [50]. Similar results were reported by Alonso *et al.* [49], where the author found that anatase can be produced at temperature far below the transition temperature (450 °C) when it is synthesized in supercritical CO₂. They were able to produce very crystalline materials at 250 °C using TTIP as the titanium precursor and ethanol as the co-solvent in SC-CO₂. Although the material obtained at high temperature were more crystalline and pure, several heat treatments were required for the preparation of the films used in the DSSCs, consequently there was no reason for working at such high temperatures and pressures.



Figure 3-8: Raman spectra of TiO_2 solid samples obtained at 60, 100, and 150 °C (AcOH/TTIP=4.0). The Raman spectrum of an anatase sample from Sigma-Aldrich (25 nm particle size) is also shown for comparison. Indicates greater crystallinity and the removal of contaminates with increasing temperature.

The effects of pressure on the reaction rate are not as pronounced as that of temperature. An increase in pressure at constant temperature will result in an increase in density and it will affect the solubility of the reactants and products (Figure 3-9) [49]. However, this outcome was not observed. Charpentier *et al.* did observe that when the pressure surpassed 41.4 MPa the TiO_2 particle size distribution became more uniform around 20 nm, but they did not notice any other change in morphology [48,51]. Because of this and safety reasons, we have not explored the effect of pressure in this thesis. The pressure was kept in the range between 21 MPa and 24 MPa.



Figure 3-9: Pressure vs density plot for carbon dioxide. Vapour-liquid saturation line (red) and CO_2 pressure at 60 °C. The highlighted region represents the pressure range covered in this study.

3.3.2 Characterization of TiO₂ Materials Obtained in SC-CO₂ and Heptane at 60°C

The morphology of the TiO_2 nanoparticles is strongly determined by the initial AcOH/TTIP ratio as indicated in the Introduction.. In heptane, an AcOH/TTIP ratio, lower than 4 resulted in non-uniform spherical nanoparticles, along with platelets, while a ratio greater than 4 resulted in the formation of long nanofibers with average diameters between 10 and 20 nm. Materials obtained at a 3.5 and 5.5 ratio are shown in Figure 3-10. As shown, the higher ratio resulted in the formation of "birds nest" like structures, along with a small amount of (< 300 nm) non-uniform particles.



Figure 3-10: SEM images of TiO_2 : a,b) 3.5 AcOH/TTIP and c,d) 5.5 AcOH/TTIP, both synthesized in heptane at 60 °C for 5 days.



Figure 3-11: TiO₂ samples synthesized in SC-CO₂ under different AcOH/TTIP ratios: a,b) 3.5, hierarchical spheres; c,d) 5.5, hierarchical spheres and fibers; and c, d) 7.0, fibers.

In SC-CO₂ with a 3.5 ratio, the solid products resembled a collection of sea urchins or round "spiky balls" with diameters from ~ 1 to 5 µm, from here on referred to as hierarchical

spheres. As the ratio increased, fibers started to grow out of the hierarchical spheres, and at a ratio of 7.0 there was no evidence of hierarchical spheres and only fibers were observed. Scanning electron micrographs of the reaction products are shown in Figure 3-11. Different magnifications were used to better illustrate the differences between materials.

The morphology of the material synthesised in heptane was significantly different than those obtained in SC-CO₂. Despite this, it is assumed that the same hexamer ring works as the basic building block in both media. These differences in morphology can be attributed to the physical properties of the two solvents that introduce differences in solubility, preferred reaction pathway, rate of esterification, surface tension, and diffusivity. Representative FTIR spectra of solid materials obtained in both media are shown in Figure 3-12, confirming that the basic hexamer building block is present in all samples [45]. The material collected from the SC-CO₂ synthesis was analysed as is, whereas the material from the heptane synthesis was heated at 80 °C for 12 h to eliminate the solvent.

The small bands around 2975 cm⁻¹ correspond to the C-H stretching mode of bridging acetates and residual isopropoxide [45]. The band around 1750 cm⁻¹ corresponds to C=O of carboxylic acid; the 1715 cm⁻¹ band is indicative of H-bonded acid, while the bands at 1028 cm⁻¹ and 1348 cm⁻¹ are associated with Ti-O-C of acetate bonded to Ti [42,45]. Even though these bands overlap with the isopropyl ligand, there are additional bands around 1120 cm⁻¹ that confirm the presence of isopropyl groups [42,52]. The intensity of this band for the fibers is extremely small indicating complete hydrolysis of the hexamer structures and removal of isopropyl groups. An indication of condensation is given by the \sim 750 and 650 cm⁻¹ bands corresponding to Ti-O and Ti-O-Ti vibration respectively [43]. In the case of fibers, a shift in the Ti-O band from 716 to 755 cm⁻¹ is observed when the acetic acid concentration is increased, which was attributed to a higher concentration of adjacent isopropyl groups [52]. The strong bands at 1454 cm⁻¹ (doublet) and 1530 cm⁻¹ belong to the symmetric and asymmetric stretching modes respectively of carboxylic group coordinated to Ti. For all the materials, the difference between these two bands is less than 100 cm⁻¹ which is indicative of bidentate bridging acetate ligands, which are expected in the case of hexamer rings formation, since for monodentate acetate ligands the difference should be around 150 cm⁻¹. The lack of signals around 1230 cm⁻¹

corresponding to C-O-C and C=O bonds of isopropyl-acetate indicates they are easily removed with purging and heating [42].



Figure 3-12: FTIR spectra of TiO_2 materials synthesized in SC-CO₂ and heptane using different AcOH /TTIP ratios. The spectra support the presence of the hexamer ring structure, and the differences in the degree of hydrolysis with different ratios.

Differential scanning calorimetry was particularly useful for determining the TiO₂ phase transition temperatures (Figure 3-13). The transition from amorphous to anatase, identified by an exothermic peak in the DSC plot, varied between 439 °C and 453 °C [53], while the transition from anatase to rutile was rarely observed around 670 °C [43]. The small changes in transition temperature depend on the degree of order in the materials [53]. The TGA shows the mass decreased as a function of temperature (20 °C/min in air) of materials synthesized under different conditions (Figure 3-14). By comparison with the TGA data of acetic acid, isopropyl alcohol, isopropyl acetate ester, and other species, each mass loss could be properly identified. All contaminants, including surface bond acetate groups, could be removed well below 500 °C.



Figure 3-13: DSC curves of TiO_2 materials synthesized in SC-CO₂ and heptane using different AcOH /TTIP ratios, offset from each other. The transition from amorphous to anatase is around 450 °C and from anatase to rutile is around 670 °C.



Figure 3-14: TGA curves of solid products obtained under different conditions and temperatures. The materials synthesized at higher temperature have fewer impurities, and purging the SC-CO₂ system removes some impurities.

As shown Figure 3-14, the solid products obtained in SC-CO₂ are relatively more pure. The material synthesized in SC-CO₂ at 100 °C and higher temperatures is clearly more pure than that obtained in heptane and low temperature SC-CO₂, in good agreement with the Raman results (Figure 3-8). This is surely due to the higher crystallinity of the solid products, and consequently a reduction of adsorbed species that were not removed during the drying (heptane) and purging (SC-CO₂) steps. The TGA results are further supported by the BET data that show the total surface area for the material synthesized at 150 °C was 165 m²/g, which is less than the material synthesized at 60 °C with a total surface area of 207 m²/g, and more than Sigma Aldrich anatase. Alonso *et al.* [49] showed that amorphous TiO₂ had a much higher surface area due to the increase in internal porosity, and it decreased with increasing crystallinity.

The material was annealed at 500 °C for 90 min to remove the absorbed acetate and other by-products and to undergo the phase transition from amorphous to anatase. As shown in Figure 3-15 the morphology of the solid products does not change dramatically after annealing.



Figure 3-15: Morphology of reaction products before and after annealing indicates no change in morphology. a) SC-CO₂ 4.0 as-synthesized b) after annealing at 500 °C for 90 min.

Raman spectroscopy was used to determine the crystalline phase of the material (Figure 3-16). At 300 $^{\circ}$ C the majority of contaminants were removed and the solid product was amorphous TiO₂. As the temperature increases the crystallite size start to increase since the activation energy is lower than the input energy [54].



Figure 3-16: Raman spectra at different annealing temperatures showing the change from amorphous (bottom) to anatase (top) phase for a sample synthesized in SC-CO₂ (AcOH:TTIP = 3.5).

After annealing at 500 °C, the main crystal phase was anatase as shown in Figure 3-17 although weak peaks corresponding to brookite are also present in all these samples at 245, 322, and 366 cm⁻¹ [21]. XRD confirmed the formation of anatase and minor amounts of brookite, in good agreement with the Raman spectrum. An attempt was made to quantify the amount of brookite in these samples using XRD. The weight fraction of each phase can be determined using the integrated intensities of the anatase and brookite peaks using the following equation for brookite [17]:

$$W_B = \frac{k_B A_B}{k_A A_A + A_R + k_B A_B}$$
(3-9)

where $k_A=0.886$, $k_B=2.721$, and A_A , A_R , A_B are the integrated intensity of the 101, 110, 121 peak of anatase, rutile, and brookite, respectively. Because of the unfavourable peak signal-to-noise ratio for brookite (inset in Figure 3-18), that made the fittings difficult, it was assumed that a negligible amount of brookite was present in all these samples.



Figure 3-17: Raman spectrum of TiO_2 showing the normal vibrational modes of anatase. Inset: small peaks corresponding to the brookite phase.



Figure 3-18: XRD spectra of TiO_2 (anatase) from different syntheses. Inset: A101 and B121 peaks of anatase and bookite respectively.

Crystallites are the primary building blocks of the annealed material and are small single crystal unit agglomerated into the secondary structure. The average crystallite size can be determined using the Scherrer (equation (3-8)) after deconvolution of the A101 XRD peak (Figure 3-18). The crystallite sizes of the material synthesized with acetic acid and titanium tetraisopropoxide ranged from 13-17 nm as shown in Figure 3-19.

It has been well established that as TiO₂ particles decrease in size below 30 nm, a nonlinear shift can be seen in the main 141 cm⁻¹ Raman anatase peak and to a lesser extent other peaks[28,54-56]. This shift seen in the Raman spectrum originates mainly from phonon confinement and can be seen most strongly in the 141 cm⁻¹ peak broadening and blue shift as particles become smaller. Berani *et al.* [57] related it with breakdown of the phonon momentum selection rule: in highly crystalline systems only phonons at the center of the Brillouin zone, q \approx 0, are involved in first order Raman scattering, while in amorphous materials the q vector selection rule does not apply because of the lack of long range order. Small particles belong to an intermediate case, where q \approx 1/D, where D is equal to the particle size and behaves non-linearly as crystallite sizes decrease [57]. The Raman shift and peak broadening were determined through the deconvolution of the 141 cm⁻¹ peak using an average of three spectra for each sample, and after calibration of the Raman spectrometer.

From the crystallite size of TiO₂, determined from the XRD, a correlation was developed between crystallite size and the Raman 141 cm⁻¹ peak shift and peak broadening. Different TiO₂ samples were prepared through multiple techniques. The crystallite size for different samples, determined with XRD, ranged in from 7 – 29 nm. Kelly *et al.* [55] found the following relationship between crystallite size and peak shift, $\Delta \omega$, and line width broadening, Γ , to be:

$$\Delta \omega = k_1 \left(\frac{1}{D^{\alpha}}\right) + \omega_o \tag{3-10}$$

$$\Gamma = k_2 \left(\frac{1}{D^{\alpha}}\right) + \Gamma_o \tag{3-11}$$

where k_1 and k_2 are fitting parameters, D is the crystallite size, Γ_0 and ω_0 are the intrinsic Raman line width and peak position for the 141 peak, respectively, and α is a constant equal to 1.55 for

TiO₂ anatase (sigma Aldrich). The Raman peak correlation with crystallite size is shown in Figure 3-19. This correlation allowed for a quick and facile way of characterizing the material without having to rely on XRD. Moreover it provided a non-destructive and *ex-situ* way of examining the TiO₂ films of DSSCs after TiCl₄ treatment and the numerous heat treatments.



Figure 3-19: Non-linear correlation of Raman peak FWHM (top) and peak position (bottom) of the 141cm⁻¹ Raman band vs crystallite size as determined by XRD. Symbols correspond to anatase samples: • SC-CO₂ 3.5, \blacktriangle SC-CO₂ 5.5, \blacklozenge Heptane 5.5, \bigstar Heptane 3.5. \blacksquare data from different syntheses. The solid line represents the fittings results using equations 3-10 and 3-11.

Table 3-4: Correlation of Raman peak position and band width to XRD crystallite size (eq 3-10 and 3-11) developed by Kelly *et al.*[55]

$y=a+b/x^{1.55}$	a (St. Err.)	b (St. Err.)	R^2
141 cm^{-1}	141 (0.22)	99.8 (10.85)	0.9029
FWHM	12.5 (0.68)	166 (32.96)	0.7324

3.3.3 Characterization of TiO₂/CNT composites

Treated carbon nanotubes (0.2 wt%) were mechanically mixed with the TiO_2 samples synthesised in heptane and SC-CO₂. The same CNTs were also added in-situ to the synthesis. With such a small amount of CNTs it was very difficult to quantify the amounts in the final samples using TGA. Moreover the FTIR bands of CNTs are very week and line up with those of TiO_2 [58]; the same applies to XRD. Despite the difficulties in characterization, the addition of CNTs had a clear effect on the synthesis of TiO_2 and the morphology of the final products. SEM images of samples obtained in Heptane 5.5, SC-CO₂ 5.5, and SC-CO₂ 3.5 are shown in Figure 3-20.

The composites synthesized in SC-CO₂ were white with no indication of CNTs. On the other hand the solids obtained in the synthesis in heptane were gray and it was evident that they were not uniformly dispersed because of agglomeration, even under stirring. After examination with SEM, it was observed that the CNTs clearly caused an alteration in the structure. There was very little resemblance between the material synthesized with CNTs and those without. Yu *et al.* [58] showed that using a conventional sol-gel method the addition of CNTs caused TiO₂ agglomerates to grow. Moreover, Jensen *et al.* [59] proposed that addition of CNTs into the supercritical CO₂ increased nucleation of the TiO₂ more than the crystal growth rate. They showed that the addition of small amounts of a seeding material, like natural fibers or hydrophobic polypropylene, acted as nucleation sites increasing crystallinity and rearranging the TiO₂ crystal. Increased nucleation could also explain the increase in reaction rate described above.

The increase in crystallinity and the decrease in crystallites size were confirmed using Raman spectroscopy. Using the correlation between crystallite size and Raman shift (Figure 3-21), the average crystallite size for the composites was estimated to be between 11 and 13 nm. The characteristic D band (1350 cm⁻¹) and G band (1580 cm⁻¹) corresponding to carbon nanotubes could not be observed in samples synthesized in SC-CO₂ and could be caused by better wetting and coating (Figure 3-21) [60]. Furthermore, differences in elemental composition of the sample were examined using back-scattered electrons (BSE), but did not indicate the presence of carbon.



Figure 3-20: SEM images of TiO₂/CNT composite material: a,b) Heptane 5.5, c,d) SC-CO₂, 5.5, e,f) SC-CO₂ 3.5.



Figure 3-21: Raman shift of TiO_2/CNT composites and anatase TiO_2 from Sigma-Aldrich. Insert D and G peaks corresponding to carbon nanotubes.

3.4 Conclusions

In summary, TiO_2 was synthesized by a sol-gel method in two different solvents, heptane and supercritical carbon dioxide (SC-CO₂). The morphology of the reaction products was modified by changing the composition of the media, the reaction temperature, or by the addition of CNTs. The materials were characterized using Raman, FTIR, SEM, XRD, TGA, and BET.

In both media, TTIP was used as metal precursor and acetic acid as an additive to control the rate of the sol-gel reaction. For synthesis at 60 °C and ~22.5 MPa, changes in the AcOH/TTIP ratio from 3.5 to 7.0 resulted in very different products. At the lowest ratio, hierarchical spheres were produced; when the AcOH/TTIP ratio was increased to 5.5, a mixture of hierarchical spheres and fibers was observed; and finally at a ratio equal to 7.0, solely fibers were formed (50-200nm in diameter and 6 μ m long). In heptane under the same temperature

conditions, globular structures were obtained at AcOH/TTIP ratios below 4 and long and thin nanofibers (10-50 nm in diameter and 2 μ m long) were formed over this limit. These results are in excellent agreement with previous studies by Chapentier and Sui et al.[42].

For all the materials synthesized at 60° C the phase transition temperature from amorphous to anatase was close to 450 °C, and that between anatase and rutile phase was around 670 °C using DSC. The average crystallite size of the TiO₂ samples determined by XRD was 15 nm.

The addition of CNTs caused a change in the morphology of the TiO_2 products in both media. Because of the difficulty in characterizing the composite materials, they were not used in DSSCs.

4 Chapter 4: Photoelectrical Characterization

4.1 Introduction

Titanium dioxide mesoporous photoanodes are a promising material for use in a DSSC, because of their abundance, low cost, low toxicity, and relatively good performance when used in combination with N719 dye and Γ_3/I_2 redox couple. It has been shown that efficiencies over 10% can be reached by combining TiO₂ with the ruthenium bipyridine dye complex, the iodide/triiodie (I₂/I₃⁻) redox couple and FTO conducting glass. This section will introduce the main experimental techniques used for studying the photoelectrical properties of the assynthesized TiO₂ materials with different morphology and with and without carbon nanotubes. I-V curves and impedance spectroscopy were used to evaluate the impact of the morphology and/or composition of the TiO₂ film on the overall performance of the photoanode. A DSSC configuration was chosen since it provides a more realistic test than the popular methylene blue degradation approach.

As mentioned in Chapter 1, TiO_2 anatase is a semiconductor and will absorb light in the ultraviolet region. The absorption of light within the semiconductor will create electron-hole pairs that can migrate to the surface and react with acceptor and donor species [20]. The efficiency of this process can be measured using incident photon to current conversion efficiency (IPCE):

$$IPCE(\lambda) = \frac{j_{ph} \cdot h \cdot c}{P_{in} \cdot e^{-} \cdot \lambda}$$
(4-1)

where j_{ph} is the photocurrent density, *h* is the Planck's constant, λ is the photon wavelength, c is the speed of light, P_{in} is the power density of the incident light, and e^{-} is the charge of an electron. Instead, dye sensitized solar cells are electrochemical devices that absorb light and convert it into electricity through multiple chemical gateways. However, electron transport through the cell is obstructed at interfaces, limited by diffusion, and impaired by chances of recombination. The ideal electrons pathway is summarized in the following table:

	Absorption of light by dye (excitation of electron)	$S + hv \rightarrow S^*$	(1)
	Electron injection into TiO ₂	$S^* \to S^+ + e^-(TiO_2)$	(2)
Photoelectrode and Counter Electrode	Electron transport in TiO ₂ to working electrode (WE)	$e^{-}(TiO_2) \rightarrow e^{-}(WE)$	(3)
	Reduction of electrolyte on counter electrode (CE)	$2e^{-}(CE) + I_{3}^{-}(CE)$ $\rightarrow 3I^{-}(CE)$	(4)
	Reduction of dye	$2S^+ + 3I^-(TiO_2)$ $\rightarrow 2S + I_3^-$	(5)
Electrolyte	I ₃ -/I ₂ diffusion	$I_{3}^{-}(TiO_{2}) \rightarrow I_{3}^{-}(CE)$ $3I^{-}(CE) \rightarrow 3I^{-}(TiO_{2})$	(6)

Table 4-1: Electron transfer reactions and transport processes in a working DSSC [61]

In this case, the IPCE is more accurately described as the product of the efficiencies of all the processes involved:

$$IPCE(\lambda) = \eta_{LHE}(\lambda)\eta_{inj}\eta_c$$
(4-2)

where η_{LHE} is the light harvesting efficiency at a given wavelength (λ), η_{inj} is the injection efficiency of the electron into the TiO₂ semiconductor, and η_c is the charge collection efficiency[10].

4.1.1 The I-V Curve

A single diode model (Figure 4-1) has been used to describe the shape of the current-voltage (I-V) curve of a DSSC under steady state operating conditions.[3,61]



Figure 4-1: Single diode equivalent circuit model: I_{ph} , photocurrent; the diode represents the recombination of electrons; R_s , series resistance; R_{sh} , shunt resistance; V_{cell} , load.

Using this model, the current cell is given by

$$I_{cell} = A \left[j_{ph} - j_d \left(e^{-\frac{e^{-}(V_{cell} + I_{cell}R_s)}{m \, k_B T}} - 1 \right) \right] + \left(\frac{V_{cell} + I_{cell} \, R_s}{R_{sh}} \right)$$
(4-3)

where j_{ph} (= I_{ph}/A) is the photogenerated density current, j_d is the dark reverse current density, R_{sh} represents the shunt resistance, an alternative pathway for the electrons (for example, recombination at the working electrode) R_s is the ohmic series resistance which takes into account sheet resistance of the FTO glasses, resistivity of the electrolyte, electrical contacts and wiring [61].

A typical a current-voltage (<u>I-V</u>) curve is shown in Figure 4-2. The efficiency of the cell and other relevant parameters can be obtained from the curve under standardized illumination conditions.



Figure 4-2: I-V curve for a DSSC. I_{sc} : short circuit current, V_{OC} : open circuit voltage, and $V_{MP_a}J_{MP}$: maximum power point.

The current associated with zero applied bias, I_{sc} , in a DSSC is called the short circuit current, Equation (4-3), and it is the largest current which can be generated from a cell. It is due to the generation and collection of photoelectrons entering the circuit. As the forward potential increases it reaches a "forward-voltage-drop" where the recombination term dominates and bends the I-V curve [3]. The I-V curve is measured in the fourth quadrant, but it is a useful convention to invert the sign of the current since the cell is generating power instead of using it.

Using the ideal diode equation, the open circuit voltage, V_{oc}, can be deduced [2]:

$$V_{oc} = \frac{mK_BT}{e} \ln\left(1 + \frac{j_{sc}}{j_d}\right) \tag{4-4}$$

where j_{sc} and j_d were previously defined, *m* is the ideality factor, usually within the range from 1 to 2 (1 for the ideal diode), *T* is the absolute temperature, K_B is the Boltzmann constant, and *e* is the electron charge. It is worth noting that the ideal diode model works better for solid state

devices than electrochemical systems like a DSSC, because the model does not take into account diffusion in the electrolyte solution.

The open circuit voltage is the maximum potential of the cell and occurs at zero current. Under these conditions, V_{oc} gives the equilibrium values for electron injection and recombination. The open circuit voltage is given by the difference between the Fermi level position of the semiconductor (TiO₂) and the reduction potential of the I_2^-/I_3^- redox couple, and its theoretical value is equal to 0.8 eV [2,10]. A greater concentration of electrons in the conduction band will shift the Fermi level to higher values [3], resulting in a decrease in recombination [10].

To determine the total solar conversion efficiency (η), the solar radiation to electrical power output is calculated using the equation [3]:

$$\eta = \frac{I_{sc}V_{oc}}{P_{in}}FF \tag{4-5}$$

where I_{sc} and V_{oc} are the short circuit current and the open circuit photovoltage respectively; P_{in} is the total incident solar power to the cell, and *FF* is the Fill Factor (FF=A/B in, Figure 4-2) which is defined as the ratio of the theoretical maximum power of the cell, $I_{sc} \cdot V_{oc}$, to the product of the current and voltage corresponding to the maximum power point, $I_{MP} \cdot V_{MP}$.

$$FF = \frac{I_{MP}V_{MP}}{I_{sc}V_{oc}} \tag{4-6}$$

Typical fill factors values for dye sensitized solar cells are in the 0.75 to 0.85 range. [10]

The series resistances, R_s , can be approximated by the slope close to the open circuit voltage point, using [62]:

$$R_{s} = \frac{V_{MP}}{I_{MP}} (1 - FF)$$
(4-7)

Similarly, shunt resistances, R_{sh} , can be approximated from the slope close to the short circuit current point:

$$\frac{1}{R_{sh}} = \frac{I_{MP}}{V_{MP}} (1 - FF)$$
(4-8)

4.1.2 Impedance Spectroscopy

In addition to efficiency measurements from I-V curves, impedance spectroscopy is an essential characterization technique because it makes it possible to separate the contributions of the different processes by studying the response of the cell (electrochemical system) to an applied small amplitude AC signal at different frequencies superimposed on a constant DC polarization potential. Because impedance spectroscopy measures a phase change in the AC circuit 0ften the data are represented graphically using a Nyquist plot as shown in Figure 4-3, where the response of a solid working electrode in a given electrolyte is shown. The resistance is constant for each component and makes up the real part; the capacitance and inductance on the other hand causes a shift in the phase angle, to lag or lead the AC current, and are represented by the imaginary part. In this case, the double layer capacitance for an electrode/electrolyte interface can be modeled by taking into account the capacitance of the double layer, C_{dl} , due to the accumulation of charges at the interface and the charge transfer resistance, R_{et} , across the interface.



Figure 4-3: (A) electrode/electrolyte interface, (B) equivalent circuit, and (C) Nyquist plot for the equivalent circuit. The diameter of the semicircle represents the resistance while the capacitance can be obtained from the maximum in the Im Z axis. Increasing frequency is indicated by the symbol ω .

The impedance is found by the following equation with the C_{dl} and R_{ct} in parallel:

$$Z(\omega) = \frac{R_{ct}}{1 + j\omega R_{ct} C_{dl}}$$
(4-9)

Each point in Figure 4-3 (C) corresponds to a frequency, the diameter of the semicircle is the charge transfer resistance and the capacitance can be found knowing the frequency of the highest imaginary Z value. As more components are added, the impedance expression becomes more complicated, and multiple semicircles and other features can be observed.

The diffusion-recombination equivalent circuit model for a DSSC

The model for a DSSC was developed independently by Kern *et al* [63] and Bisquert[64], to describe electron transfer and recombination in nanocrystalline TiO_2 porous electrodes and is represented in Figure 4-4.



Figure 4-4: Transmission line model for a DSSC used in impedance spectroscopy. r_t – electron transport resistivity; r_r – recombination resistance, C_{μ} – chemical capacitance at TiO₂/electrolyte interface, R_s – series resistance, R_{DL} – double layer resistance at working electrode, C_{DL} - double layer capacitance at working electrode, R_{pt} – double layer resistance at counter electrode, C_{pt} – double layer resistance at counter electrode, C_{pt} – double layer capacitance at counter electrode [2,61,64,65].

By measuring the impedance of the cell and fitting it to this equivalent circuit allows for the evaluation of all the components of the system, because of the very different time constants or characteristic frequencies of the processes involved. These contributions pertain to: electron
transport and charge recombination in the TiO_2 film; resistance and capacitance at the interface of electrolyte/TiO₂, electrolyte/Pt electrode, and electrolyte/working electrode; and electrolyte diffusion [2].

The impedance is related to the slope of the I-V curve (the resistance) for the corresponding operating point (DC voltage),

$$Z_{cell}(\omega) = \frac{V_{AC}(\omega, t)}{I_{AC}(\omega, t)}$$
(4-10)

by taking the limit at zero frequency,

$$\lim_{\omega \to 0} Z_{cell}(\omega) = \frac{\partial V_{cell}}{\partial I_{cell}} = R_{cell}$$
(4-11)

(1 11)

the resistance of the cell, R_{cell} , can be determined. The cell resistance is comprised of several different contributions: R_s , the ohmic series resistance of the cell (resistance of the FTO substrate, resistivity of the electrolyte, and cell electrical contacts), the diffusion resistance of the electrolyte, R_D , the resistance of the counter electrode, R_{Pt} , and the overall resistance of the TiO₂ porous electrode, R_{TiO2}

$$(4-12) R_{cell} = R_S + R_D + R_{Pt} + R_{TiO_2}$$

 R_{TiO2} accounts for the overall resistance of the TiO₂ photoelectrode and includes the electron transport and electron recombination, R_t and R_r , respectively.

The impedance spectrum will depend on the external applied DC potential; a low, intermediate, or high applied DC voltage (V_{app}) will amplify certain characteristics of the cell and it will make it possible to reduce the number of fitting parameters required to reproduce the experimental results. Moreover, the impedance spectrum of a cell tested in the dark will be very different from the spectrum of the same cell under illumination conditions. The definition of low,

intermediate, and high potential is based on the value of the open circuit voltage, V_{OC} . A high applied potential will have $V_{app} \sim V_{OC}$.

For this equivalent circuit model, the impedance expression for the TiO_2 porous photoanode of the cell accounts for the two competing electron pathways: transport through the film and recombination with the electrolyte:[2]

$$Z(\omega) = \left(\frac{R_t R_r}{1 + \left(\frac{i\omega}{\omega_r}\right)^{\beta}}\right)^{1/2} \operatorname{coth}\left[\left(\frac{\omega_r}{\omega_t}\right)^{\beta/2} \left(1 + \left(\frac{i\omega}{\omega_r}\right)^{\beta}\right)^{1/2}\right]$$
(4-13)

where ω_r and ω_t are the characteristic frequencies of recombination and electron transport; R_r and R_t are the total macroscopic recombination and transport resistances; and β is a constant with values between 0.85 and 1.0 [66]. It has been assumed in more recent papers that β =1[65]. The total resistance and capacitance of the film can be express in terms of the components of the equivalent circuit using the following relationships:

$$R_t = r_t d;$$
 $R_r = \frac{r_r}{d};$ $C_\mu = c_\mu d$ (4-14)

where r_t is the transport resistance, r_r is the recombination resistance, c_{μ} is the chemical capacitance, and *d* is the thickness of the TiO₂ film. The two characteristic frequencies can also be expressed in terms of components of the transmission line,

$$\omega_t = \frac{1}{R_t C_\mu} = \frac{1}{r_t c_\mu d^2}; \qquad \omega_r = \frac{1}{R_r C_\mu} = \frac{1}{r_r c_\mu}$$
(4-15)

At the dc limit ($\omega=0$), two distinct limit cases can be reached:

$$Z_{dc} = \frac{1}{3}R_t + R_r ; \quad R_t < R_r$$
 (4-16)

$$Z_{dc} = (R_t R_r)^{1/2} ; \quad R_t > R_r$$
(4-17)

The shape of the overall impedance spectrum is modulated by the ratio of the characteristic frequencies of electron transport and recombination

$$\frac{\omega_d}{\omega_r} = \frac{R_r}{R_t} = \left(\frac{L}{d}\right)^2 \tag{4-18}$$

where ω_d , is the transport characteristic frequency, and *L* is the diffusion length. The characteristic frequency for recombination, ω_r , for the cells is related to the electron lifetime, τ_n , through

$$\omega_r = \frac{1}{\tau_n} = \frac{1}{R_r C_\mu} \tag{4-19}$$

Moreover the transport characteristic frequency, ω_d , is related to the diffusion coefficient, D_n , through

$$D_n = \frac{\omega_d}{L^2} = \frac{1}{R_t C_\mu} \tag{4-20}$$

By combining all these equations, three independent parameters can be derived: electron lifetime, the electron diffusion coefficient, and the ratio between recombination resistance and transport resistance R_r/R_t . A more detailed description of the impedance model and related equations can be found in reference [2]

4.2 Experimental

4.2.1 Materials and Methods

The chemicals used for the fabrication of the DSSC were AR grade and used without further purification. Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'- dicarboxylato) ruthenium(II) (N-719 dye, 95%, Sigma-Aldrich); acetonitrile (99.8%, Sigma-Aldrich); *tert*-Butanol (99.5%, Sigma-Aldrich); lithium iodide (99.99%, Sigma-Aldrich), iodine

(99.99%, Sigma-Aldrich); 1,2 dimethyl-3-propylimidazolium iodide (DMP II, TCL America); 4ter-butylpyridine (TBP, 96%, Sigma-Aldrich); 3-methoxypropionitrile (MPN, 98%, Sigma-Aldrich); glacial acetic acid (Sigma-Aldrich) ; hydrochloric acid (HCl, 37%, Sigma-Aldrich); titanium tetrachloride (TiCl₄, 99.995%, Sigma-Aldrich); TiO₂ Degussa P25 (Sigma-Aldrich); silver conductive paste (Sigma-Aldrich); Cerasolzer soldering alloy, α -terpineol (96%, Sigma Aldrich); ethyl cellulose solution (viscosity 10 cP, 5%, Sigma-Aldrich).

4.2.2 DSSC Fabrication

This section summarizes the different steps involved in the preparation of a DSSC. As shown, the procedure involved: (a) deposition and syntherization of a TiO₂ film (~15 μ m in thickness) and a TiO₂ scatter layer on a conductive FTO glass; (b) adsorption of a ruthenium dye (sensitizer) onto the surface of the TiO₂ nanoparticles; (c) cell assembly (sandwich the photoanode and the Pt counter-electrode together using a polymeric gasket); and (d) filling the cell with the Γ/I_3 electrolyte solution.



Figure 4-5: Different steps involved in the fabrication of a DSSCs. From left to right: TiO₂ film, Pt counter-electrode, sensitizer adsorption, and cell assembly.

i- Film preparation and film thickness characterization

FTO glasses from MTI (with a sheet resistance of 6-8 Ω /sq) were cleaned using hydrochloric acid, washed with ultra-pure water (18 M Ω ·cm) until neutral pH, and dried in an

oven at 120 °C. The clean substrates were treated with a 40 mM TiCl₄ solution and dried at 70 °C for a minimum of 30 min. This very thin layer of TiO₂ enhances the adhesion of the TiO₂ nanoparticles and acts as a blocking layer, reducing electron recombination from the FTO with the electrolyte [2].

A couple of experimental procedures were tested for the preparation of the films, including a doctor blade method and screen printing with multiple paste formulations. The doctor blade method, which involved spreading the TiO_2 paste over a 1 cm² area onto a FTO glass masked by scotch tape (3M) using a glass slide, was fast, but it was not reproducible. In addition, the films did not show a good adherence to the substrate.

The screen printing approach was slow, but it was extremely reproducible and the adherence of the film was also very good. The main steps of this preparation method are summarized in the flow chart shown in Figure 4-6. The reasons for such a long procedure was to produce films with strong adhesion to the FTO substrate, that do not crack when sinterized at high temperature, and have a uniform distribution of interconnected particles. As in other studies, acetic acid was used to prevent particle agglomeration due to the strong chemical interaction between TiO₂ and carboxylic acid groups. The subsequent addition of water contributed to the formation of surface hydroxyl groups (-OH) on the TiO₂ particles, allowing chemical bonding between the particles and the FTO glass through dehydration during sinterization step. The α -terpineol is less volatile than ethanol and along with ethyl cellulose provided stability to the mixture paste and an adequate viscosity for screen printing after elimination of other volatile components.



Figure 4-6: Screen printing paste preparation procedure.

A typical TGA run of the paste carried out in air at a gas flow rate of 20 mL/min is shown in Figure 4-7. It can be seen that very little ethanol (boiling point 78 °C) remains because there is almost no mass decrease before 140 °C. At that point absorbed water and acetic acid (boiling point 118 °C) start to leave, as well as α -terpineol (boiling point 217 °C), which constitutes around 50% of the total mass. The free ethylcellulose decomposes around 360 °C, and the adsorbed ethylcellulose decomposes at around 400 °C accounting for about 30% of the total mass. The final 20% is TiO₂. These values are in good agreement with other formulations [67].



Figure 4-7: TGA and DSC results for a representative screen printing paste prior sinterization in air at a heating rate of 20 °C/min and a 20 mL/min gas flow rate.

Care was taken on the addition of CNTs to the material so that they would not decompose during the numerous heat treatment steps in air. CNTs will start to decompose around the temperatures needed for sintering the TiO_2 particles; this problem is not generally discussed in the literature where referring to TiO_2/CNT composite photoelectrodes.

The purification of the CNTs reduced their onset decomposition temperature when compared to pristine CNTs (Figure 4-8). This is a result of the addition of defects through the purification procedure [68].



Figure 4-8: TGA and DSC runs for pristine and purified CNTs in air at a heating rate of 20 °C/min and a 20 mL/min gas flow rate. The figure shows the change in the decomposition of CNTs with temperature after the purification step.

The TGA and DSC results shown in Figure 4-7 and 4-8 were used to develop the following heating procedure. The sample were heated in air up to 375 °C held for 90 min to insure the additives were removed, then heated to 500 °C under argon and held for another hour, Figure 4-9.



Figure 4-9: Heating procedure for TiO_2/CNT composites in air and argon. Run conditions: 20 °C/min, 30 °C up to 375 °C, then hold for 90 min, followed by 20 °C/min up to 500 °C then hold for 60 min.

The number of layers required to prepare 15 μ m TiO₂ films varied between 5 and 7 prints, as determined using a profilometer. In all cases, the following treatment was adopted to make the photoanode. After a TiO₂ layer was printed, the film was allowed to settle for 10 min, and then dried on a hotplate at 80 °C for 5 min before the next layer was applied. The TiO₂ film was annealed at 500 °C in air for 1 hour, unless CNTs were used in which case they were heated to 375 °C in air, held for one hour under these conditions, and then heated to 500 °C under nitrogen and held for another hour (Figure 4-9). When the film had cooled it was treated once again with TiCl₄ at 60 °C for 30 min. This was followed by another heat treatment, similar to the last one but up to 400 °C. The film was cooled under nitrogen and then placed immediately into a dye solution to minimize contact with moisture.

The TiO_2 solids used to prepare the photoanodes along with the synthesis media are shown in the following table:

	Degussa P25	Degussa P25	P25
A CONTRACTOR OF THE OWNER	Hierarchical Spheres	SC-CO ₂ 3.5	HS
	Hierarchical Spheres and Fibers	SC-CO ₂ 5.5	HSF
	Nanofibers	Heptane 5.5	NF

Table 4-2: Labelling of the material tested in a DSSC configuration.

ii-Dye Solution Preparation

The 5 mM N-719 dye solution was prepared in a glove bag under nitrogen to minimize contact with moisture. The solvent was a 1:1 mixture of anhydrous acetonitrile and tert-butanol, which is used to increase the solubility of the dye and be sure the amount of dye is enough to saturate the films. The TiO_2/FTO glasses were immersed in the dye solution for at least 24 hours in sealed containers and dark conditions.

Dye loading was determined by desorbing the dye from the photoanode in a solution of 0.1 M NaOH in ethanol and water (1:1) over 3 h. In an alkaline solution the affinity of the dye by the metal decreases and the dye can be removed from the TiO_2 film. The dye concentration in solution was measured using a Cary 50 UV-visible spectrometer (Figure 4-10) [69].



Figure 4-10: UV-visible spectra of the N-719 dye in 0.1 M NaOH (1:1 ethanol; water) after desorption from the films. \bullet NF \blacktriangle P25, \blacklozenge HS, \blacksquare HSF.

iii-Electrolyte Solution

The electrolyte formulation was taken from Chiba Y *et al.*[70] since I_3/I_2 proved to be an effective mediator and stable under the operation conditions [2]. The electrolyte solution composition is given below:

Table 4-3: Electrolyte solution composition

Chemical	Concentration (mol/L)
Lithium iodide (LiI)	0.1 M
Iodine (I ₂)	0.05 M
Ter-butylpyridine	0.5 M
1,2 dimethyl-3-propylimidazolium iodide (DMPII)	0.6 M
3-Methoxypropionitrile (MPN).	Solvent

The additive *ter*-butylpyridine was added to minimize the reduction of triiodide (interception) by adsorption onto bare spots on the TiO₂ films, while 1,2 dimethyl-3-propylimidazolium iodide (DMPII) was added to decrease the viscosity of the solution [2].

iv-Preparation of the Platinum Counter-Electrode

Two holes were very carefully drilled into the FTO glass used to prepare the platinum counter electrodes. The electrodes were cleaned with 0.1 M HCl solution and washed with ultrapure water. A 1 cm² area was masked with scotch tape and 5 layers of Plastisol T paint (Solaronix) were applied to the FTO glasses, waiting a minute for drying before applying each subsequent layer. The counter electrodes were then heated at 450 °C for 15 min to remove organic materials and produce the Pt film.

v-DSSC Cells Assembly

In this step the photoanode and the Pt counter-electrode were sandwiched together, using a 25 μ m Meltonix gasket (Solaronix) to keep them from touching and to leave space for the electrolyte solution. The inner 1 cm² section was cut away to match the area of the TiO₂ photoanode and platinum counter electrode. The gasket was fused to the glasses using a hot press to form a strong seal. The electrolyte was introduced into the cell through a hole in the counter electrode and was pulled through by capillary forces. The two holes were then sealed using a 60 μ m Meltonix film and a thin glass microscope cover using a soldering iron. The copper wire connections were made using Cerasolzer soldering alloy, which is designed to adhere to glass, and coated with silver paste to decrease the contact resistance.

4.2.3 I-V Curves and Impedance Spectroscopy Measurements

The efficiency and other important cell parameters were determined using a solar simulator under standardized conditions: an air mass of 1.5 (AM1.5); intensities of 100 mW/cm²; and a cell temperature of 25 °C. The I-V curves corresponding to DSSCs with photoanodes prepared with TiO₂ powders with different morphology were acquired with a Gamry Instruments

Reference 600 potentiostat using a Newport Oriel Sol 3A sun simulator under 1.5 AM D, 100 mW/cm², direct illumination (see Section 1.1). The I-V curves for P25 with and without a scattering layer and with and without CNTs were collected with a using an Optical Associates Inc, TriSol solar simulator, under 1.5 AM, 100 mW/cm², global illumination. Global illumination takes into account diffuse irradiation caused by the atmosphere [6]. The fill factor and the efficiencies were calculated using equations (4-5) and (4-6)

The impedance measurements were done on the cells using a Gamry Instruments Reference 600 potentiostat at different applied voltages, in the dark and under illumination, from 100 Hz to 10 mHz, taking 20 point per decade with a AC amplitude of 10 mV. A two electrode configuration was used for the measurements with the working and working sense electrodes both connected to the photoanode, and the reference and counter electrode both connected to the cathode. The DC applied bias potential for each run was -0.5V vs I_2/I_3 unless otherwise stated. The curve fittings were done with the Gamry Echem Analyst software. The resistance and chemical capacitance at the platinum counter electrode were found using a blank cell consisting of two platinum electrodes and I_2/I_3 electrolyte; the series resistance was found as the onset value along the real axis.

4.3 Results and Discussion: Photovoltaic Properties of a DSSC

This is the first study on dye sensitized solar cells in Gaspari's and Trevani's research groups and a systematic procedure for preparing the TiO_2 pastes, assembling the cells, and testing their performance using a solar simulator and impedance spectroscopy was developed as part of this thesis with the valuable contribution of Simone Quaranta (Dr. Gaspari's PhD student)

The methodology was used to prepare several DSSCs with the materials synthesized in Chapter 3. The performance of these cells was studied using I-V curves and impedance spectroscopy. The reproducibility for a single cell was used as a reference when comparing the performance of the cells prepared with different TiO₂ materials. Ongoing work in our laboratories will provide the statistical analysis required to confirm and/or improve these initial findings.

In one set of experiments, the performance of cells prepared with TiO₂ films comprised of hierarchical spheres (HS, 3.5 AcOH/TTIP, SCCO₂), hierarchical spheres and fibers (HSF, 5.5 AcOH/TTIP, SCCO₂), and nanofibres (NF, 5.5 AcOH/TTIP, heptane) were examined. In a second set of runs, the performance of TiO₂ Degussa P25, a commercially available product, with and without CNTs and scattering layers consisting of hierarchical spheres was investigated.

Efficiency Determination from IV Curve Data

The I-V curves for DSSCs with photoanodes prepared with TiO_2 solids with the morphologies illustrated in Table 4-2 are shown in Figure 4-11. The corresponding values of efficiency and other cell parameters are summarized in Table 4-4. It can be seen that the open circuit voltage (V_{oc}) remains constant. The short circuit current is the main difference between the different cells, with values between 4.46 and 7.50 mA cm⁻². The efficiencies for HSF , HS, and NF are 1.72%, 2.15%, 2.77%, respectively.

The morphologies of solids used to prepare the film would affect the film structure and the surface area; these two parameters could have a significant impact in dye loading and electron transfer. The short circuit current, I_{sc} , is dependent on the amount of photogenerated electrons that can make it into the circuit, meaning it depends on light harvesting capabilities and rates of electron transfer and recombination [61].



Figure 4-11: I-V curves for DSSCs prepared with TiO₂ solids with the following morphologies: \blacksquare -NF, \forall P25, \bullet -HS, \blacktriangle -HSF. The data were acquired with a Newport Oriel Sol 3A sun simulator under 1.5 AM D, 100 mW/cm², direct illumination. Scan rate: 0.1 V/s

Table 4-4: DSSC efficiencies and I-V curve parameters of DSSCs prepared	with TiO ₂ solids
with different morphologies. The data were acquired with a Newport Oriel Sol under 1.5 AM D , 100 mW/cm^2 , direct illumination.	3A sun simulator

I _{sc}	V_{MP}	I_{MP}	FF	R _s	R_{sh}	Eff:
(mA/cm ²)) (V)	(mA/cm^2)	FF	(Ohm)	(Ohm)	Efficiency
3 7.50	0.43	6.43	0.559	29.67	150.6	2.8%
2 5.75	0.42	5.11	0.574	35.1	192.2	2.2%
9 4.46	0.46	3.75	0.577	51.7	290.8	1.7%
4 6.94	0.44	6.33	0.592	28.1	171.8	2.8%
°) 5557.	$\begin{array}{c} c & I_{sc} \\ \hline & (mA/cm^2) \\ \hline 53 & 7.50 \\ \hline 52 & 5.75 \\ \hline 59 & 4.46 \\ \hline 74 & 6.94 \\ \hline \end{array}$	$\begin{array}{ccc} & I_{sc} & V_{MP} \\ \hline & (mA/cm^2) & (V) \\ \hline 53 & 7.50 & 0.43 \\ \hline 52 & 5.75 & 0.42 \\ \hline 59 & 4.46 & 0.46 \\ \hline 74 & 6.94 & 0.44 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

^a Result obtained using global irradiance.

The dye loadings were determined for films of different morphologies prepared using an alternative screen printing paste. The normalized results for the dye loadings are shown in Figure 4-12



Figure 4-12: Dye loadings for films prepared with TiO_2 solids with different morphologies, normalized by film thickness.

Indeed it was found that the dye loading was higher for those morphologies that showed higher efficiencies. Structurally this is seen in the transparency of the films in Figure 4-13, where the morphologies with greater efficiencies were more opaque than the others. Notice that P25 has the greatest transparency, but better dye absorbance than HSF. A reason for this could be because of the small particle size, dense structure, and good connectivity between particles, however, P25 would not scatter the light as effectively as HSF (hierarchical spheres interspaced by fibers).



Figure 4-13: Transparency of TiO₂ films of different morphologies. Film thickness: \sim 15µm. Square area indicates the scattering ability of the film.

Lee *et al.* [71] showed that nanofibers performed poorly compared to nanoparticles in DSSCs and correlated the decrease in efficiency to fibers having less surface area and poorer dye loading [24]. However, these preliminary results indicate NF performs better than other morphologies. In the case of HSF, the relatively poor efficiency could be associated to a low dye loading, as well as, to a reduced transparency compared to the other morphologies. The BET surface area after sinterization for a synthesis in SC-CO₂ with 4.0 AcOH/TTIP (which resembles HS) was 67 m²/g; for P25 the surface area was 49 m²/g, which is expected to decrease upon sinterization [71]. The higher dye loading of HSF and HS could also be due to a more optimal pore size between that of P25 and HSF.

Recently Liao *et al.* [24] examined fibers, hierarchical spheres, spheres and ellipsoids synthesized using a solvothermal method. The performance of these matererials were studied in a DSSC configuration. The authors reported very high efficiencies with their material, but it should be noted that the cell area was 0.16 cm^2 . In addition they used a 150 nm sputtered blocking layer to increase TiO₂ particle connectivity with the FTO working electrode and reduce the shunt resistance. Their different morphologies and efficiencies are shown in Figure 4-14.



Figure 4-14: Different morphologies produced by Liao *et al*.: a) nanoparticles, b) nanofibres, c) hierarchical spheres, d) ellipsoids. Reproduced from ref [24].

A light scattering layer is often used to improve the efficiency of DSSCs; the layer usually contains larger particles which can scatter the light back into the mesoporous film and increase the average optical mean path [6]. In this work HS was tested as a scattering layer because of its good dye loading, and ability to scattering the light. It was tested on P25 and P25/CNT composites. Figure 4-15 shows the I-V curves of the composite material.



Figure 4-15: I-V curves for DSSCs prepared with Degussa P25 TiO₂ anatase with and without the addition of CNTs: \blacksquare -P25+HS, \blacklozenge -P25, \lor -P25+CNT+HS, \blacktriangle -P25+CNT. The data were obtained using a TriSol solar simulator, under 1.5 AM, 100 mW/cm², global illumination. Scan rate: 0.1 V/s

As shown, the scattering layer increased the efficiency for the P25 and the P25 composite material by 12.5% and 10% respectively. On the other hand, the open circuit voltage can be seen to decrease from 0.674 to 0.622V when CNTs were added. The V_{oc} depends on the difference between the Nernstian potential of the electrolyte, and the Fermi level of the TiO₂, with a theoretical maximum around 0.8 eV for a Γ/I_3 system [2]. The processes that decrease the V_{oc} are: increased rates of recombination, and low rates of charge transfer (Equation (4-4)). Carbon is known as a catalyst in the reduction of triiodie [72], it has been used as a counter electrode [73], and it has been used in the photodegradation of pollutants such as methylene blue [30]. A cause of the decrease could be associated to the fact that carbon nanotubes were mechanically mixed into the paste of TiO₂ to make the photoelectrode, they were not added to the synthesis, thus limiting the intimate contact between TiO₂ and the CNTs [74]. The presence of "naked" carbon nanotubes in the photoanode that are in direct contact with the electrolyte could act as recombination sites and reduce the open circuit voltage [72].

Samula	V_{oc}	I _{sc}	V_{MP}	I _{MP}	Fill	R _s	R_{sh}	~0/
Sample	(V)	(mA/cm^2)	(V)	(mA/cm^2)	Factor	(Ohm)	(Ohm)	1[70
P25	0.674 (±3.2mV)	6.94 (±2.2mA)	0.44 (±0.2 mA)	6.33 (±2.3mA)	0.592 (±0.23)	28.1	171.8	2.8% (±0.07)
P25+HS	0.652	7.90	0.45	7.10	0.620	24.1	166.9	3.2%
P25 + CNTs	0.622	4.83	0.42	4.27	0.600	39.6	244.0	1.8%
P25+CNTs+HS	0.626	4.95	0.46	4.39	0.654	36.5	300.8	2.0%

Table 4-5: DSSC efficiencies and I-V curve characteristics of P25 with CNTs and scattering layer collected with a TriSol solar simulator, under 1.5 AM, 100 mW/cm², global illumination.

The short circuit current also decreased with the addition of CNTs, which could be due competition for light absorbance between the dye and CNTs. Others have reported an increase in short circuit current with the addition of small amounts of CNTs due to increased electron mobility, less trapping, and less recombination with the dye due to the Schottky barrier effect[31,72]. The opposite effect observed in our composite materials could be caused by an excess of CNTs added and the catalytic effect mentioned above. Because of the complexity of

the problem, impedance spectroscopy was used to evaluate the different processes that could explain the differences. Some preliminary results are presented in the following section.

Impedance Spectroscopy Results

As mentioned in Section 4.2.3, the position of the Fermi level at the interface between the TCO and TiO₂ film can be controlled by an external applied potential. The impedance spectra of a DSSC with a Degussa P25 TiO₂ photoanode in the dark at two different applied potential are compared in Figure 4-16 and Figure 4-18. At a high applied potential, over the open circuit voltage, V_{OC}, the Fermi level is close to the TiO₂ semiconductor conduction band which increases the concentration of electrons in the TiO₂ network and reduces the transport resistance of the film ($R_r \gg R_t$). Under this condition, the transmission line required to fit the impedance data can be simplified to that shown in Figure 4-17.

The impedance spectrum for a DSSC with a TiO₂ Degussa P25 photoanode in the dark, at a high applied potential of -0.7 V (Figure 4-16), shows three distinct regions (semicircles). Based on the transmission line in Figure 4-17, the low frequency arc is associated to electrolyte diffusion, the middle arc at intermediate frequencies is linked to electron recombination and chemical capacitance at the TiO₂ surface, and finally the semicircle at high frequency values is linked to the counter electrode charge transfer resistance and capacitance. [2].



Figure 4-16: Impedance spectrum of a DSSC (Degussa P25 photoelectrode) in the dark under a - 0.75V bias vs Γ_3/I_2 (high applied potential). Frequency range: 100 Hz to 10 mHz, AC amplitude 10mV.



Figure 4-17: Transmission line model at high applied potentials for describing the impedance spectrum shown in Figure 4-16.

When operating at low DC applied potentials, the Fermi-level is close to the valence band and the electrons cannot be injected into the TiO₂ due to the extremely high electron transport resistance ($R_t \rightarrow \infty$) and the main contribution to the impedance spectrum in Figure 4-18 is the parallel combination of the charge transfer resistance of the FTO/electrolyte interface, R_{DL} , at the bottom of TiO₂ film and the C_{DL} , resulting in an open high resistance arc [2].



Figure 4-18: Impedance spectrum of a DSSC with a TiO_2 photoelectrode film made from Degussa P25, in the dark under -0.25 V bias vs. I_2/I_3^- (low applied potential), 100 Hz to 10 mHz, and 10 mV AC amplitude.

At high frequencies (inset) the contribution of the counter electrode interface can also be observed. The resistance for reducing the electrolyte at the Pt counter is insignificant compared to the charge transfer resistance at the working electrode [2]. The diffusion of the electrolyte is not seen because it occurs at very low frequencies [2,75]. For this case the DSSC can be modeled using the equivalent circuit shown in Figure 4-19.



Figure 4-19: Equivalent circuit of a DSSC at low applied potentials for describing the impedance spectrum shown in Figure 4-18.

At intermediate potentials, that is close to the maximum power point of the cell, the full transmission line model is required to fit the impedance data (Figure 4-20 and Figure 4-21). At this applied potential the transport resistance in the TiO₂ film is close to the recombination resistance with the electrolyte ($R_t \approx R_r$). In the case of $R_t < R_r$, the diffusion of the electrons in the film is observed at high frequencies with a slope higher than the characteristic 45° Warburg feature (inset in Figure 4-20). At low frequencies a deformation associated with the recombination resistance (R_r) and capacitance (C_{μ}) can be seen overlapping with electrolyte diffusion at even lower frequencies. As the applied potential decreases in this intermediate region, the recombination resistance becomes smaller than the electron transport resistance, $R_t > R_r$, and the semicircle becomes unsymmetrical, this is what is referred to as Gerischer impedance [2,75].



Figure 4-20: Impedance spectrum for a DSSC prepared using hierarchical spheres-fibers (HSF) at intermediate potentials in the dark. Applied bias potential: -0.5 V, frequency range: 100 Hz to 10 mHz, and AC amplitude equal to 10mV.



Figure 4-21: Equivalent circuit for a DSSC at a potential close to the maximum power point in Figure 4-20

Different processes are observed in the dark and under illumination, since in the latter case, electrons are injected into the TiO_2 conduction band and electron transport becomes negligible like in the case of high applied bias potentials (Figure 4-22).



Figure 4-22: Impedance spectra of a DSSC prepared using hierarchical spheres (HS) under illumination and dark at intermediate potentials. Applied bias potential: -0.5 V, frequency range: 100 Hz to 10 mHz, and AC amplitude equal to 10mV.

This thesis is primarily interested in the changes in electron transport in the TiO_2 films caused by the different morphologies and by addition of CNTs. For this reason, the impedance study was carried out at an intermediate potential, -0.5 V, close to the maximum power point of the cell, in the dark. The impedance spectra of the DSSCs analysed in this work are shown in Figure 4-22and Figure 4-23.



Figure 4-23: Impedance spectra for all the materials investigated in this study collected in the dark at a bias potential of -0.5 V. The solid lines represent the fittings using the equivalent circuit in Figure 4-21.



Figure 4-24: Impedance spectra for the materials shown in Figure 4-24. The solid lines represent the fittings using the equivalent circuit in Figure 4-21.

The transmission line in Figure 4-20 was used to fit the IS data. The corresponding diffusion coefficient, electron lifetime, and R_r/R_t ratio derived from fitting the impedance spectra are summarized in Table 4-6.

Table 4-6: DSSC efficiencies, diffusion coefficients, electron lifetimes and relative recombination resistances obtained from the impedance spectroscopy runs.

Sample	η(%)	$D_n(cm^2s^{-1})$	$\tau_n(s)$	R_r/R_t	
HSF	1.7%	2.6×10^{-5}	0.05	0.92	
HS	2.2%	1.8×10^{-6}	0.60	0.76	
NF	2.8%	2.0×10^{-5}	0.06	0.89	
P25	2.8% (2.5) ^a	1.7×10^{-5}	0.05 (0.06) ^a	0.89	-
P25+HS	3.2%	6.0×10^{-6}	0.20	0.94	
P25 + CNTs	1.8%	4.0×10^{-5}	0.03	0.51	
P25+CNTs+HS	$2.0\% (3.9)^{a}$	2.3×10^{-5}	0.03 (0.04) ^a	0.64	
	1 [01]				_

^a values taken from Quaranta *et al.* [31]

In the impedance spectra of the HS, the central arc corresponding to recombination resistance is not a true circle, and the linear portion at high frequencies, corresponding to the transport resistance, is very small indicating strong recombination $(R_r < R_t)$ [2,61]. In this case a form of Garischer impedance should be used; however, by doing so the diffusion coefficient and R_r/R_t cannot be determined. As a result the transmission line model in Figure 4-21 was used to fit the HS data. However, this introduces a greater error in R_r/R_t and the diffusion coefficient when compared with other samples in Table 4-6[61]. The higher recombination for HS could be caused by trapping and recombination at the many spiky projections on the particles. The low diffusion coefficient, almost an order or magnitude lower than the diffusion coefficient for the other TiO₂ morphologies, and the long electron lifetime, which incorporates the transport lifetime and time stuck at trapping sites, supports this hypothesis.

The diffusion coefficient, electron lifetime, R_r/R_t and efficiencies of HSF and P25 are very similar even though the transparency of the electrodes is different. The cause of this is partly due to: the better contacts used for the P25 studies evident in the low series resistance; and the use of direct light for HSF as opposed to global irradiance for the P25, which increases the energy input for the later. Unfortunately, the solar simulator used for the initial studies had to be changed before the work was completed. What is notable about the HSF impedance spectra is that recombination is relatively low; this could be attributed to one-dimensional semiconductors theoretically have fewer grain boundaries [72]. The slight decrease in diffusion coefficient for NF is possibly due to the smaller size of the fibers, but electron lifetime and diffusion coefficient are close to those of HS. The difference in efficiency must be a result of the morphology. The shunt resistance for HSF is very high compared to the others morphologies and could be another indication of the open structure and not many contact sites on the FTO.

Liao *et al.* [24] used diffuse reflectance spectroscopy and incident-photon-to-current efficiency (IPCE) to examine light scattering and harvesting abilities of the different morphologies. They saw that hierarchical spheres had the highest efficiency and performed better at scattering and harvesting the light. They attributed this result to the larger over all particle size and better dye loading. On the other hand they saw that the transport and recombination was better in more crystalline material and nanofibres, concluding that light harvesting and scattering is one of the key parameters in determining the efficiency.

The addition of the scattering layer reduced the diffusion coefficient and increased the electron lifetime, as expected. The values represent the mixture of poor performance of the HS and good performance of the P25. In the same respect, the open circuit voltage was lowered because of increased recombination due to the surface traps from the scattering layer. However because of the increase in light absorption, a shift in the Fermi level, and shallower electron trapping/detrapping, the electron transport increased (R_t/R_t) [76].

The CNTs increased the electron diffusion coefficient because of their high conductivity. On the other hand, electron lifetime was lower and R_r/R_t was low due to increased recombination, supporting the catalytic effect of the CNTs. With the addition of the scattering layer, the diffusion decreased and the electron lifetime increased with respect to the P25/CNT film because of the averaging of the properties of the two different layers.

4.4 Conclusions

In conclusion, a procedure was developed to fabricate DSSCs and characterize in-house synthesized materials. TiO₂ nanofibers produced in heptane performed better than hierarchical spheres and the mixture of hierarchical spheres and fibers. These results indicate that higher dye loading, as well as a more efficient light scattering, were crucial in the performance of the cells and their efficiencies. When CNTs were added to the synthesis, contrary to previous reports a decrease in efficiency was observed. The reduction in the recombination resistances (R_r/R_t in Table 4-6) after the addition of carbon nanotubes to Degussa P25 and P25+HS is a major factor in reducing the efficiency of these cells. Further research needs to be conducted to see if better efficiencies can be obtained through chemical linkages between the TiO₂ network with the CNTs. The reproducibility of the cells needs to be investigated further for these results to be statistically relevant.

5 **Conclusions and Future Work**

 TiO_2 films of different morphologies were synthesized using different reaction media, supercritical carbon dioxide and heptane. The photoelectrical properties of the materials were tested using DSSC devices. Furthermore, the impact of carbon nanotubes on the photoelectrical properties of TiO₂ was investigated by mixing CNT's with Degussa P25 commercial TiO₂ films followed by testing in a DSSC device.

In order to produce nanomaterials in supercritical CO_2 , a high temperature, high pressure system was developed, tested and calibrated. It was able to withstand and hold pressures of 24 MPa and temperatures of 150 °C over multiple days. The system contained features such as a precursor injection system, a temperature range from 0 to 150 °C, capability of recording realtime temperatures and pressures, could work under flow conditions and had safety features such as a rupture disk, a materials trap and proper ventilation.

The morphologies of the different films were characterized using FTIR, Raman, XRD, SEM and TGA. By controlling the ratios of acetic acid-to-titanium tetraisopropoxide, we were able to obtain a variety of nanostructures in different media, including: globular structures and fibers in heptane, hierarchical spheres in SC-CO₂ and mixtures of nanospheres and fibers.

The synthesised material was tested in DSSCs using a solar simulator to record the I-V curve and impedance spectroscopy to examine the electron diffusion, lifetime, and recombination. A procedure to fabricate DSSCs was successfully implemented, and cells with efficiencies above 3% were created and tested. Impedance spectroscopy showed that at low potentials the spectrum was dominated by diffusion of the electrolyte; at high potentials all three components could be clearly seen, that is: the impedance caused by the counter electrode, the TiO_2 film, and the electrolyte; at intermediate potential the impedance due to electron transport and recombination was dominant. When operated under illumination a reduction in recombination resistance occurred due to increased electron transfer from the dye to the TiO_2 conduction band.

The morphologies tested in a DSSC device included: nanofibres synthesised in heptane (heptane 5.5), hierarchical spheres (SC-CO₂ 3.5), and hierarchical spheres and fibers (SC-CO₂ 5.5). It was found that the nanofibres obtained in heptane performed the best (2.77%) due to higher dye loading, good scattering of the light and good electron diffusion from their 1-D structures. Hierarchical spheres had a decrease in efficiency (2.17%) because of greater recombination due to all the spiky projections, but they had good dye loading and light scattering. The mixture of hierarchical spheres and fibers had the worst performance (1.72%) due to their open structure causing bad dye loading and scattering. For completeness future work should test fibers synthesized in SC-CO₂ and the globular structures from heptane, and work should continue to perfect the art of making DSSCs to increase the efficiency.

This work confirms the high impact of different morphologies on the photoelectrical properties of TiO₂, as reported also by Liao *et al.* [24], but indicates a better performance of nanofibers with respect to nanospheres, contrary to Liao's findings. We conclude that the combination of morphology and relative size of the nanostructures is responsible for the differences in performance.

It should be noted that, when CNTs were added to the synthesis, there was also a clear change in morphology. Nanofibers no-longer appeared in synthesis with heptane and large blocks appeared in the SC-CO₂ synthesis. The change in morphology was caused by TiO_2 nucleation on the CNTs.

A scattering layer on top of the Degussa P25 sample proved to be effective at increasing the efficiencies of DSSCs, and the electron transport properties and recombination of the cell took on properties of both materials. When CNTs were added to these cells, the efficiency was seen to decrease due to recombination at the interface of the CNT and electrolyte. However, it was not possible to test similar properties with the different morphologies obtained in this work.

Future work should focus on the types of morphologies that can be obtained in SC-CO₂ using AcOH/TTIP as precursors and seeding it with CNTs. Future work should also include examining the functionalization of CNTs with TiO₂, verify that SC-CO₂, on achieving better coatings of CNTs with TiO₂, possibly with SC-CO₂, and re-examine the quantity of CNTs needed to increase the efficiency.

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