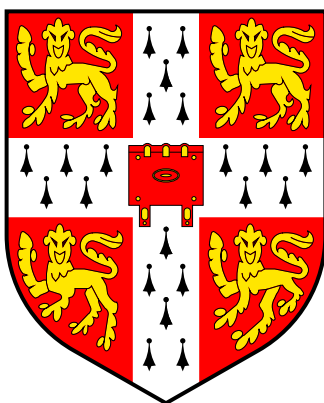


Block Copolymer Patterning of Functional Materials



Edward Crossland

May 2008

A dissertation submitted for the degree of Doctor of Philosophy

University of Cambridge

Cavendish Laboratory

Corpus Christi College

Declaration

This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text.

I declare that no part of this work has been submitted for a degree or other qualification at this or any other university.

This dissertation does not exceed the word limit of 60,000 words set by the Physics and Chemistry Degree Committee.

Edward Crossland, May 2008

Preface

This thesis is the result of work carried out with the Thin Films and Interfaces Group at the Cavendish Laboratory, Cambridge, between October 2004 and December 2007 and was funded through an Engineering and Physical Sciences Research Council Project Studentship.

I would like to thank first of all my supervisor Prof. Ullrich Steiner whose boundless enthusiasm, knowledge and insight remains a constant inspiration. Also to Prof Marc Hillmyer who spent a sabbatical year watching me drop his precious copolymers before they could be put to good use, thank you, and sorry! Dr Henry Snaith also has a lot to answer for; without his ideas and immense expertise this work would never have come so far. Dr Sabine Ludwigs helped me out right at the start and has always been there for valuable discussions and guidance. Thank you also to Miha Nedelcu and Team Solar, we are in this together! Marleen Kamperman, Prof. Ulrich Weisner, Gilman Toombes, and Detlev Smilgies from Cornell University were all extremely kind in offering their time and considerable expertise in X-ray scattering and all things morphological. I have been privileged to work in superb scientific environment and learn from some incredible people. My thanks to the Biological and Soft Systems Sector in the Cavendish, and the Cambridge Nanoscience Centre and all the wonderful support staff and researchers there.

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To mum and dad, who got me here, and made sure I could stick it out at the end, thank you! Marie, you know I can never thank you enough for keeping me (marginally) sane, and always being there for me. Thank you mi pequeña.

Block Copolymer Patterning of Functional Materials

Edward Crossland

The objective of this work is to develop and apply the use of block copolymer self assembly as a precision patterning tool on the 10 nm length scale for functional materials in thin films. These methods and resulting structures are interesting for a wide range of applications in nanotechnology, however the specific motivation for this work is the patterning of thin film mesoscale semiconductor composites for next generation solar cells. The proof of principle is demonstrated by fabricating dye-sensitized solar cells incorporating structured arrays of TiO₂.

The first part of this thesis introduces the operating principles of the solar cell as a means of producing electrical energy from sunlight and outlines some of the most promising approaches to low-cost solar technologies, particularly those incorporating organic components. The search thus far has led to the concept of excitonic solar cells, which rely on specific cooperative semiconductor material architectures in order to produce efficient solar energy conversion. *Chapter 2* contains the principles of self assembly in block copolymers and important aspects of their use as sacrificial or partially sacrificial templates for selected functional materials. Here, block copolymers containing a minority poly(lactide) component, which is selectively degradable under mild chemical conditions, are used to form mesoporous polymer films with well-defined internal porosity. In *Chapter 5*, an electric field is used to align standing cylindrical copolymer domains that are removed to leave a template for electrochemical deposition of ordered standing nanowire arrays with 12 nm diameter and packing densities of over 10^{11} cm^{-2} . A simple in situ electrochemical technique for monitoring the removal of the poly(lactide) component from thin films with a range of morphologies is described in Chapter 6.

The thin film behaviour and electrochemical replication of the bicontinuous gyroid block copolymer phase is summarized in *Chapter 7*. Dye-sensitized solar cells incorporating a TiO₂ gyroid network are characterized in *Chapter 8*. These results are the first reported application of a gyroid structure in a functioning electronic device. In *Chapter 9*, the performance of nanowire and gyroid networks are compared directly to ‘traditional’ disordered state-of-the-art mesoporous TiO₂ materials. The stability of the freestanding nanostructures is found to be a key requirement in fabricating real composite devices. The network-based gyroid and nanoparticle structures therefore considerably outperform the standing nanowire arrays in solar cells despite their impressive electronic properties.

Chapter 10 presents preliminary results achieved using a functional copolymer of poly(lactide) in which the template material itself demonstrates charge transport characteristics. The PLA component again provides a means of introducing a well defined internal porosity to a charge transport medium, enabling a more direct approach to the fabrication of intimate, distributed semiconductor junctions.

Motivation : The Solar Energy Challenge

The human race generates and consumes a staggering 4.1×10^{20} Joules of energy each and every year, equivalent to continuous consumption of 13 TWⁱ. Technological development and population growth will drive our future energy demands still higher, more than doubling to 30 TW by 2050, even if we learn to use energy more efficientlyⁱⁱ. Our energy hungry society is currently driven almost entirely (80 to 85%) by non renewable energy sources such as combustible fossil fuels and nuclear fission. Even if the planet could tolerate the harmful side effects of pollutants and climatic change caused by atmospheric emissions, we are now forced to consider the inevitable exhaustion of these resources. A clean, renewable source of energy must be developed, capable of delivering at least 10 TW of power for an extended period of time. To put this in perspective, generating this amount of energy using nuclear fission alone would require the construction of a new 1 GW plant somewhere in the world every day for the next 25 years.

The energy carried by solar radiation represents a huge and virtually untapped resource. The total incident power flux taken over the globe is 120,000 TW, many orders of magnitude greater than our current and foreseeable future needs. To comprehend the scale of this energy, the world's most powerful hydrogen bomb, detonated over the island of Novaya Zemlya on the 30th October 1961, released 58 megatonnes of energy in a single blast; six thousand times more powerful than the Hiroshima bomb and almost thirty times greater than all the explosives used by all sides in World War II. This energy, an astonishing 210,000 TJ, arrives here on earth every 2 seconds from the sun.

The challenge, of course, lies in harvesting this seemingly abundant solar resource. Photons from the sun are distributed over the globe with a correspondingly low energy density. Solar energy is therefore far more difficult to harvest than the convenient, high energy density deposits of fossil fuels on our doorsteps. In the world today, only 0.015 % of electricity production comes directly from solar energy. But all is not lost, a coverage of just 0.16 % of the earth's surface with 10 % efficient solar farms would generate 20 TW of power - the equivalent of 20,000 1 GW nuclear fission plants. In practical terms, the required land area in the US to meet America's domestic energy needs is roughly ten times the roof area of all single family residential rooftops or comparable to the area of all numbered federal roads.

However, solar energy technology remains too expensive to compete with fossil fuel sources; the current cost of electricity produced by solar cells is \$0.30/kW h, compared to just \$0.03/kW h for electricity from natural gas. Our great challenge is to develop robust, scalable, and cheap technologies to make solar energy economically competitive with non-renewable resources. Nanotechnology can certainly play a significant role in meeting this challenge. Light interacts with materials on the length scale of its wavelength, a few hundreds of nanometres. Energy capture occurs via excited electron states which interact with interfaces and defect structures typically on the 1-10 nm scale. Therefore the manipulation of specific nanoscale structures enables us to derive significantly enhanced performance from otherwise low cost material systems. Advances in the design and precision engineering of these systems are rapidly expanding the prospects for viable solar energy production from a new generation of device technologies.

ⁱBasic energy sciences workshop on solar energy utilization. 2005 U.S. Department of Energy, Available at: www.sc.doe.gov/bes/reports/abstracts.html.

ⁱⁱE. Cartlidge. Bright outlook for solar cells. *Physics World*, 20(7):2024, 2007.

Contents

1	Excitonic Solar Cells	1
1.1	Photovoltaics and Conventional Solar Energy Conversion	1
1.2	Organic Solar Cells	2
1.2.1	Excitonic solar cells	3
1.3	Bulk Heterojunctions	5
1.3.1	All Organic Junctions	7
1.3.2	Hybrid Organic/Inorganic Junctions	9
1.4	Dye Sensitized Solar Cells	10
1.4.1	Solid State Dye-Sensitized Solar Cell	13
1.4.2	Structuring of Inorganic layers for DSSCs	16
2	Principles of Block Copolymer Self Assembly	27
2.1	Microphase separation in block copolymers	27
2.2	Block copolymers and nanotechnology	32
2.2.1	Block copolymer thin films	33
2.2.2	Alignment of the microphase	36
2.2.3	Patterning of functional material systems	39
3	Techniques and Instrumentation	55
3.1	Structural Characterization: Imaging and Scattering Methods	55
3.1.1	Electron Microscopy	55
3.1.2	Small Angle X-ray Scattering	59
3.1.3	Wide Angle X-ray Diffraction	63
3.1.4	Scanning Force Microscopy	63
3.1.5	Ellipsometry	65
3.2	Electrochemical Deposition	67
3.2.1	Electrochemical Surface Area Measurements	68
3.3	Photovoltaic Device Characterization	70
3.3.1	Photovoltaic Performance: Definitions	70
3.3.2	Transport and Recombination	74
3.3.3	Photovoltaic set-up: device testing	76
4	Experimental	81
4.1	Materials	81
4.2	Block Copolymers	82
4.2.1	Synthesis of Poly(D,L-lactide) [PLA]	83
4.2.2	Synthesis of Poly(4-fluorostyrene)- <i>b</i> -poly(D,L-lactide) [PFS- <i>b</i> -PLA]	84

4.2.3	Synthesis of Poly(styryltriarylamine)- <i>b</i> -poly(D,L-lactide) [PSTA- <i>b</i> -PLA]	85
4.3	Substrate preparation	85
4.4	Thin film deposition	86
4.5	Copolymer Electric Field Alignment	89
4.6	Electrodeposition of Ti(IV)oxide	91
4.7	Electrodeposition of Platinum	93
4.8	DSSC Device Assembly	93
4.8.1	TiCl ₄ surface treatment	93
4.8.2	Solid-state DSSC device assembly	93
4.8.3	Liquid electrolyte DSSC device assembly	95
5	Nanowire Arrays	99
5.1	Introduction	99
5.2	Experimental	100
5.3	Templating of Freestanding Nanowire Arrays	101
5.4	Templating of thick nanowire arrays	109
5.5	Summary	113
6	In situ Measurements of PLA etching in block copolymer templates	117
6.1	Introduction	117
6.2	Experimental	119
6.3	Results and Discussion	120
6.3.1	Homopolymer PLA Etching	120
6.3.2	Etching of PFS- <i>b</i> -PLA templates	122
6.4	Conclusion	124
7	Templating the Double Gyroid	127
7.1	The gyroid phase in block copolymers	127
7.1.1	Patterning using the gyroid phase	129
7.2	Experimental	130
7.2.1	Simulation of the double gyroid phase	131
7.3	Results and discussion	134
7.3.1	Bulk phase behaviour	134
7.3.2	Low temperature thin film behaviour	135
7.3.3	High temperature thin film behaviour	144
7.4	Summary	153
8	The double gyroid solar cell	159
8.1	Introduction	159
8.2	Experimental	160
8.3	Freestanding titania gyroid network arrays	161
8.3.1	Structural characterization	161
8.3.2	TEM Cross sectioning	169
8.3.3	Material characterization	170
8.4	Liquid electrolyte dye-sensitized solar cells	172
8.5	Solid-state dye-sensitized solar cells	172
8.6	TiCl ₄ surface treatment	175
8.7	Titania deposition growth rate effects	178
8.8	Discussion	179
8.9	Summary	182
9	StructureFunction	189
9.1	Introduction	190

9.2	Experimental	191
9.3	Nanowire, Gyroid and Nanoparticle Structures	192
9.3.1	Nanocrystalline morphology of structured arrays	196
9.4	Dye-Sensitized Solar Cell Performance	198
9.4.1	Nanowires in solid-state dye-sensitized solar cells	198
9.4.2	Liquid electrolyte dye-sensitized solar cells	199
9.5	Charge Transport and Recombination	201
9.6	Summary	203
10	Semiconducting Block Copolymers	209
10.1	Introduction	210
10.2	Experimental	211
10.3	PSTA Hole Mobility	213
10.4	Porous PSTA films	214
10.5	Electric Field Alignment of PSTA- <i>b</i> -PLA	216
10.5.1	Application of DC fields	216
10.5.2	Application of AC fields	222
10.6	Summary	224
11	Summary and Outlook	231
11.1	Summary	231
11.2	Further Work	235

Excitonic Solar Cells

The following chapter will give an overview of the important concepts in photovoltaic devices incorporating novel and low-cost material systems. These approaches have in common the application of semiconductor-semiconductor interfaces or ‘heterojunctions’. The nanometer scale structural organization of these architectures is a crucial factor in their ability to convert incident light to electronic energy. The dye-sensitized solar cell concept is introduced along with a brief review of state-of-the-art nanostructure fabrication as motivation for this work.

1.1 Photovoltaics and Conventional Solar Energy Conversion

The photovoltaic effect is the generation of an electric potential difference upon light irradiation. The principle is the basis for a variety of approaches to converting solar radiation into electrical energy using a solar cell [1]. Effective solar energy harvesting using a photovoltaic device requires completion of two sequential tasks:

- I. Photoexcitation of charge carriers in light absorbing material.
- II. Separation and extraction of free charge carriers to external electrodes.

The first of these tasks is controlled by the electronic structure of the absorber such that an electron is promoted into a higher electronic state on absorption of an incident photon. Ideally the absorption should match the solar spectrum. Some inherent asymmetry, such as a compositional gradient or

material junction is then necessary to separate and extract the excited charge before it can relax back to its original state. The residual energy of the separated charges allows an electrical potential to build at the external electrodes and thus drive an external load.

Traditional inorganic technologies which dominate the current world market for solar modules are based on a flat junction between n and p-type inorganic semiconductors. Such a junction can be created in a thin silicon wafer for example by n and p-type doping of adjacent layers. Absorption of a photon of $h\nu > E_{\text{bandgap}}$ can occur anywhere in the bulk of the active layer and results in the excitation of an electron from the valence band to the conduction band. The electron and its conjugate hole are essentially free carriers following excitation. In order to absorb a significant fraction of incident light, the layer must have a minimum thickness dependent on the absorption cross section of the material. Silicon is an indirect bandgap semiconductor and as such requires a relatively thick ($\sim 100\mu\text{m}$) active layer. An asymmetry for charge separation is provided by the electric field present in the junction depletion region which sweeps electrons and holes in opposite directions towards extracting electrodes. Because both electrons and holes coexist in the same bulk volume, the cell is extremely sensitive to the presence of crystal defect sites and trace impurities which can act as efficient recombination centres. To avoid excessive loss of photogenerated charge the semiconductor must therefore be of exceptionally high purity and crystallinity. There is significant fundamental cost, in terms of materials and high temperature processing in fabricating layered devices on an industrial scale using crystalline inorganic materials. The high production cost of Si solar cells remains a barrier to their wider adoption for commercial power generation despite decades of Si processing development.

1.2 Organic Solar Cells

The high cost of traditional photovoltaic technologies has driven the search for alternative approaches using material systems compatible with low cost, large scale production methods such as reel-to-reel processing. Solar cell concepts that incorporate one or more organic components are very promising in this regard [2]. Organic materials are relatively cheap to synthesize and are naturally amenable to well established solution based processing methods (reel-to-reel, dip and spin coating, ink jet and screen printing) as well as dry deposition techniques such as vapour phase deposition [3]. A further

advantage is the versatility of organic materials born of modern molecular design and synthesis that allows tuning of important physical properties such as band-gap, charge transport, solubility and morphological characteristics [4]. Organic photovoltaic technology does however have a number of shortcomings, which must be addressed before it becomes a viable option for the generation of electric power: (1) photoactive polymers absorb light mainly in the visible spectral band but not in the infrared, making use only of part of the solar spectrum, (2) only a small fraction of the charge carriers find their way to the electrodes, and (3) their life-time is limited by the photooxidation. While (1) and (3) are largely challenges of molecular design and synthesis, aspect (2) can be addressed by innovative structuring of multiple device components. The possibilities in this regard are best appreciated by understanding organic solar cells as an example of an *excitonic* photovoltaic system.

1.2.1 Excitonic solar cells

The mode of operation in organic solar cells is fundamentally different to that of conventional inorganic *p-n* junctions. Indeed it is possible to broadly categorize existing solar cells as either conventional silicon *p-n* junction type or excitonic solar cells (XSCs) according to their mode of operation [5]. Firstly the charge transport mobilities of organic semiconductors are orders of magnitude less than crystalline inorganic materials. The highest reported hole mobility for semi-crystalline polymers is around $0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [6] (which is itself several orders of magnitude greater than the mobility in typical amorphous organic materials applied in organic solar cells) compared to $450 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in silicon [4]. Low charge mobility limits the feasible thickness of the organic layer in solar cells to a few hundred nanometres [7]. The second and most important distinguishing feature is the nature of electronic excitation following photon absorption. In organic semiconductors, the excited electron remains in a bound state with its conjugate hole known as an *exciton*. In fact, excitonic states arising from the Coulomb attraction of electron hole pairs also exist in crystalline inorganic systems. However, the binding energy of the exciton here is very small (a few meV) owing to strong dielectric screening from the crystal lattice, so that the electron and hole thermally dissociate very easily at room temperature. With relatively weak intermolecular forces and a lack of ordered crystallinity (except in a few cases) organic semiconductors do not have a fully delocalized electronic band structure. This and the absence of strong dielectric screening result in a tightly bound exciton that will

not spontaneously dissociate at room temperature (binding energy $\gg kT$). Generation of *free* charge carriers is therefore not concurrent with light absorption as in conventional cells.

One very effective means of facilitating exciton dissociation is to introduce an interface with a second material which has molecular or band energy levels such that it is energetically favourable for forward charge transfer of an electron or hole across the interface. Free charges are both generated and simultaneously separated via exciton dissociation at this donor-acceptor interface known as a *heterojunction*. Following separation, both charge species move to external electrodes with work functions chosen to favour charge extraction. The schematic operation of an excitonic solar cell, showing photon absorption, exciton diffusion and dissociation, and charge extraction is shown in Figure 1.1.

Power conversion efficiency, defined as the ratio of electrical power delivered to the incident flux of radiative energy, is the headline quantifier of solar cell performance. The external quantum efficiency (EQE), the ratio of electrical current to incident photon flux is also a key figure of merit as it describes in a direct manner the conversion of photons to extracted charges. It is useful to consider

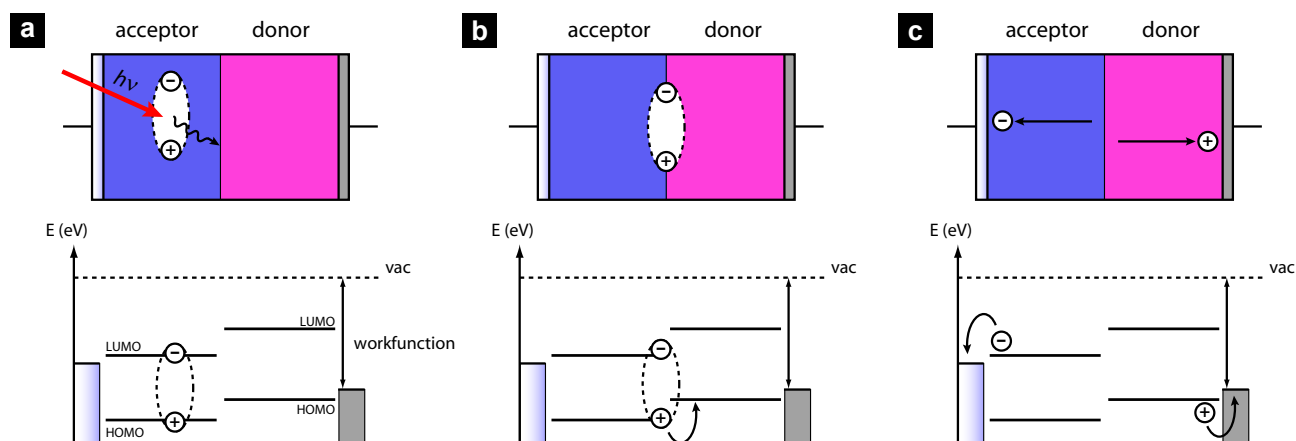


Figure 1.1: Schematic representation of XSC operation at a donor-acceptor interface. (a) Light absorption in the body of either donor or acceptor phase produces a bound exciton. The electronic structure of lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO) of the two phases and external electrode workfunction is shown underneath a schematic of the device structure. **(b)** The exciton diffuses to the interface where the electron or hole undergoes forward charge transfer to the adjacent phase leading to simultaneous free charge generation and separation. **(c)** transport and collection of charge from each phase to external electrodes.

the EQE of an excitonic cell relying on a donor-acceptor interface as a product of efficiencies at each sequential stage of photovoltaic operation [7]:

$$EQE = \eta_A \eta_{ED} \eta_{CC} \quad (1.1)$$

Where η_A is the light absorption efficiency (the fraction of incident photons absorbed in active layer), η_{ED} is the exciton dissociation efficiency (the fraction of photo-generated excitons that successfully reach and dissociate at the heterojunction) and η_{CC} is the charge collection efficiency (the fraction of free charges that subsequently reach the electrodes).

A major problem with XSC operation is the strong tendency for the exciton to recombine before it reaches the interface; the exciton diffusion length in typical organic materials is only of the order 10 nm [8]. Therefore only material within around 10 nm of the interface produces excitons that can contribute to the photocurrent while hundreds of nanometres of material may be required for significant light absorption (high η_A). Organic based devices based on a simple planar bilayer heterojunction (Fig. 1.2a) are therefore compromised by either a low η_{ED} (when too thick) or low η_A (when too thin) and a poor overall EQE [9, 10].

1.3 Bulk Heterojunctions

An XSC with high EQE can be made by finely distributing the donor-acceptor interface throughout the thickness of the device layer to form an interpenetrating *bulk heterojunction*. An effective bulk heterojunction has to fulfil two requirements: (1) the average domain size should be comparable to the exciton diffusion length (high η_{ED}) and (2) both phases form mutually continuous charge transport pathways through the device to the respective external electrodes (high η_{CC}).

Bulk recombination is suppressed in a XSC as there are essentially no free minority carriers present in either phase (i.e. free electrons and holes exist in different material phases). However, recombination by back electron transfer across the interface remains a loss mechanism that can compete with charge extraction and lead to low η_{CC} . This is a particular issue in a bulk heterojunction since charges might never be a significant distance from the interface. Extraction pathways should therefore be as direct as possible through a phase with a reasonably high charge mobility so that the in-

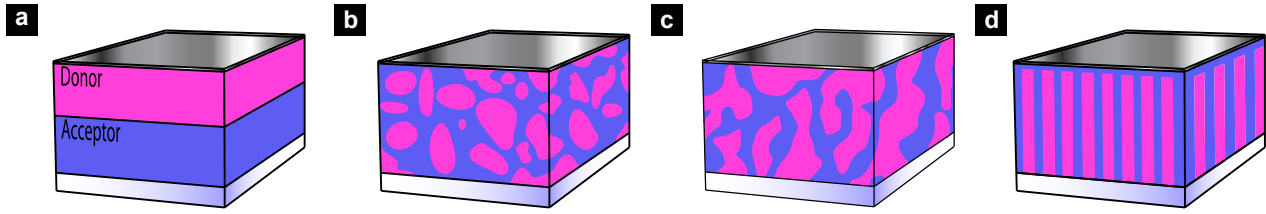


Figure 1.2: **Schematic representation of possible donor:acceptor heterojunction phase morphologies in photoactive thin layers (cross-sectional view).** (a) Flat bilayer structure. (b) Generic de-mixed phase morphology, unsuitable for a photovoltaic device because of the lack of connectivity of the minority phase to the electrodes. (c) A near-bicontinuous morphology (d) Conceptually ideal interdigitated junction on lateral scale of exciton diffusion length and thickness on the scale of the optical depth.

terfacial recombination rate is not competitive with transport time out of the device. This competition means that the overall efficiency is extremely sensitive to the morphology of the bulk heterojunction [7]. Figure 1.2 shows a series of possible schematic forms for the interface. The highly dispersed morphology in Figure 1.2b is effective in exciton dissociation, but not in charge extraction owing to a lack of continuity in both phases. The disordered, bicontinuous morphology in Figure 1.2c allows both efficient charge separation and charge transport in each phase. The comb-like interdigitation of the two phases (Fig. 1.2d) is a conceptually ideal structure to simultaneously optimize η_A , η_{ED} , and η_{CC} .

Self Assembly of Bulk Heterojunctions

The nanometre scale imposed by the exciton diffusion length makes bulk heterojunction fabrication extremely difficult using top-down lithographic patterning alone. Large area, low cost production of these structures must therefore rely on a degree of self assembly of the component materials during processing. Broadly speaking there are two approaches to bulk heterojunction self assembly:

- I. Co-deposition and self assembly of the constituent phases
- II. Patterning of one phase followed by infiltration of a second active material into intimate contact.

The primary advantage of the direct approach (1) is the simplicity at the point of device assembly. The difficulty is in design and selection of materials with required electronic properties and deposition parameters that will spontaneously form an optimized junction architecture. Examples of this

concept are co-sublimation or solution deposition of small molecules [11, 12], spin coating of polymer/polymer [4] or polymer/nanoparticle [13] blends from a single solvent or phase separation of block copolymers [14]. The sequential deposition approach (2) introduces additional sacrificial components or templates to act as structure directors for the active materials. In this way the self assembly of well studied and developed systems can be transferred into a wide range of functional materials. There are a greater number of (potentially costly) fabrication stages required to assemble the device, however the pay-off is better control of the junction morphology and a much wider choice of active material components.

Block copolymers and their spontaneous self assembly on macromolecular length scales offer in principle an ideal route to efficient bulk heterojunction architectures. Chapter 2 will introduce block copolymers and outline both direct and indirect approaches to patterning of functional materials. The remainder of this chapter is devoted to a review of state-of-the-art approaches to bulk heterojunction fabrication. Emphasis is given to a particularly promising subclass of bulk heterojunction device: the dye-sensitized solar cell (DSSC), which was chosen as a proof of principle system for the functional nanostructures developed in this thesis.

1.3.1 All Organic Junctions

Organic Blends

Perhaps the most straightforward and implementation of the bulk heterojunction concept is found in polymer/polymer and polymer/small molecule blend devices. A distributed junction can be formed by simple demixing during co-deposition of the two components, for example by spin coating from a single solution. Once all solvent has left the film, the phase morphology of glassy components is frozen in. The domain size and morphology is dependent on a complex interplay of a number of factors: solution composition and relative solubilities of the components, interaction parameters between each component and with the substrate, layer thickness, deposition method, drying process and subsequent annealing [7, 4]. Optimizing the bicontinuous morphology in Fig. 1.2c on a sufficiently small length scale corresponds to a very narrow range of sample preparation parameters and is therefore difficult to achieve [15, 16].

Blends of conjugated polymers with organic molecules such as a soluble methanofullerene derivative of C₆₀ (6,6)-phenyl C₆₁-butyric acid methyl ester (PCBM) constitute some of the most efficient all-organic solar cells to date. PCBM acts as an electron acceptor from donor polymers such as poly(phenylenevinylene) (PPV) derivatives or poly(3-hexylthiophene) (P3HT). The concept was first demonstrated in 1993 by Sariciftci *et al.* using a flat bilayer cell of C₆₀ evaporated on a spin coated poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene) (MEH-PPV) layer with an EQE of 9% at 514 nm illumination [10]. In 1995 Yu *et al.* made a MEH-PPV:PCBM bulk heterojunction blend which achieved a dramatically improved EQE of 45 % under low intensity illumination [17]. Further developments in control of the demixed morphology have led to P3HT:PCBM devices showing over 5% power conversion efficiency under simulated solar illumination [18, 19]. The first polymer/polymer blend devices were produced in 1995 by Halls *et al.* [20] and Yu *et al.* [21] using MEH-PPV and CN-PPV (cyano-para-phenylenevinylene) conjugated polymers. Chemical modifications to the polymers to improve solubility and optimization of phase morphology through processing parameters have steadily improved photovoltaic device performance. The record power conversion efficiency of these blends has now reached 1.7 % under simulated solar illumination [4].

Conjugated Block Copolymers

The complex interplay of processing parameters and intrinsic material properties has a profound and often unpredictable effect on the morphology and performance of blend-based heterojunction devices. It is therefore very difficult to systematically achieve the same, controlled morphology with new materials in order to optimize the intrinsic electronic properties of the components. Block copolymers on the other hand offer extremely well defined phase-separated morphologies that can be tuned by control of molecular design. Moreover the natural length scale of copolymer microphase separation (~ 10 nm) is well matched to the exciton diffusion length in many organic semiconductors. The most direct approach is to couple the donor and acceptor polymer components into a single block copolymer molecule so that the bulk heterojunction is formed by in-situ microphase separation within the film. There are, however, several other approaches to the transfer of block copolymer structures into functional material systems which are discussed in Chapter 2.

1.3.2 Hybrid Organic/Inorganic Junctions

Nanocrystal:Polymer blends

A simple mixing approach has also been used to produce hybrid organic/inorganic blend devices. The inorganic component is included in the form of nanocrystals with a range of geometries such as quantum dots, rods, or tetrapods dispersed in a matrix of conjugated polymer. The first cells of this kind were made using a blend of MEH-PPV polymer with CdS and CdSe nanoparticles [22]. Both materials can contribute to light absorption allowing extension of the spectral response, while the shape of the nanocrystal can be chosen to provide better pathways for electron transport. Highly elongated rods for example offer better connectivity in the blend than simple dots and result in dramatically improved transport. Hunyh *et al.* made P3HT:CdSe blends with rods of lengths 7, 30 and 60 nm which showed improved EQE with increasing nanocrystal aspect ratio [22]. The best devices were 200 nm thick, with 55 % EQE and showed 1.7 % power conversion efficiency [13].

Tetrapods consisting of tetragonally branched four-limb CdSe nanocrystals naturally result in elongated transporting structures which extend partially perpendicularly rather than parallel to the substrate. Cells made from CdSe tetrapods show 45% EQE at 480 nm, approximately double that of a device made with the equivalent weight fraction of 65 nm rods [23]. The tetrapod device achieved 1.8 % power conversion efficiency under simulated solar illumination. Vertical alignment of high aspect ratio nanorods has recently been demonstrated by the application of electric fields during slow solvent evaporation [24, 25]. These techniques could lead to further improvements in the performance of these blend devices.

Structured Inorganic:Polymer Devices

Backfilling a polymer into a pre-structured inorganic layer is an example of the sequential patterning route to bulk heterojunction architectures. The most common approach is to structure an inorganic metal-oxide semiconductor such as TiO₂ (titania), which has the advantage of being readily available and non-toxic. In addition to this, technology for producing structured ‘mesoporous’ TiO₂ electrodes with continuous pathways for electron transport has been well developed since the discovery of its photocatalytic properties [26, 27] and its use in dye-sensitized solar cells (Section 1.4). The most

common, and still the most successful method is to create a mesoporous layer from sol-gel processed sintered nanoparticles (~ 20 nm diameter). The layer is deposited as a viscous paste containing polymer binding agents which are burnt off during high temperature (500°C) sintering to leave a sponge-like mesoporous layer with $\sim 60\%$ porosity and an internal surface area some 100 to 140 times greater than the equivalent flat substrate per micron in film thickness [28].

Heterojunction PVs have been made by infiltrating either MEH-PPV or P3HT conjugated polymers into mesoporous TiO_2 nanoparticle films [29]. The limited success of these devices (power conversion efficiency $\leq 0.16\%$) is attributed to the presence of a distribution of pore sizes in the disordered nanoparticulate layer. Large (50-100 nm) polymer domains filling the largest pores, result in recombination of a significant fraction of excitons before they reach the interface, while the smallest nanopores hinder effective infiltration of the viscous polymer solution [30]. McGehee *et al.* made mesoporous TiO_2 films using a block copolymer directed sol-gel synthesis that resulted in well ordered and connected 8 nm spherical voids. While complete infiltration could be achieved from a P3HT melt the EQE remained low ($\sim 10\%$), most likely indicating that holes generated on the P3HT chain deep in the layer cannot escape before undergoing recombination with electrons in the titania phase [31, 32]. This was attributed to the highly nonlinear infiltration pathway into the film, leading to twisted chains with reduced charge transport mobility. The development of an open and well ordered porosity on the 10 nm length is expected to lead to significant improvements in polymer infiltrated hybrid devices [8, 33].

1.4 Dye Sensitized Solar Cells

Dye sensitized solar cells (DSSCs) are strictly speaking a subset of the hybrid inorganic organic excitonic cell [5]. The basic operational principle is to sensitize a wide bandgap inorganic semiconductor (such as a metal oxide) to the solar spectrum by attaching a surface-adsorbed monolayer of an organic dye [34, 35]. If the redox potential of the photo-excited dye lies above the conduction band edge of the inorganic semiconductor then an electron may be injected into the layer, as shown in Figure 1.3, process 1. The oxidized dye is regenerated by electron transfer from a surrounding donor species (process 2). The first, and still the most successful version of this concept uses a donor species dis-

solved in a liquid electrolyte, usually an organic or ionic liquid solvent containing the I^-/I_3^- redox couple [28]. The oxidized donor diffuses away to a counter electrode where it is subsequently reduced to complete the cell circuit (process 3). The principle loss mechanisms in DSSC photovoltaic operation are: back transfer of the injected electron into the dye ground state (process 4) and recombination with acceptor species in the electrolyte (process 5). The voltage generated under illumination corresponds to the difference between the quasi Fermi level in the semiconductor electrode and the redox potential of the electrolyte.

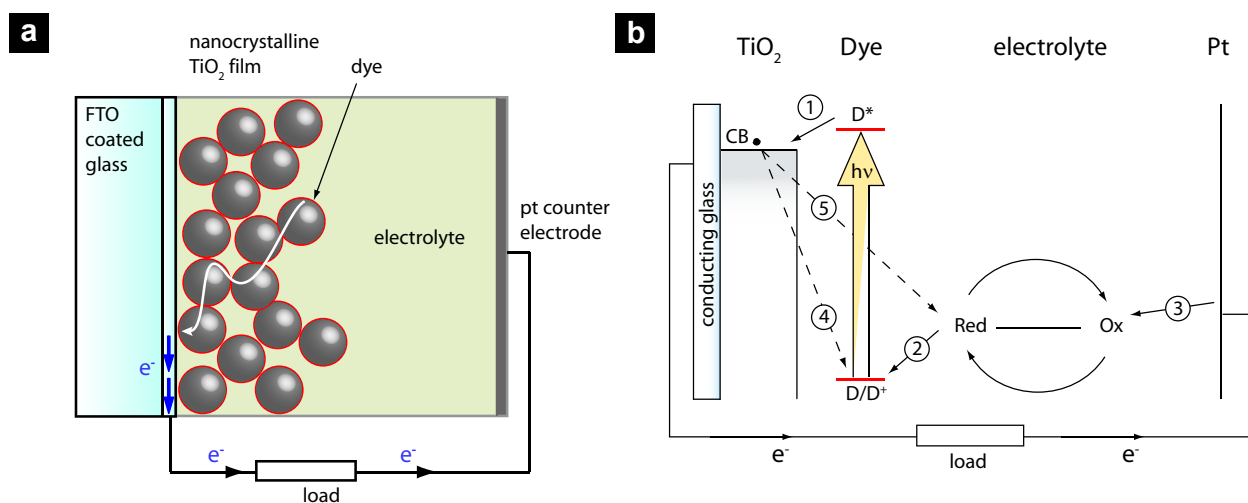


Figure 1.3: **Schematic liquid-electrolyte device architecture and electronic energy level structure.** (a) The electrolyte surrounds a dye-sensitized mesoporous inorganic layer on a conducting transparent electrode. A platinum counter electrode completes and seals the device. (b) Mechanism of photovoltaic operation on photoexcitation of the dye: (1) electron injection into TiO₂ conduction band, (2) dye regeneration, (3) reduction of oxidized species in electrolyte from Pt counter electrode. Principle loss mechanisms: (4) back transfer of electron into dye ground state, (5) electron recombination with acceptor species in electrolyte.

The problem of exciton diffusion is avoided since all excited states are generated already at a charge separating interface. However, the confinement of the cell's absorbing component to a single interfacial monolayer makes it very difficult to achieve significant light absorption. As with the fully organic XSCs, the solution is offered by a highly structured inorganic layer that provides a much increased surface to load with dye. Electron transport to the anode occurs via diffusion of electrons through the nanocrystalline inorganic layer [36], again calling for a fully continuous network structure. Using a typical transition metal complex dye such as N719 (absorption coefficient

$13,900 \text{ mol}^{-1} \text{ cm}^{-1}$) [37], a surface area enhancement of ~ 1000 over the flat surface equivalent is needed to achieve a significant optical depth ($\eta_A \sim 90 \%$).

The first DSSCs exploiting a bulk heterojunction structure were developed in the 90's by O'Regan and Grätzel using mesoporous TiO_2 nanoparticulate films [28]. In order to reach high photon-to-electron conversion efficiencies, a number of conditions must be fulfilled. Firstly, the dye regeneration process must be at least an order of magnitude faster than the recapture of conduction band electrons by the oxidized dye [38]. Secondly, the lifetime of the carriers (limited by recombination processes) must be substantially greater than the time they require to reach the external electrodes. A number of comprehensive reviews of DSSC device physics exist in the literature describing important aspects of dye and electrolyte design in developing high efficiency cells [39, 40, 34, 41]. The characteristic time scales for the various charge carrier reactions in nanoparticulate TiO_2 DSSCs are shown in Table 1.1. With these kinetics parameters in optimized liquid-electrolyte cells over 90 % of incident photons near the dye adsorption maxima result in extracted charges and deliver over 10 % power conversion efficiency under solar illumination [42].

With such impressive quantum efficiency, further optimization of the TiO_2 electrode structure for direct charge extraction would likely result in relatively marginal direct improvement in the performance of the liquid-electrolyte DSSC. However, improvements in charge transport properties make the system more tolerant to increases in recombination rate that might occur for example in developing dyes with better solar spectrum overlap, or in new electrolyte formulations that could increase device lifetime or reduce toxicity [40]. A further significant advance would be offered by a patterning technique that remove the high temperature ($\sim 500^\circ\text{C}$) sintering stage required for nanoparticle layer fabrication; a development that would significantly reduce the processing cost and enable straightforward manufacture on flexible substrates.

Table 1.1: Dynamics of charge-carrier reactions in liquid-electrolyte and solid-state DSSCs [34].

	Injection	Regeneration	Recapture	Recombination
Solid-state	fs	0.3 - 1 ns	$100 \mu\text{s}$	μs - ms
Liquid-electrolyte		2 - $10 \mu\text{s}$		ms - s

1.4.1 Solid State Dye-Sensitized Solar Cell

One area of concern regarding commercialization of the liquid electrolyte DSSC arises from the volatile and corrosive nature of the iodide/triiodide electrolyte. Effective sealing of the device is difficult, and conventional current collector grids cannot be used since even silver or gold grids are not long-term resistant to corrosion from the electrolyte. These worries have driven efforts to replace the liquid electrolyte with a solid state hole transporting material (HTM) [43, 38]. The functioning principles of this all-electronic solid-state dye-sensitized solar cell (sDSSC), shown in Figure 1.4, are similar to the liquid electrolyte cell. However, the oxidized dye is now regenerated by electron transfer from a neighboring hole conducting molecule.

Both wide band-gap p-type inorganics such as CuI [44] or CuSCN [45] and molecular organic semiconductors [43, 46] are candidates for the hole transporting medium. The key HTM requirements are: (1) suitable electronic levels to act as a donor species with oxidized dye state, (2) good charge transport properties, and (3) ease of infiltration into the pores of the structured layer to make intimate contact with the dye coating. One of the most successful HTMs identified is the organic molecular

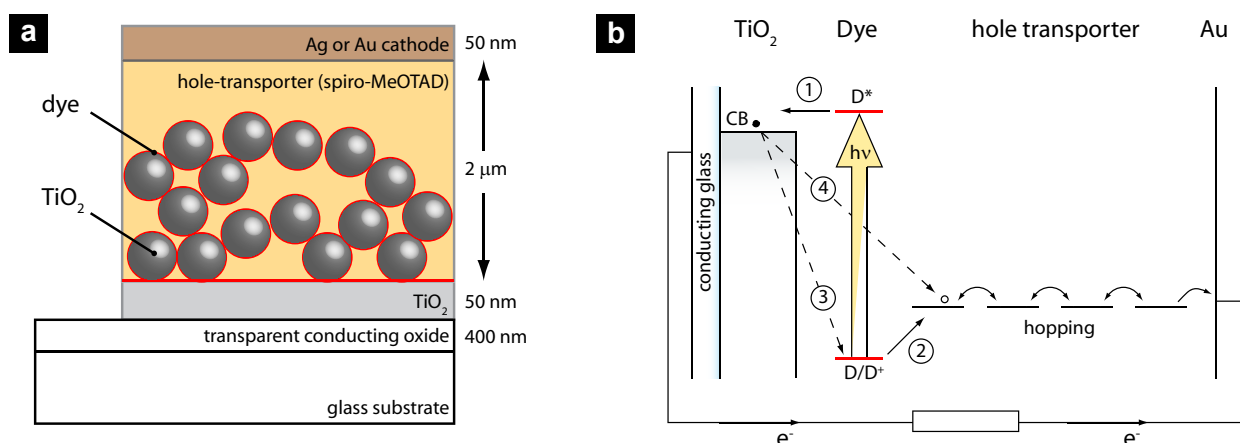


Figure 1.4: **Nanoparticulate solid-state device cross section and electronic energy level structure.** (a) sDSSC schematic device structure in cross section. The dye-sensitized mesoporous layer is infiltrated with spiro-MeOTAD by spin coating from a concentrated solution. An Ag or Au counter electrode completes the device. (b) Mechanism of photovoltaic operation on photoexcitation of the dye: (1) electron injection into TiO_2 conduction band, (2) dye regeneration by hole transfer to spiro-MeOTAD molecule. Principle loss mechanisms: (3) back transfer of electron into dye ground state, (4) electron recombination with holes in the hole-transporter [34].

semiconductor 2,2',7,7'-tetrakis(N,N-di-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD) based on a spiro centre (a tetrahedral carbon linking two aromatic moieties). The chemical structure of spiro-MeOTAD is shown in Figure 1.6. The material is amorphous with $T_g = 120^\circ\text{C}$; crystallization is not desirable in the HTM since this inhibits intimate electronic contact with the dye layer [38]. The first dye sensitized heterojunction devices using spiro-MeOTAD were reported by Bach *et al.* in 1998 [43, 47]. For the solid-state device, the optimized film thickness of the mesoporous TiO_2 is usually between 2 and $3\ \mu\text{m}$ [48, 49], i.e. less than the optical depth of the active layer. Figure 1.5 shows the trend in solid-state device efficiency and short-circuit current with increasing layer thickness for nanoparticulate devices sensitized with a ruthenium bi-pyridyl complex dye (K51).

Studies of charge-carrier mobility in spiro-MeOTAD infiltrated into TiO_2 films have shown that charge recombination and collection lifetimes became comparable under standard operating conditions near the open-circuit potential [50]. This implies that many charges recombine within the composite when operating at high potential. Hence, significant improvements in device performance should be possible either by enhancing the mobility in mesoporous TiO_2 or by slowing electron-hole recombination. Several recent studies have indicated that the most critical factor limiting the performance of thicker sDSSC layers is effective infiltration of the HTM into the mesoporous structure [51, 52, 53]. Both wetting of the TiO_2 pore surface, and complete filling of the pore voids is important; hole transport through a surface wetting layer of HTM is not only slower than through fully continuous 3D domains, but also confines the holes to a thin film adjacent to the TiO_2 phase and thus promotes recombination [51, 54]. The disordered pore distribution in nanoparticulate films is unlikely to be ideal for infiltration of a solid-state HTM. The smallest pores will act as restrictions for effective infiltration and in thick layers, insufficient material can be transported into the pore structure to fill all the voids. Control of TiO_2 mesoscale morphology could address both electron transport properties (by providing direct extraction pathways) and infiltration issues (with a well defined monodisperse pore-network). There remains therefore significant room for improvement in sDSSCs by introduction of an ordered, inorganic mesostructure, with direct charge transport routes out of the device layer.

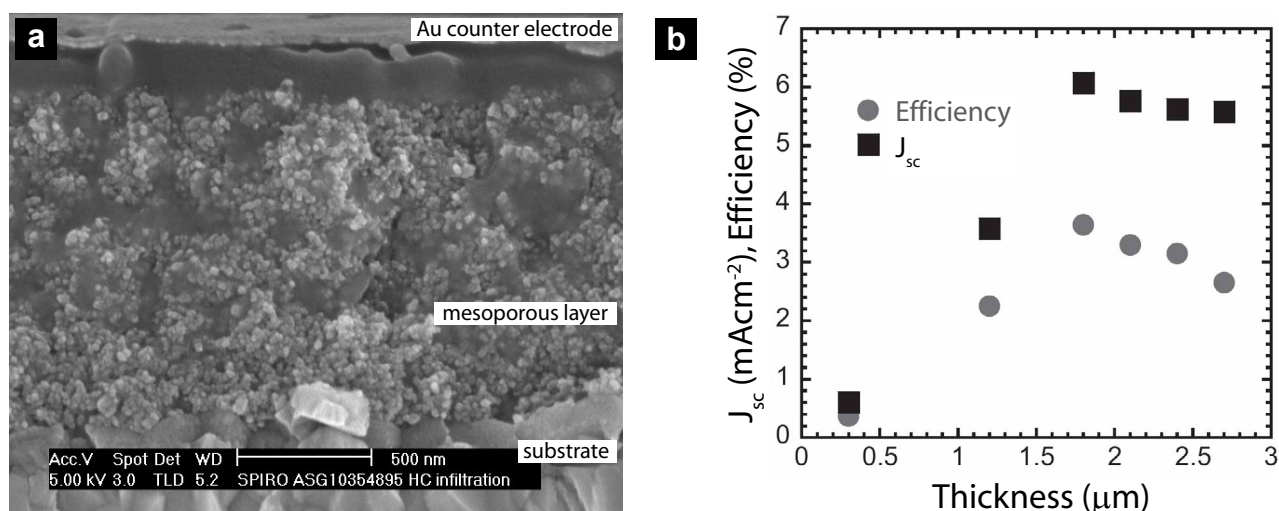


Figure 1.5: **Nanoparticulate TiO₂ solid-state device performance using spiro-MeOTAD hole transporter.** (a) SEM cross sectional image of a sDSSC made by infiltration of spiro-MeOTAD into a TiO₂ nanoparticulate layer. The grey areas are spiro-MeOTAD while the bright features are the sintered TiO₂ nanoparticles. An Au or Ag counter electrode completes the device. (b) Short-circuit current and power conversion efficiency under AM 1.5 solar illumination of 100 mW cm^{-2} are shown as a function of mesoporous layer thickness for sDSSCs sensitized with K51 ruthenium bi-pyridyl complex dye [34, 55].

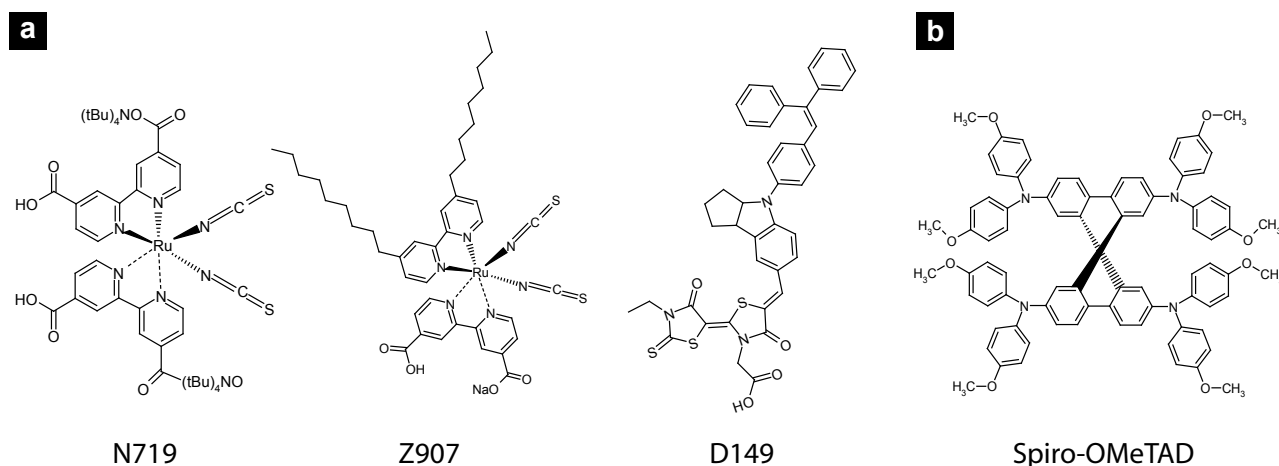


Figure 1.6: **Chemical structures of light-adsorbing dyes and solid-state hole transporting material used in this work.** (a) N719, Z907 and D149 dyes. (b) Hole transporter Spiro-MeOTAD

Dye Sensitizers for DSSCs

The light-adsorbing dye molecule plays the important role of light harvesting and charge generation in the DSSC. Therefore in order to create a highly efficient cell, the dye should have an ad-

sorption closely matching the solar spectrum, be able to attach to the semiconductor surface, inject electrons rapidly and with high quantum yield into the conduction band, and be stable for many years of exposure to natural light [40]. A high extinction coefficient is also important since this determines the necessary dye loading (and therefore surface area) of the active layer in order to adsorb a significant fraction of incident photons. The dyes used in this study are shown in Figure 1.6. N719, cis-bis(isothiocyanato)bis(2,20-bipyridil-4,40-dicarboxylate) ruthenium (II) bis-tetra-n-butylammonium, was developed by Nazeeruddin *et al.* in 1999 and is a widely used dye in liquid electrolyte cells [37]. Z907, Ru(4,40-dinonyl 2,20-bipyridine)(NCS)₂ developed by Wang *et al.* is an amphiphilic dye with similar absorption coefficient to N719 and improved thermal stability [56]. Z907 performs particularly well in solid-state DSSCs where the dye assembles into compact layers on the TiO₂ surface with outfacing hydrophobic chains acting as an effective blocking layer for charge recombination between hole conductor and TiO₂ [49, 57]. D149 is a metal-free organic dye with an absorption coefficient of 68,700 mol⁻¹ cm⁻¹, five times higher than N719 under the same conditions [58]. Efficiencies of up to 4.1 % have been recorded in solid-state DSSCs with mesoporous TiO₂ nanoparticle films 1.6 μm thick sensitized with D149 [59].

1.4.2 Structuring of Inorganic layers for DSSCs

A large part of this thesis concentrates on the growth of titania arrays grown in porous block copolymer templates and their application in liquid-electrolyte and solid-state DSSCs. A number of approaches to producing nanostructured inorganic layers for bulk heterojunction cells have been explored in the literature. Substrate-based nanostructured arrays of a wide range of materials including titania can be electrochemically grown into templates made for example from block copolymer films [60], anodized alumina [61], colloidal crystals [62] or track-etched polycarbonate membranes [63, 64]. A comprehensive review of titania nanostructures is contained in reference [27]. Various interesting and high aspect ratio mesoscale titania objects such as sheets, rods, tubes and multi-core fibrils [65] have been synthesized in modifications of the standard solvothermal and hydrothermal nanoparticle synthesis route. Sintered pastes containing nanowire/nanoparticle composites have been used to fabricate liquid-electrolyte cells with power conversion efficiencies up to 8.7 % [66]. An interesting in-situ patterning approach is to etch into a substrate rather than deposit additional material.

High aspect-ratio nanotubes [67] or nanorods [68] of titania can be obtained by oxidation of titanium metal foils by direct chemical oxidants or under anodization. Zhu *et al.* made liquid electrolyte DSSCs from 30 nm wide tubes six microns in length showing efficiencies of up to 3 % [69].

Sol gel processing using in-situ structure-directors such as block copolymers has proven a promising approach to pattern mesoporous titania layers [33]. A commercially available triblock copolymer poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol) known as P123 has been a particularly successful material in this regard. Wei *et al.* recently demonstrated 10 % efficient liquid electrolyte cells made from mesoporous TiO₂ that was ground-down and deposited as a paste in the same manner as traditional nanoparticle films [70]. Zúkalová *et al.* prepared P123-patterned TiO₂ mesoporous layers with well defined 5-8 nm pores and remarkably high surface areas (466-fold enhancement in a 1 μ m layer). Solid-state DSSCs made from these films showed up to 4 % power conversion efficiency, around a 50 % improvement on the equivalent nanoparticle film [71]. These results show that it is possible to improve bulk heterojunction cell performance by control of the interface morphology. With the exception of vertical nanowire arrays however, few existing approaches have produced both well ordered and *oriented* structures conceptually ideal for electronic performance and infiltration of solid-state components.

Further progress is also expected in the field from the exploration of materials other than TiO₂ in DSSC devices [38, 40]. Development of mesoporous ZnO nanoparticle films is now approaching the performance of titania in liquid-electrolyte cells [72]. Crystalline ZnO nanowire arrays can be grown hydrothermally from seeded substrate layers [73]. Liquid-electrolyte DSSCs with power conversion efficiencies of 1.5 % were made using wires up to 25 μ m long with diameters of 130 to 200 nm [74]. The device performance was limited by low surface areas for dye absorption (maximum surface area enhancement of ~ 200 in a 25 μ m thick array) despite showing up to two orders of magnitude faster charge transport out of the device layer [75]. A significant advantage of the templating approach to heterojunction structuring is the general access to a range of potentially interesting electrode materials permitting broad exploration in future research for device applications.

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Principles of Block Copolymer Self Assembly

The following chapter introduces the microphase separation of diblock copolymers and discusses various routes to exploit their self assembly for nanotechnology patterning applications. Particular emphasis is given to aspects relevant to the structuring of bulk heterojunction architectures for photovoltaic applications.

2.1 Microphase separation in block copolymers

Polymers are a class of macromolecules made up of covalently tethered repeat units (monomers). While homopolymers consist of a single type of monomer, the term copolymer refers to chains containing two or more chemically distinct monomers. Block copolymers [1] represent a particularly interesting subclass in which the different monomer units (say A and B) are arranged in linear blocks, the simplest example of which being an AB diblock copolymer (Figure 2.1).

Very few pairs of homopolymers are miscible in the melt; indeed the tendency of a blend of polymers to macrophase separate is much greater than that of an equivalent blend of the unconnected monomers. The thermodynamics of polymer melts is governed by the competing influence of energetic and entropic terms in the free energy of mixing. The energy of mixing (ΔU_{mix}) is proportional to the number of monomers present while the entropy contribution (ΔS_{mix}), which favours homogenous mixing, is proportional to the number of polymer chains. The entropy of mixing per monomer is therefore decreased by a factor of the degree of polymerization (N) for the polymer blend compared

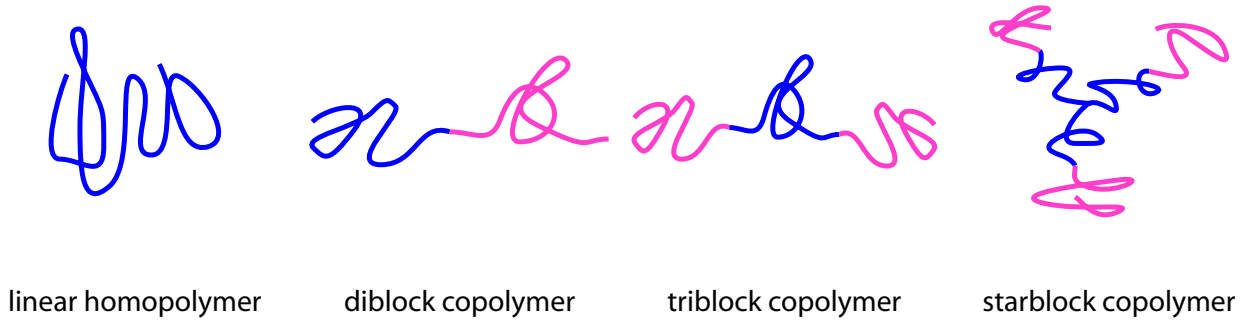


Figure 2.1: **Simple homopolymer and block copolymer architectures**

to a blend of the unconnected monomers. The Flory-Huggins free energy of mixing per monomer (ΔF_{mix}) for a blend of polymers A and B at temperature T , with degree of polymerization N and volume fractions f_A and f_B respectively, is given by:

$$\Delta F_{\text{mix}} = \Delta U_{\text{mix}} - T\Delta S_{\text{mix}} \quad (2.1)$$

$$\frac{\Delta F_{\text{mix}}}{k_B T} = \frac{f_A}{N} \ln f_A + \frac{f_B}{N} \ln f_B + \chi f_A f_B \quad (2.2)$$

where χ is the dimensionless Flory interaction parameter describing the strength of the energetic cost per monomer of contacts between A and B monomers:

$$\chi = \chi_{AB} = \frac{Z}{k_B T} (\epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})) \quad (2.3)$$

where Z is the number of nearest-neighbour contacts in a lattice model of the polymer, and ϵ_{AB} is the interaction energy per monomer between A and B monomersⁱ

Polymer mixing is therefore controlled by the product χN rather than χ as is the case for the monomer blend. A critical value of $\chi N = 2$ separates the situation in which mixtures of all compositions are stable ($\chi N < 2$) from the situation in which mixtures at some compositions will phase separate ($\chi N \geq 2$). Since N can be extremely large, only a very small positive value of χ (i.e. even very weak repulsive monomer interactions) is required for the free energy of mixing to favour phase

ⁱIn practice χ may have more complex dependence on the temperature, for example $\chi = A/T + B$. In general, since $\chi k_B T$ is an energy density, values should be stated along with the model lattice size

separation over a single phase mixture of polymer chains.

In block copolymer melts, repulsive monomer interactions are again a strong driving force for phase separation of the two blocks into A and B rich domains. However, since each block is covalently tethered to its reluctant partner the scale of the phase separation is limited to macromolecular ('mesoscopic') dimensions. The result is spontaneous formation of a rich spectrum of periodic, ordered structures on the 5-100 nm length scale, known as *microphase separation*. At sufficiently elevated temperatures, as with homopolymer blends, entropic terms overwhelm the energetic interaction terms in the free energy and result in a single disordered phase. The transition from a homogeneous melt of copolymer chains to the chemically heterogeneous ordered microdomains occurs on cooling at a critical value of χN and is known as the order-disorder transition (ODT). The morphology of the microphase and the temperature of the ODT depend on the composition of the copolymer, i.e. the volume fraction of one block f_A (with $f_B = 1 - f_A$). The microphase morphology adopted must balance minimizing unfavourable A-B interactions with the entropic penalty of stretching the two blocks away from each other as the chain adopts an extended configuration. For example, a symmetric diblock ($f_A = f_B$) will microphase separate into an alternating lamellar morphology with a flat interface, illustrated in Figure 2.2a. A simplified but illuminating treatment of this situation was given by Bates & Fredrickson [2]. At low temperatures (large χ), the lamellar microdomains are nearly pure in A or B components, separated by interfaces much narrower than the lamellar period λ ; so-called 'strong segregation'. Assuming that the chains are uniformly stretched, an approximate expression for the free energy per chain for the lamellar phase (F_{LAM}) is given by:

$$\frac{F_{\text{LAM}}}{k_B T} = \frac{3(\lambda/2)^2}{2Na^2} + \frac{\gamma A}{k_B T} \quad (2.4)$$

The first term in Equation 2.4 is the entropic stretching penalty for a Gaussian chain of N monomers, each of size a , extended to a distance equal to half the lamellar domain period (λ). The second term represents the repulsive energetic interactions confined to the (sharp) A-B interface, as a product of the contact area per chain (A) and the interfacial tension (γ). A simple treatment of the polymer-polymer interface for highly immiscible polymersⁱⁱ provides an estimate for the interfacial tension

ⁱⁱSee for example Reference [3]

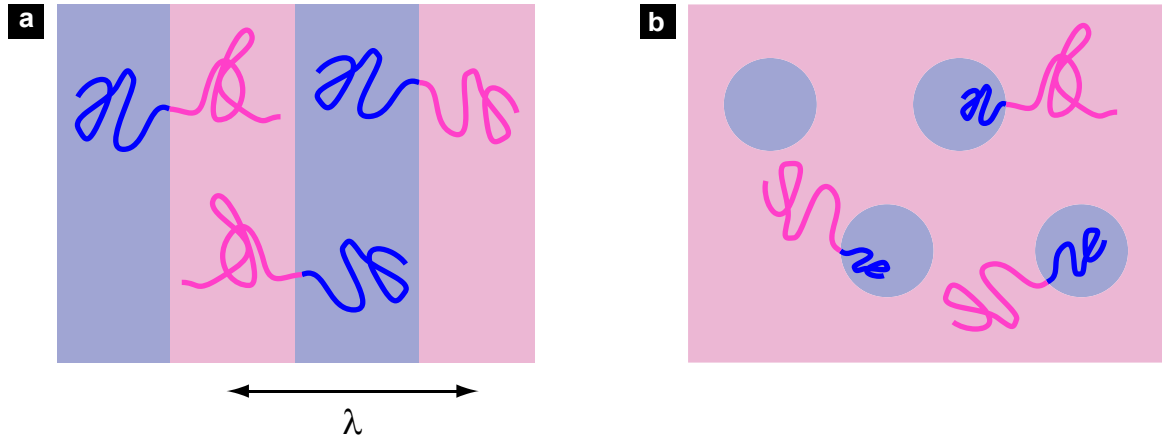


Figure 2.2: **Microphase separation in diblock copolymers.** The shaded regions represent domains rich in A or B monomers. **(a)** $f_A = f_B = 1/2$, lamellar phase separation with flat domain interfaces. **(b)** $f_A > 1/2$ Spontaneous curvature of domains towards the minority phase in cylindrical or spherical morphologies. The characteristic domain spacing λ is in the range 10 - 100 nm.

$\gamma = (k_B T / a^2) \sqrt{\chi}$. The volume filling condition (assuming incompressibility) constrains the contact area per chain, $A\lambda/2 = Na^3$. Now, minimizing Equation 2.4 with respect to λ we obtain an expression for the equilibrium lamellar period (λ_0):

$$\lambda_0/2 \sim a\chi^{1/6}N^{2/3} \quad (2.5)$$

The corresponding free energy of the lamellar phase can be used to estimate the order-disorder boundary. The free energy per chain in a homogeneous disordered phase (F_{DIS}) can be approximated simply by the A-B contact energy:

$$\frac{F_{\text{DIS}}}{k_B T} \approx \chi f_A f_B N = \chi N/4 \quad (2.6)$$

Setting $F_{\text{DIS}} = F_{\text{LAM}}(\lambda_0)$ predicts a critical value of $\chi N \sim 10.5$ as the location of the order-disorder transition. From this simple argument (in good agreement with more rigorous mean field calculations), we find that symmetric diblocks of high molecular weight or with strong incompatibility ($\chi N > 10.5$) are predicted to microphase separate into ordered lamellae with a period that scales as the two thirds power of the molecular weight. Smaller diblocks on the other hand, with more compatible blocks ($\chi N < 10.5$) are expected to form a single homogeneous phase.

More sophisticated mean-field and analytical theories have been developed to describe microphase separation[4, 5]. Three regimes are generally defined according to the extent of segregation (or ‘degree of incompatibility’) of the blocks: weak ($\chi N \sim 10$), intermediate ($\chi N \sim 10 - 100$) and strong ($\chi N \geq 100$). The above discussion strictly speaking applies to the strong segregation limit. These theories have been used to map ‘phase diagrams’ for copolymers, such as shown in Figure 2.3, that include the microphase behaviour below the ODT for non-symmetric copolymers. As the copolymer is made steadily asymmetric by increasing f_A , there comes a point when the free energy can reduce overall by curving the interface towards the shorter block. The morphology changes from lamellar (L) to hexagonally packed cylinders (C) of the B block surrounded by a matrix of the majority A block (Figure 2.2b). With further asymmetry a body-centred cubic spherical phase (S) forms, followed by a narrow region of close-packed spheres (CPS) before a disordered phase at the compositional extremes. A more complex, bicontinuous gyroid (G) phase is stable in a small region of phase space between the L and C phases, bringing the total to 5 ordered microphases with regions of thermodynamic stability (Figure 2.4)ⁱⁱⁱ.

The gyroid phase was first observed in block copolymers in 1986 when Thomas and co-workers

ⁱⁱⁱMathematical Sciences Research Institute (MSRI) <http://www.msri.org>

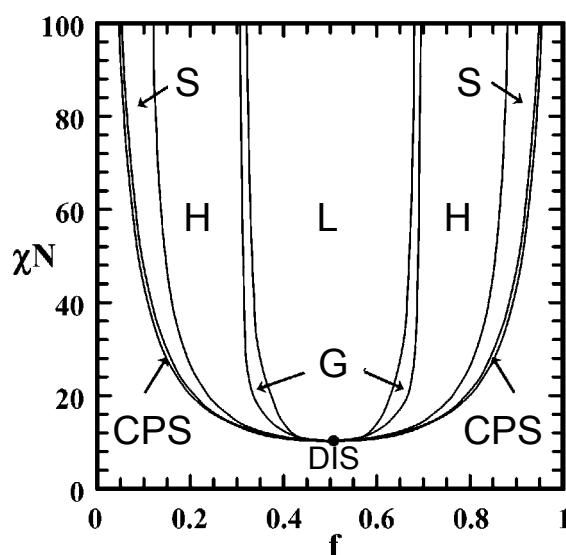


Figure 2.3: Diblock copolymer phase diagram parameterized by f and χN , calculated by Cochran *et al.*[6]

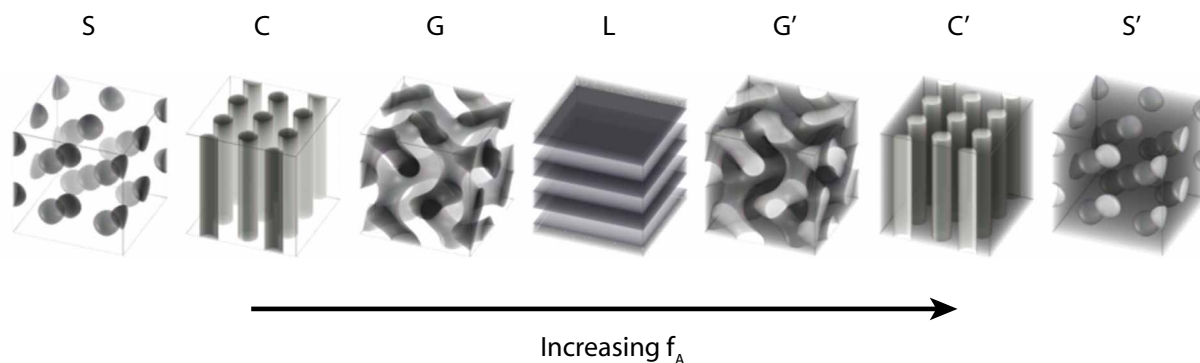


Figure 2.4: **Equilibrium phase morphologies of AB diblock copolymers as a function of component A volume fraction f_A :** (S) Spheres (body centred cubic lattice), (C) Cylinders (hexagonal lattice), (G) Gyroid, (L) Lamellar.

observed a new morphology, lying between L and C that was originally characterized as an ordered bicontinuous double-diamond (OBDD) [7]. In 1994 the true symmetry and form of the gyroid was identified by two groups independently [8, 9] and led to a re-evaluation of the OBDD to the G phase [10]. The gyroid phase, in which both A and B domains are continuous in three dimensions, is of particular technology and scientific interest, and will be discussed in detail in Chapter 7.

The general form of experimentally determined phase diagrams agrees remarkably well with those predicted by theory [11]. One notable discrepancy is the observation in real systems of a hexagonally perforated lamellar (HPL) phase between C and L. Recent experimental and theoretical studies have shown however that the HPL is a long-lived transient or metastable structure rather than a thermodynamically stable phase [12, 13, 6].

2.2 Block copolymers and nanotechnology

The self assembly of block copolymer microphases make these materials an extremely useful tool in a wide range of applications [14]. They are now used routinely as industrial additives to convey desirable bulk properties such as enhanced toughness to commodity plastics and polymer blend composites. Applications requiring surface modification such as medical implants or colloidal stabilization also benefit from carefully selected block copolymer components. Self assembly of copolymer micelles in the solution phase has been used to direct synthesis of nanoparticles [15] or as capsules

for drug delivery [16]. Many potential applications of block copolymers rely on the coupling of microphase morphologies to materials with carefully selected intrinsic properties, where control of mesoscale architecture conveys specifically enhanced functions. Firstly, there are applications such as photovoltaic devices that call for extremely large area internal junctions between semiconducting materials [17]. Heterogenous catalysis, molecular sieves and supports, energy storage media and fuel cell electrodes call for functional materials with well defined internal mesoscale pore structures [18]. Nanoscale dots and wires on substrates in specific orientations and in specific materials form the basis of a new generation of miniaturized electronics, data storage and sensors that may be directed using copolymer microphases [19, 20]. Self assembly of functional components represents a hugely attractive alternative to top-down lithographic patterning methods owing to the potential for large area, high throughput structuring on extremely small dimensions [21].

Many of the most promising copolymer applications exist naturally in a thin film or layer geometries on supporting substrates. There are fundamental differences between a bulk volume of a material and a thin film where the majority of the system is close to or at an interface of one sort or another [22]. An understanding of the behaviour of block copolymers in thin films and at interfaces is therefore crucial in order to realize their full potential. The following discussion will outline current approaches to copolymer technology in thin films, and describe ways to design and process these materials to control their self assembly.

2.2.1 Block copolymer thin films

The term ‘thin film’, when applied in the context of block copolymers, often refers to layer thicknesses comparable to the characteristic domain spacing of microphase separation - 10 to 100 nm. In photovoltaic applications the thickness of the active layer is determined by the need for near complete optical absorption of incident illumination [23]. For many conjugated polymers this means several hundred nanometres, while in many inorganic dye-sensitized systems optical paths of several microns are needed for efficient light harvesting [24]. For these applications therefore, film thicknesses of the order 10 to 100 times the domain spacing are most relevant. On the other hand, lithographic patterning of magnetic dots, or surface oriented nanowires calls for ‘ultra thin’ films which are comparable or thinner than the domain spacing. In both systems, interaction with the two external interfaces

(substrate and free surface) can dominate the phase behaviour of the copolymer.

In the region of an external interface, such as a free surface or supporting substrate, differences in the surface free energies or affinities of each block towards the substrate ($\Delta\gamma$) have a strong influence on copolymer morphology. When the asymmetry is sufficiently large, the free energy of the system can reduce by preferential segregation of one or other component to the interface. Russell and coworkers first studied these effects experimentally in lamellae-forming poly(styrene)-*b*-(methylmethacrylate) (PS-*b*-PMMA) copolymers using neutron reflectivity [25] and dynamic secondary ion mass spectroscopy (SIMS) [26]. After phase separation the lamellae were found to orient parallel to both gold and silicon substrates (a so-called $L_{\parallel}$ morphology). On silicon substrates, the total film thickness is $(n + 1/2)\lambda$ where λ is the lamellar period and n is the number of periods, while on gold the thickness is $n\lambda$. The differences are explained by the symmetry or asymmetry of affinities for each block at the free surface and substrate surface, illustrated in Figure 2.5. If the initial film is not commensurate with these quantized thicknesses then on thermal annealing, islands and holes will form on the free surface to avoid the elastic penalty of stretching or compressing chains required to alter the domain spacing.

Parallel domain alignment at an interface will propagate into the bulk of a copolymer film to a degree dependent on the magnitude of the substrate affinity asymmetry or ‘surface field’ $\Delta\gamma$. TEM studies on a PS-*b*-PMMA lamellar system found a critical thickness (linearly dependent on $\Delta\gamma$) below

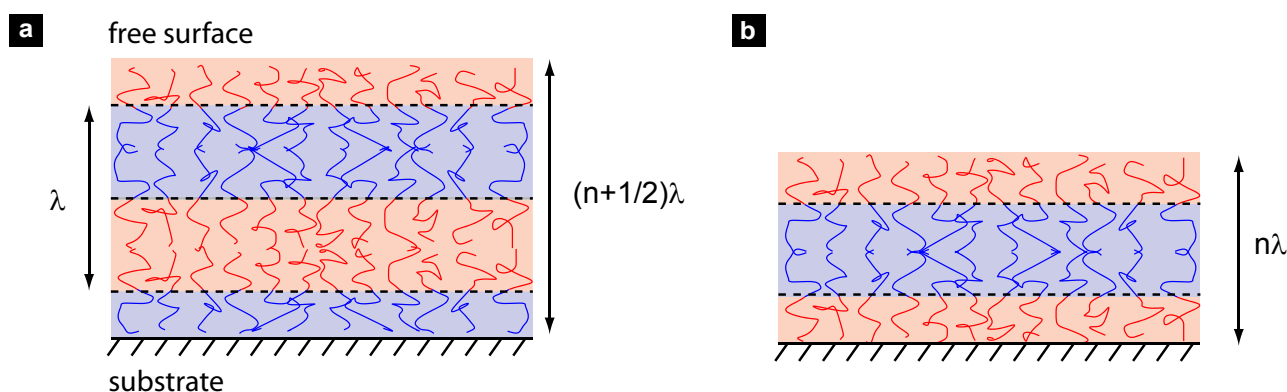


Figure 2.5: **Quantization of film thickness in lamellar forming copolymer thin films.** (a) *Asymmetric* affinity of one block to the substrate and another to the free surface results in film thicknesses quantized in units of $(n + 1/2)\lambda$. (b) *Symmetric* affinity of one block to both the substrate and free surface results in quantization in units of $n\lambda$.

which surface fields are enough to cause the entire film to adopt a $L_{||}$ alignment.[27] For example, the critical thickness was ~ 10 lamellar periods when $\Delta\gamma \sim 50 \text{ nJ cm}^{-2}$, corresponding to a film some 400 nm thick. In films thicker than this critical thickness the coherence of the parallel alignment was lost some ~ 3 lamellar periods from the interface. Substrate interactions can be tuned in an extremely well controlled manner to favour either copolymer block by surface grafting of random copolymer brushes with varying fractions of each component [28]. A ‘neutral substrate’, with $\Delta\gamma \sim 0$ has no energetic preference for either copolymer block. Approximately neutral surfaces can also be made using self assembled monolayers (SAMS) such as alkane thiol layers on gold [29]. On neutral surfaces, the lamellar microdomains are found to orient normal the surface [28, 30], which removes commensurability constraints between the film thickness and λ so that consequently, the surface of the film remains smooth.

The behaviour of cylinder-forming copolymers in the vicinity of a planar interface is perhaps less intuitive than lamellae. In this system, the bulk symmetry is broken regardless of orientation so that the microdomains are forced to adjust. Here the balance of film thickness and surface fields leads to various alignments of the phase, or indeed to a complete change from the bulk morphology known as ‘surface reconstruction’. Knoll *et al.* studied this effect in great detail the using poly(styrene)-*b*-(butadiene)-*b*-(styrene) triblock copolymer thin films in conjunction with molecular dynamic simulations [31]. In addition to parallel alignment effects similar to a lamellar copolymer, they found wetting layers, perforated lamellae, and lamellar reconstructions with increasing strength of the surface field. The averaged mean curvature of the domain interfaces decreases in order to adopt to the planar symmetry of the surface. In light of the modulating confinement effects of film thickness, cylinder forming copolymers can be induced form spontaneous standing morphologies (C_{perp}) spanning the entire film with judicious choice of film thickness and weak surface fields [32, 33]. These structures are particularly intriguing for data storage since each cylinder is potentially addressable, or for lithographic and nanostructuring applications where open access to the substrate is desirable [34]. While simulations and theory predict that $C_{\perp}$ could be formed in much thicker films [31], in practice the greatest aspect ratio of a film-spanning $C_{\perp}$ microphase in a pure copolymer on a neutral planar surface is around two. This can be increased by incorporating a small amount of additional minority component homopolymer which segregates in the blend to the centre of the cylinders. Spanning

vertical cylinders with aspect ratios of up to ~ 10 can be made in this way [35].

2.2.2 Alignment of the microphase

Tailoring block copolymer structures to a chosen application requires general control over the orientation of the microphase. For example, films with fully spanning perpendicular microphases (cylinders or lamellae) have particular technological advantages for any application requiring access to the substrate; either for replication of high aspect-ratio standing nanostructures, or for lithographic masks or porous membranes. On the other hand, some applications such as electronic arrays and addressable memory, call for long range order and alignment in the plane of the film. A great deal of research effort has been dedicated to developing generalized approaches to microphase alignment, and a number of comprehensive reviews exist in the literature [22, 36].

The alignment and optimization of long-range *in-plane* order comprises a fascinating field of research in itself. However, such features are not key requirements in photovoltaic systems targeted in this work. In brief, topographically (graphioepitaxy) [37, 38] and chemically (heteroepitaxy) [39, 40] pre-patterned substrates exploit surface fields and in-plane confinement to guide and order standing cylinders, spheres, or lying nanowire structures. Similar confinement-alignment effects can be achieved by patterning the copolymer film itself into using for example nanoimprint lithography (NIL) [33]. Long range order and alignment can be encouraged using zone casting [41] or temperature gradients [42] which direct the microdomains via a sweeping propagation of an ordering front.

Russell and coworkers reported an interesting method of inducing standing alignment in strongly immiscible cylinder-forming copolymer films by exposure to a controlled solvent atmosphere ('solvent annealing') followed by solvent extraction [43, 44]. In this case an ordering front propagated down through the layer on removal of the solvent, rather than a horizontal sweeping gradient induced during zone-casting. After solvent annealing the vertical alignment is coupled to extremely high degrees of in-plane hexagonal ordering.

Shear flow fields are a remarkably effective means to orient copolymer microdomains. Large amplitude oscillatory shear (LAOS), and extrusion are common methods used to align bulk copolymer melts and solutions [45]. Thomas and coworkers developed the use of roll casting to expose relatively thick films to a shear flow alignment field [46, 47]. Recently, a step-like deformation of pre-cast films

confined under a rubber stamp been shown to align single layer films of molten cylinders [48]. The general application of shear flow fields to thin films, however, is not straightforward, and in particular may not be suited to producing vertical rather than in-plane alignment for film thicknesses several times the domain spacing.

Extremely precise local control of domain alignment can be achieved in a wide range of sample geometries using *electric fields*. While these provide in many cases a weaker alignment field than shear flow, they make up for this in the ability to apply spatially specific fields either in-plane or out-of-plane by control of electrode geometry.

Electric field alignment

Directing the orientation of an anisotropic dielectric object in an electric field relies on the coupling of the electric field to induced polarization charges, whose distribution depend on the orientation of the object. When an external electric field is applied to a dielectric material by means of a constant potential difference across external electrodes, the electrostatic contribution to the free energy of the system (F) is given by:

$$F = F_0 - \frac{1}{2} \int (\epsilon(\mathbf{r}) \mathbf{E}(\mathbf{r})^2) \cdot d^3\mathbf{r} \quad (2.7)$$

Where F_0 is the free energy in the absence of the field, $\epsilon(\mathbf{r})$ is the local dielectric constant and $\mathbf{E}(\mathbf{r})$ the electric field [49]. We assume a linear dielectric response.

Thurn-Albrecht *et al.* gave an informative evaluation of Equation 2.7 for the simplified picture of an infinitely long, isolated cylinder enclosed in an infinite matrix, with dielectric constants ϵ_1 and ϵ_2 respectively [50]. Solving Maxwell's equation ($\nabla \cdot [\epsilon(\mathbf{r})\mathbf{E}(\mathbf{r})] = \rho_{\text{free}}$) to find the field distribution and substituting into Equation 2.7, the difference in free energy per unit volume between states with the long axis parallel ($F_{\parallel}$) or perpendicular ($F_{\perp}$) to the field vector is:

$$\Delta F = F_{\parallel} - F_{\perp} = -\frac{1}{2} \epsilon_0^2 \frac{(\epsilon_1 - \epsilon_2)^2}{\epsilon_1 + \epsilon_2} \quad (2.8)$$

Since ΔF is always negative, the orientation of the cylinder axis parallel to the applied field is the lower free energy state, whether $\epsilon_1 > \epsilon_2$ or $\epsilon_1 < \epsilon_2$. With this orientation, all spatial gradi-

ents of dielectric constant (sharp interfaces in this picture) are perpendicular to the field vector; that is, *dielectric interfaces tend to align parallel to the electric field*. The material heterogeneity of a microphase-separated copolymer has an associated spatial variation in the dielectric constant. As a consequence, anisotropic copolymer phases such as L and C will favour an orientation with their long axes parallel to the electric field vector. Admundson *et al.* calculated the free energy contribution for a more realistic description of arrays of block copolymer microdomains by expanding the dielectric constant in powers of the local composition amplitude (the volume fraction of one component minus its mean value) [51, 52]. The essential physics of electric field alignment for domains with sharp interfaces is however captured by Equation 2.8. Most importantly, the driving force is proportional to both the square of the dielectric contrast ($\Delta\epsilon$), and the square of the electric field strength.

There are numerous theoretical [53, 51, 52] and experimental [54, 55, 56, 57] studies of electric field alignment of block copolymers using both in-plane and vertical fields. Wang *et al.* found that ion complexation to one block can cause a significant increase in dielectric contrast and a corresponding increase in the electric field alignment response [58, 59]. Tsori *et al.* have also proposed that mobile ions contained in the copolymer contribute a further free energy reduction for domain alignment [60]. Electric fields can also induce complete phase morphology changes such as that the spheres-to-cylinder transition observed by Xu *et al.* [61].

In a thin film geometry, a vertical electric field such as that applied in a parallel plate capacitor geometry drives a normal alignment of $L_{\perp}$ or $C_{\perp}$ microdomains. There is therefore a competition between the electric field and the surface fields that favour parallel domain alignment $L_{\parallel}$ or $C_{\parallel}$. The free energy of Equation 2.7 is modified in a simple model to include distinct contributions from the surface interactions and the electric field response:

$$F = F_0 + F_{el} + F_{surf} = F_0 - \frac{1}{2} \int_{V_{el}} (\mathbf{r}) \cdot \mathbf{E}(\mathbf{r})^2 \cdot dV + \int_A \sigma(\parallel, \perp) \cdot dA \quad (2.9)$$

Where F_{surf} contains a surface integral of $\sigma(\parallel, \perp)$ from interfacial interactions over the substrate area A . V_{el} is the sample volume (extending out from the surface) over which the surface and electric field alignment forces are in competition, driving alignment perpendicular or parallel to the electric field, respectively. In the notation of Equation 2.8 there is a critical field at which $\Delta F_{el} = -\Delta F_{surf}$ and the two contributions are balanced. Thurn-Albrecht *et al.* found that V_{el} was independent of the film

thickness, indicating a finite boundary layer at the substrate at which F_{surf} is able to dominate F_{el} [50]. Slightly below the threshold field, the $C_{\parallel}$ boundary layer coexists with $C_{\perp}$ in the rest of the film. Only above the threshold does the electric field dominate everywhere and produce ‘complete’ alignment, i.e. $C_{\perp}$ microdomains that pass continuously from surface to substrate. Detailed theoretical studies have described the orientation of lamellar microdomains in symmetric BCP thin films taking account of the competition between electric (E) and surface fields [53, 62]. In the strong segregation regime, there are two critical fields E_1 and E_2 when there are strong, preferential interfacial interactions. For $E < E_1$, surface fields dominate and an $L_{\parallel}$ morphology is favoured while for $E > E_2$, the electric field dominates and a $L_{\perp}$ is favoured. For intermediate fields, $E_1 < E < E_2$, a mixed orientation of microdomains is predicted with $L_{\parallel}$ near the films interfaces and $L_{\perp}$ in the center of the film.

The strength of the electric field, dielectric contrast, interfacial energies and film thickness therefore all play a role in achieving the desired alignment. Complete vertical alignment of domains can be achieved in two ways: (I) strengthening the electric field driving force by increasing the field strength and the dielectric contrast, and/or (II) reducing the surface fields by making the substrate ‘neutral’ to both blocks. Xu *et al.* found that in a lamellae-forming PS-*b*-PMMA copolymer, complete alignment could only be achieved once surface interactions were neutralized with a random copolymer surface-grafted brush [56].

2.2.3 Patterning of functional material systems

Despite over three decades of development, there remain remarkably few examples of functioning device applications that exploit the ordered self assembly of block copolymers. The reason for this is to a large extent the difficulty in transferring the structural order from model block copolymers into systems with interesting intrinsic material properties. Broadly speaking there are three approaches to this challenge: (I) synthesize the copolymer directly from interesting functional polymers, (II) use a phase separated block copolymer as a sacrificial mesoporous template for functional material growth, or (III) blend the block copolymer with precursors for functional material synthesis and use microphase separation as an in-situ structure director.

As mentioned in Chapter 1, route (I) is perhaps the most intuitive and direct approach to achieving a well-defined mesoscale bulk heterojunction. However, these copolymers are generally extremely

difficult to synthesize, limiting the available materials. Despite this, recent progress has been reported in coupling donor (D) and acceptor (A) semiconducting polymers in block copolymers that exhibit successful microphase separation [63, 64, 65, 66, 67, 68, 69]. Tu *et al.* coupled a poly(3-hexylthiophene) (one of the most promising and widely explored macromolecular semiconductors) acceptor block with cyano-substituted poly(phenylenevinylene) (CNPPV) donor prepolymers to produce a D-A-D triblock copolymer. However, further tuning of the HOMO and LUMO levels of the donor and acceptor blocks was still needed in order to favour charge transfer and separation at the internal interface [65]. Sommer *et al.* achieved successful charge separation at a copolymer D-A interface formed by a polyacrylate chain with triarylamine sidegroups coupled to a second with perylene diimide side groups [67, 68]. Absorption and electron transport was achieved via the perylene diimide side groups while the (amorphous) triarylamine block made up the hole conducting phase. The microphase morphology after thermal annealing was made up of ~ 13 nm diameter worm-like minority domains of $\pi - \pi$ stacked perylene sidegroups in a hole transporting matrix. Single active-layer solar cell devices showed up to an order of magnitude improvement over equivalent macrophase separated blends, attributable to the increased D-A interface [67]. While these results demonstrate the great potential of these materials, the power conversion efficiency remains low (0.32 %), at least in part because of high series resistance (and therefore low photocurrents) stemming from a lack of vertical microdomain alignment to provide effective charge extraction pathways.

A templating approach to block copolymer structural transfer (route II) is certainly more within the grasp of today's copolymers, and significantly widens the potential choice of functional materials. One block is made selectively removable by etching after microphase separation, leaving a well defined internal pore structure in the remaining polymer which forms the template for deposition of a chosen material [18, 70]. There are at least four copolymer systems reported in the literature amenable to selective etching of a single component to produce mesoporous materials: hydrolysis of polyesters [71], HF cleavage of alkylsiloxanes [72], ozonolysis of polydienes [73, 74] and UV-etching of poly(methylmethacrylate) [32]. The selective etching functionality may also take the form of a single cleavable linkage in the copolymer, such that the one phase is freed from the other which can be subsequently removed by selective solvents [75].

Filling the mesoporous template may be achieved in a number of ways. Thurn-Albrecht *et al.*

were the first to demonstrate electrochemical deposition into a porous block copolymer using a PS matrix left by UV removal of C_{60} PMMA domains from a PS-*b*-PMMA film on a Au substrate [76]. An electric field was used to induce the standing alignment, and the template-supported Co nanowire array thus produced had a density in excess of $1.9 \times 10^{11} \text{ cm}^{-2}$. Other viable filling techniques include solution phase reaction [74, 77, 78], or atomic layer deposition [79].

There are two closely related variants of the sacrificial templating scheme, which are outlined schematically in Figure 2.6. In a ‘partially sacrificial’ templating route (Figure 2.6b), the copolymer itself contains a functional material component. Removal of the sacrificial component leaves a porous functional template which is filled with a second functional material of choice to immediately produce the desired composite. In ‘doubly sacrificial’ templating (Figure 2.6a), a freestanding functional material replicate of the polymer template is produced by etching away the template polymer matrix. The second functional material component (if required) is back-filled around the nanostructures to form the desired composite; no trace of the original copolymer remains in the finished composite.

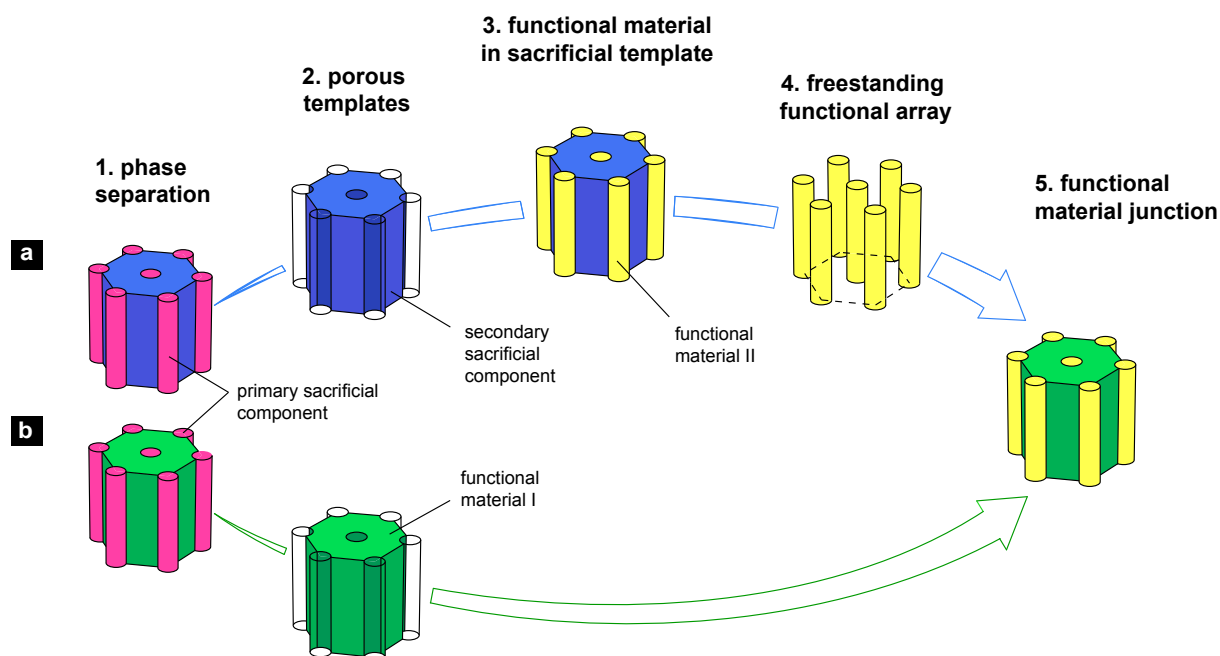


Figure 2.6: **Partial and doubly sacrificial templating strategies using block copolymer self assembly**

The primary advantage of the partially sacrificial template is that fewer processing stages are required to produce the final composite. However, there are now severe restrictions placed on the processing conditions in order to avoid damaging the functional mesoporous polymeric template. First and foremost this means a mild selective degradation of the primary sacrificial block; hydrolysis of polyesters such as found in poly(lactide) is one example of a suitably non-aggressive selective etching technique. UV exposure or ozonolysis would result in severe damage to most semiconducting polymers. Secondly, deposition and processing of the backfilled material may not approach the high temperatures often required to produce inorganic materials with a high degree of crystallinity. There are however many examples of low temperature ($< 100\text{ }^{\circ}\text{C}$) electrochemical routes to inorganic semiconductors [80, 81, 82].

A doubly sacrificial templating strategy avoids many of the problems associated with processing damage to soft functional materials since the inorganic material may be deposited first followed by a high temperature annealing stage. The disadvantage of this technique are twofold: firstly an increase in the number of required fabrication steps and secondly the need to work with a freestanding nanostructured functional material array. These structures are potentially mechanically unstable and therefore restrict subsequent processing parameters in deposition of a second functional material.

The third approach to structural transfer (route III), in which the copolymer acts as a structure director in a co-operative organization of organic and inorganic components was mentioned in connection to TiO_2 DSSC patterning in Chapter 1. More generally, Weisner *et al.* demonstrated this technique using poly(isoprene)-*b*-(ethyleneoxide) (PI-*b*-PEO) copolymers mixed with nanoparticulates produced by hydrolysis of aluminium and silicon alkoxide precursors [83]. The nanoparticulate hydrolysis products of the precursors preferentially swell the PEO phase. The organic components can be burnt out to leave, in this case, aluminosilicate ceramics with a range of mesostructures similar to those on a typical copolymer phase diagram, depending on the ratio of inorganic to organic components. Stucky *et al.* have used related methods to produce mesoporous samples (up to 14 nm pore size) of a range of metal oxides from inorganic salt precursors and amphiphilic poly(alkylene oxide) copolymers directors [84].

The primary focus of this work is the use of a doubly sacrificial templating approach to patterning of bulk heterojunction photovoltaics using poly(4-fluorostyrene)-*b*-poly(D,L-lactide) (PFS-*b*-PLA)

copolymer films. Encouraging preliminary results are also presented using a partially sacrificial template of poly(styryltriarylamine)-*b*-poly(D,L-lactide) (PSTA-*b*-PLA) in which the majority polymer component exhibits hole transport characteristics.

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Techniques and Instrumentation

3.1 Structural Characterization: Imaging and Scattering Methods

3.1.1 Electron Microscopy

Imaging features smaller than the diffraction limited resolution of optical microscopes (some hundreds of nanometres) require an illumination source with a much smaller wavelength. Electron microscopes use a stream of electrons accelerated through a high voltage (1 kV to ~ 400 kV) which are gathered and focused using a column of electromagnetic lenses to illuminate the sample. It is the interaction of these electrons with the sample that makes sub-optical imaging possible.

The incident electrons interact with a finite volume of the sample in a number of different ways. Transmission electron microscopy (TEM) makes use of electrons exciting the transmission side of a thin foil specimen which may have (I) passed through the sample without interacting, (II) scattered (i.e. deflected from their incident path) elastically (without loss of energy) or inelastically from atoms in the interaction volume (see Figure 3.1). On the other hand, the electron-sample interaction also leads to electrons emitted from the same side of the sample as the incident beam: they may (III) undergo backscattering, (IV) ionize a sample atom causing emission of low energy (<5 keV) secondary electrons and (V) Auger electrons. Both X-ray and optical photons (cathodoluminescence) may also be emitted as a result of energy transfer to the sample atoms from the incident electrons.

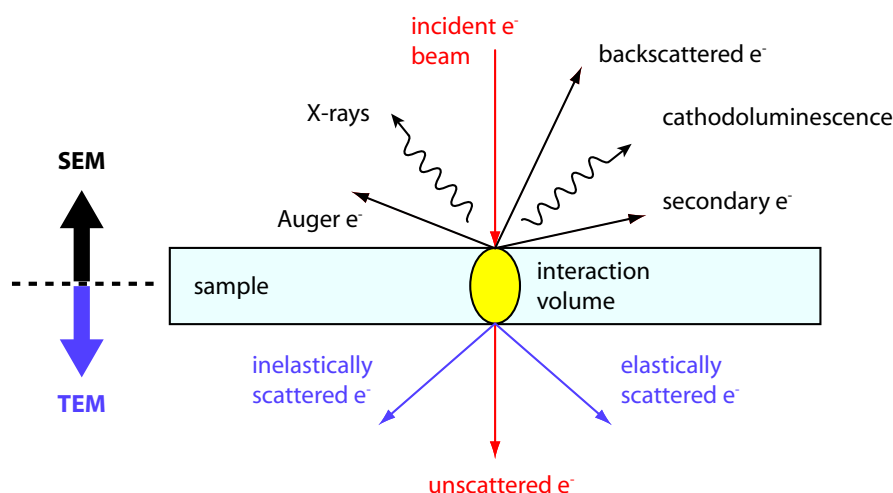


Figure 3.1: **Schematic representation of possible interactions of an incident electron beam with a specimen in electron microscopy.** Electrons on the transmission side of a thin foil sample are used in TEM while electrons emitted on the incident side are collected for SEM.

Scanning Electron Microscopy

In scanning electron microscopy (SEM) the electron beam is focused to a very small spot size and scanned over the surface of a sample. Various detectors exist to collect either electron or photon emissions from the interaction volume which may be used to gather information on the local structure. Perhaps the most common SEM technique uses a secondary electron detector to count secondary electron emission during irradiation. Emission of secondary electrons from the sample is highly dependent on topography. Since they are of relatively low energy, only secondary electrons that are very near the surface (<10 nm) can exit the sample and be detected. The number of secondary electrons counted during the dwell time of the incident beam is translated into a pixel intensity built up over the scanned area. Therefore while the images produced by secondary electron SEM images are sensitive to topography of the sample, they do not produce quantitative surface height information.

The resolution is limited by the size of the interaction volume, the spot size of the focused beam, or the extent to which the material interacts with the electron beam. The interaction volume is extremely dependent on the sample material, and charging effects caused by secondary electrons that are not able to dissipate in a poorly conducting materials. Polymers therefore are sometimes coated with a thin continuous metal coating (between 2 and 5 nm depending on sample topography) to reduce surface charging effects and improve resolution. In this study however it was found that even in thick polymer

films (up to 5 μm) sufficient secondary electron resolution of topographic features on the 10 nm scale could be achieved without additional coating. The primary microscope used was a LEO ULTRA 55 SEM with field emission source operated at 5 kV electron acceleration voltage. Additional images were also acquired using a FEI Philips XL30 with field emission source at an accelerating voltage of 10 kV.

Transmission Electron Microscopy

In transmission imaging mode the scattered electrons pass through an electromagnetic objective lens and aperture before exposure of a photographic film or CCD camera. The objective aperture is necessary to generate phase contrast in the image. In bright-field mode the weakly scattered and transmitted electrons are selected by positioning the aperture on the optic axis such that dark areas in the image correspond to strongly scattering regions of the sample. A FEI Philips Tecnai 20 TEM, with an accelerating voltage of 200 keV (LaB₆ source filament) and a CCD camera was used for imaging of polymer phase morphologies in this study.

Specimens of low electron density hydrocarbon materials such as polymers should be of the order of 100 nm thick to allow sufficient transmission. This is achieved in practice with a precision cutting apparatus known as a ultramicrotome. The microtome is commonly used in preparation of ultra-thin (~ 30 nm and upwards) uniform sections from the exposed face of an epoxy-embedded specimen. The sample is first fully embedded in an epoxy matrix, mounted onto a mechanical arm and roughly cut to size using a fixed glass knife-edge. A small (~ 1 mm²) face is left exposed and is cut using a diamond blade with a reservoir of water behind in order to collect the sections. The floating sections are picked up from the water surface using Cu TEM mounting grids.



Contrast in polymer samples was achieved using ruthenium tetroxide (RuO₄) - a selective staining agent for aromatic and olefinic double bonds [1, 2]. An RuO₄ vapour is generated by the reaction of hydrated ruthenium trichloride (RuCl₃·3H₂O) with a 15-20 % aqueous solution of sodium hypochlo-

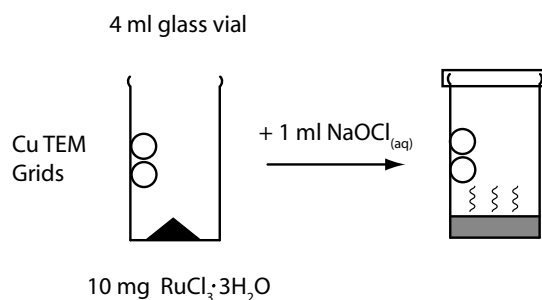


Figure 3.2: **Selective polymer staining with RuO₄ vapour for TEM imaging.** Sealed 4 mL glass vials used to expose polymer samples to RuO₄ vapours generated from the reaction in Equation 3.1. 1 ml of 15-20 % NaOCl_(aq) was added to 10 mg RuCl₃·3H₂O powder immediately before sealing the vial. All staining was conducted inside a fumehood and handled using protective gloves.

rite (Equation 3.1) in a sealed glass vial containing the microtome sections (Figure 3.2).

TEM Tomography

Three dimensional images known as ‘tomograms’ can be reconstructed from a series of TEM images taken over a range of specimen tilt angles. This technique allows detailed examination of internal structure for thicker (but still transmissive) polymer samples. Copolymer films were embedded and sectioned into 300 nm thick and stained in the standard manner and mounted on standard Cu TEM grids. Images were recorded every 2° from +65° to -65° using a Fischione ultrahigh-tilt tomography holder model 2020 and a FEI Tecnai F20 field emission gun transmission electron microscope operated at 200 kV in scanning transmission electron microscope (STEM) mode. Image acquisition was undertaken using the FEI software package Xplore3D and aligned sequentially using Inspect 3D. Reconstructions were performed using an iterative routine that constrains the reconstructed volume to match the original images when re-projected back along the original tilt directions. Selected-volume projections were constructed in Inspect 3D, and surface rendering (after a segmentation process) was undertaken using Amira software. Image acquisition and 3D rendering was done by Dr Ana Hungria in the Electron Microscopy Group, Department of Materials Science and Metallurgy, Cambridge.

High Resolution Transmission Electron Microscopy

High resolution transmission electron microscopy (HRTEM) is capable of atomic resolution imaging of the crystal lattice in inorganic samples. This technique is used to study directly the relationship between crystal domain structure and the mesoscale (10 nm) confinement imposed by the templating techniques described in this work. HRTEM was performed by Dr Caterina Ducati in the Department of Materials Science and Metallurgy, Cambridge using a Jeol 4000 EX microscope, with 400 kV acceleration voltage and a point resolution of 0.17 nm.

The electron diffraction pattern arising from constructive interference of scattered electrons in the sample is formed in the back focal plane of the TEM. Comparison of the electron diffraction pattern to a library of material diffraction patterns can be used to identify the material and crystalline polymorph.

3.1.2 Small Angle X-ray Scattering

Scattering experiments were performed at the G1 line at Cornell High Energy Synchrotron Source (CHESS) by Marleen Kamperman. All primary analysis and simulation was done by Marleen Kamperman, Dr Detlef Smilgies and Dr Gilman Toombes.

Small angle X-ray scattering (SAXS) is an extremely widespread and useful tool for the study of mesoscale material structures such as block copolymer phase morphologies. SAXS provides information about phase separated domains averaged throughout the bulk of a sample. The incident X-rays are scattered elastically from electrons in the polymer, therefore a diffraction pattern with well defined intensity maxima will arise if there is sufficient electron contrast between the polymer components.

A beam of monochromatic X-ray radiation (wavelength λ) is incident on a phase-separated polymer sample and the scattered intensity recorded as a function of the scattering angle θ (Figure 3.3). The same principles that give rise to Bragg diffraction peaks in the diffraction pattern of a crystalline solid apply to the scattered intensity from a copolymer morphology; however the peaks occur at smaller angles reflecting the larger scale periodicity. The peaks are typically broadened in comparison to crystalline solid patterns owing to the diminished degree of long range order.

The copolymer microphase morphology can be effectively represented by a lattice of points with matching symmetry. The 'reciprocal lattice' is constructed from the real space lattice such that each

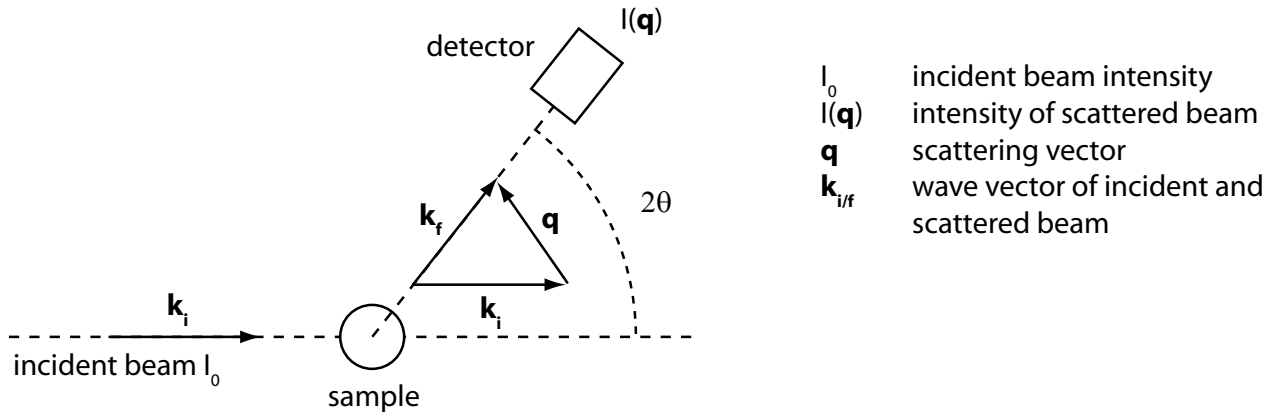


Figure 3.3: SAXS Experimental Schematic

reciprocal lattice point represents a set of lattice planes as a normal vector to this plane with length $G = 2\pi/d$. The scattering angle of the detector (θ) defines the scattering vector or ‘momentum transfer’ probed according to:

$$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i = \frac{4\pi \sin \theta}{\lambda} \quad (3.2)$$

Constructive interference of scattered beams from a set of real space lattice planes occurs when the momentum transfer matches a reciprocal lattice vector. That is, the reciprocal lattice points are the values of momentum transfer where the Bragg diffraction condition is satisfied for a particular set of lattice planes:

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.3)$$

where $n = 1, 2, 3...$ is the order of peak and d_{hkl} is the spacing of lattice planes (hkl) in real space. The observed peak spacings can be compared to characteristic sequences from model lattices representing the candidate copolymer morphologies. Table 3.1.2 summarizes the ratio of consecutive Bragg spacings for cylindrical, lamellar, and gyroid symmetries.

		Scattering Maxima					
		1	2	3	4	5	6
Cylinders	q_{hkl}/q_{100}	1	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{7}$	$\sqrt{9}$	$\sqrt{12}$
	d_{hkl}/d_{100}	1	0.577	0.500	0.378	0.333	0.289
	hkl	100	110	200	210	300	320
Gyroid	q_{hkl}/q_{100}	$\sqrt{6}$	$\sqrt{8}$	$\sqrt{14}$	$\sqrt{16}$	$\sqrt{20}$	$\sqrt{22}$
	d_{hkl}/d_{100}	0.408	0.354	0.267	0.250	0.224	0.213
	hkl	211	220	321	400	420	332
Lamellae	q_{hkl}/q_{100}	1	2	3	4	5	6
	d_{hkl}/d_{100}	1	0.500	0.333	0.250	0.200	0.167
	hkl	100	200	300	400	500	600

Table 3.1: Bragg spacings for model cylindrical, gyroid and lamellar morphologies [3]

Grazing-Incidence Small-Angle X-ray Scattering

Grazing-incidence small-angle X-ray scattering (GISAXS) is an important technique used in the investigation of nanoscale material structures and/or the shape of nanoscopic objects at surfaces or in thin films. Block copolymer thin films are therefore ideally suited to characterization with this method. The X-ray beam is directed at a defined grazing incident angle α_i close to the critical angle of total external reflection of the polymer film, and the off-specular intensity is probed by a 2D detector. Sample-averaged information about the lateral structure both inside the film plane and along the film normal can be obtained in a single two-dimensional detector exposure (Figure 3.4a).

Analysis of the scattering patterns can identify not only the phase morphology, but also its orientation in both lateral and vertical directions in the film, for example to distinguish between standing and parallel lamellar microdomains [4]. Other phases to be characterized in this way include spheres [5], standing cylinders [6, 7], and more complex phases such as HPL, and G [8, 9, 10]. A great advantage of GISAXS is the ability to probe films on their native substrates 'as-made', avoiding difficult and invasive sample preparation and allowing the detailed study of processing effects such as temperature annealing or solvent treatment on the copolymer phase morphology [11].

Analysis of the scattering pattern requires simulation of an expected pattern using the symmetry of a proposed film morphology. GISAXS differs to SAXS in that the model must account for the passage

of the incident beam wavevector through the model film layer; i.e. for so called dynamical effects, such as refraction on entering and exiting the film, and reflection at the film- substrate interface. Figure 3.4b shows the paths considered in simulation of the diffraction pattern of both direct and reflected beam paths using the distorted wave Born approximation (DWBA) [4].

For the proposed gyroid morphology, the allowed peak selection rules for an $Ia\bar{3}d$ symmetry were

	X-ray wave- length (Å)	Sample- detector distance (mm)	Exposure time (s)	α_i (°)	α_{crit} (°)
Bulk PFS- <i>b</i> -PLA	1.538	1319	3.00	-	-
Voided PFS template	1.223	1920	0.02	0.18	0.12
Hydrated Ti(IV) oxide films	1.223	1920	0.10	0.18	0.14
Calcined mesoporous titania	1.538	1936	0.20	0.19	0.15

Table 3.2: X-ray operating conditions

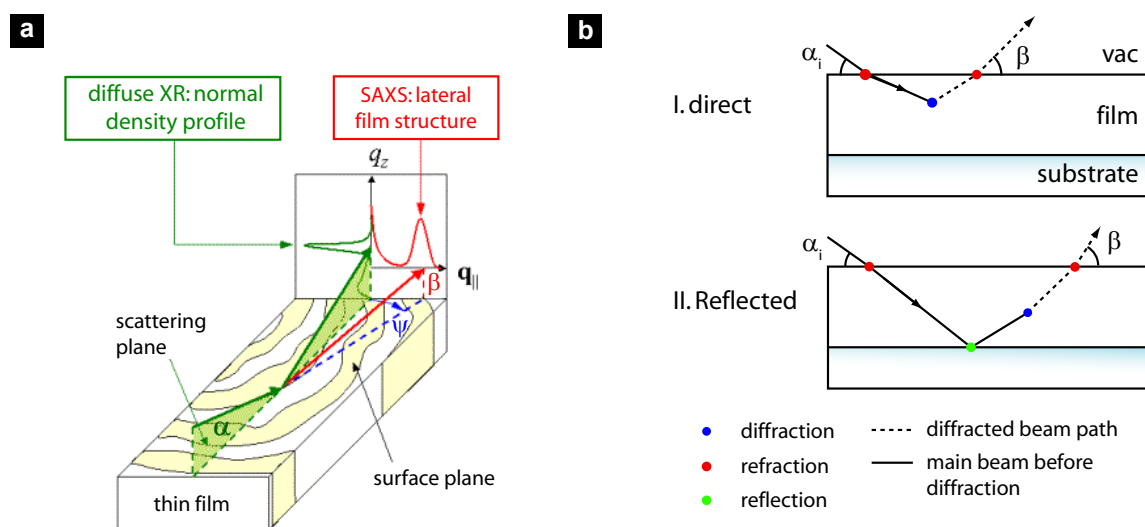


Figure 3.4: **GISAXS scattering geometry.** (a) Incident angle α_i , in-plane scattering angle ϕ , and exit angle β . The normal density profile corresponds to a detector scan in diffuse reflectivity while lateral film structure gives rise to SAXS-like scattering parallel to the substrate. (b) Schematic cross section showing schematic beam paths considered in the simulation of 2D diffraction patterns using the DWBA scheme. ‘Direct beam’ diffraction occurs without reflection from the substrate layer. ‘Reflected beam’ diffraction spots arise after reflection from the substrate interface. Image (a) reproduced from ref [11].

taken from Reference [3]. In practice the simulated 2D GISAXS patterns were calculated using Matlab routines following the index scheme devised by Smilgies *et al.* [12] The fitting parameters for the model are the unit cell orientation and dimension (including an optional degree of structural compression perpendicular to the substrate), and critical angle of incidence for the layer (α_{crit}), which depends on the effective refractive indices of the layers. The operating conditions (including the fitted critical angle) are shown in Table 3.1.2.

3.1.3 Wide Angle X-ray Diffraction

The principles behind wide angle X-ray diffraction (XRD) as a probe for crystalline material composition are similar to those described in the context of SAXS for the study of mesoscale copolymer morphologies. However, in order to probe much smaller structural symmetries of the atomic lattice, the X-ray detector is set to record the much greater scattering angles (corresponding to greater q values). The diffraction pattern obtained from XRD is able to identify both the material via its crystal symmetry and unit cell size, which are documented in the International Centre for Diffraction (ICDD) Powder Diffraction Database.

Grazing incidence X-ray diffraction (GIWAXS) is the wide-angle detector equivalent of GISAXS, and is useful for characterizing thin films of crystalline material on the substrate ‘as-made’. GIWAXS was also conducted on the G1 line at Cornell High Energy Synchrotron Source (CHESS) by Marleen Kamperman. The data were collected at a X-ray wavelength of 1.21 Å. The powder spectra were calibrated by comparison to simulated spectra of cassiterite using the crystal structure visualisation program ‘Mercury’ (Cambridge Crystallographic Data Centre).

3.1.4 Scanning Force Microscopy

Scanning force microscopy (SFM) is an extremely useful tool to probe surface structures and material heterogeneities. The basic principle is to scan an extremely sharp tip mounted on a cantilever with a certain spring constant (usually between 1 and 100 N/m) over the surface to be studied. The displacement of the cantilever provides a measure of the combined distance-dependent surface forces acting on the tip. The cantilever displacement is measured using the deflection of a laser beam fo-

cused on its the upper surface. The voltage difference of upper and lower quadrants in a 4-quadrant photodiode detector is proportional to this deflection. The SFM feedback electronics aim to keep the deflection constant by dynamically changing the tip-sample distance using the piezo crystal translation. A schematic of a typical SFM set up is shown in Figure 3.5. This mode of operation is known as ‘contact mode’ and produces an output of the surface topography mirrored by the required z -height compensation while scanning. There are several disadvantages to contact mode: the probe exerts locally high pressures which can deform or even destroy the surface especially when imaging soft samples. The surface is also subjected to large lateral forces caused by the scanning motion.

‘TappingModeTM’ SFM is a modified operation mode that maps topography by lightly tapping the surface with an oscillating probe tip. The cantilever initially undergoes a driven oscillation close to its natural free resonance frequency with an amplitude of the order 10 nm. At close enough tip-sample distances the tip experiences the steep repulsive force gradient which causes an increase in the resonance frequency above the free resonance until ultimately a new dynamical equilibrium is reached with an amplitude which corresponds to the imposed mean tip-sample distance. The reduction in amplitude can be used as a feedback parameter again compensated by changing the tip-sample separation, thus producing an output mirroring the surface topography. The phase of the cantilever

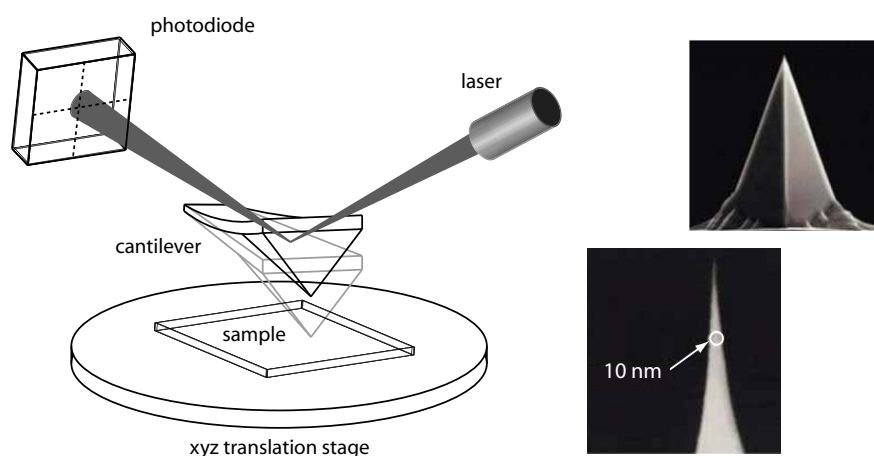


Figure 3.5: **Schematic of a typical Scanning force microscope (SFM).** The reflection of a laser beam focused on the top side of the cantilever is monitored by a 4-quadrant photodiode and provides a measure of tip deflection. A piezoelectric translation stage controls motion of the sample in three dimensions. The SEM images on the left show the end of the tip with a radius of curvature less than 10 nm (SEM tip images: www.pacificnano.com)

oscillation response relative to the driving force provides information about the energy dissipation from the cantilever into the sample which often reveals material contrast at the surface.

SFM images in this study were generated in tapping mode on a Veeco Dimension 3100 AFM with Nanoscope IV controller using NSG20 supersharp silicon tips (tip radius < 10 nm) with resonant frequency in the range 250 to 400 kHz (purchased from NT-MDT, Europe). In this instrument the $x - y - z$ motion is generated by a segmented piezo tube onto which the cantilever is mounted.

3.1.5 Ellipsometry

Ellipsometry is an optical technique for the study of surfaces and coatings by measuring the changes in polarization state of monochromatic illumination upon reflection. The theory of ellipsometry is based on the Fresnel equations for reflection and transmission for light incident on interfaces in planar multi-layered materials [13]. In nulling-ellipsometry, monochromatic light from a laser source is elliptically polarized by passage through a linear polarizer (P) and quarter-wave plate (the ‘compensator’, C). The reflected beam passes through a second linear polarizer (the ‘analyzer’, A) before being detected by a CCD. The optical components can be independently rotated. A minimum (‘null’) intensity is detected when P and C are aligned such that the reflected beam is linearly polarized in direction perpendicular to A. These values are used to determine the reflection coefficients parallel and perpendicular to the sample surface. In practice the nulling condition is found and recorded for a range of incidence angles (or illumination wavelengths), and the data fitted to an optical model of the reflecting surface.

Nulling ellipsometry was carried out using a Nanofilm EP3 imaging ellipsometer (Nanofilm, Germany) with single wavelength (532 nm laser) illumination. The technique was used to monitor the gradual reduction in thickness of a poly(D,L-lactide) (PLA) thin film on silicon substrate caused by ester hydrolysis in basic water. This experiment required a liquid-cell geometry shown in Figure 3.6.

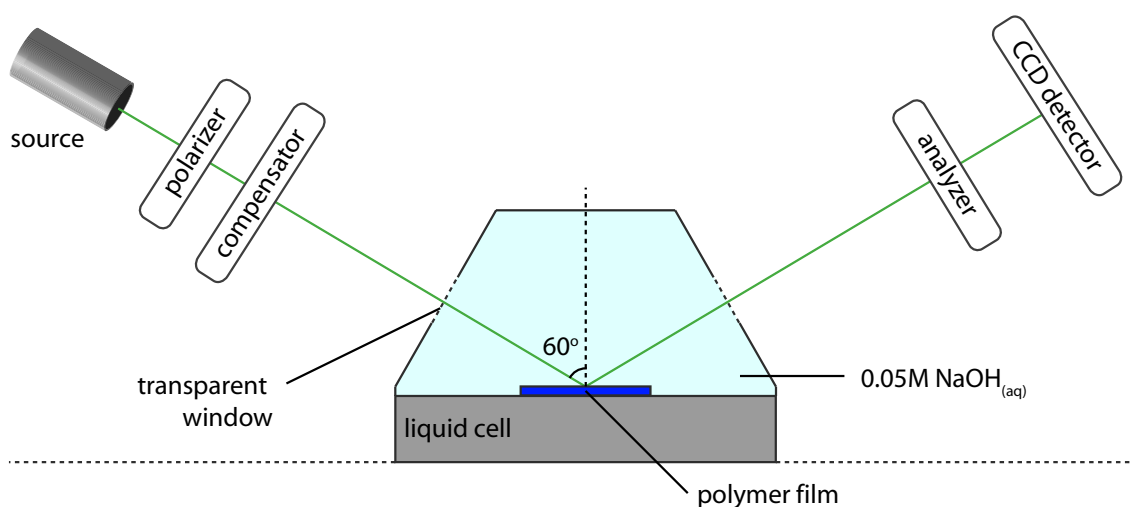


Figure 3.6: **Schematic representation of null ellipsometry experiment for a polymer film submerged in liquid.** Monochromatic illumination from the laser source is elliptically polarized by passage through a linear polarizer and a quarter-wave plate compensator. The beam reflects from the polymer/silicon surface at an incident angle of 60° such that it passes at normal incidence through transparent windows in the liquid cell. The reflected beam passes through a second linear polarizer (the analyzer) before detection in a CCD photo-detector.

Table 3.3: Optical parameters at 532 nm illumination obtained by ellipsometric fitting to model layers

Material	Refractive index n	Extinction Coefficient k	Thickness (nm)
Silicon	4.15	0.02	-
Silicon oxide	1.5	0	1.6
Poly(lactic acid)	1.46	0	110
0.05 M NaOH _(aq)	1.37 ^a	0	-

^a Refractive index of 0.05 M NaOH_(aq) was determined in the liquid cell over an incidence range 59° to 61° . All other fitting was done using an angle of incidence spectra over a 10° range with at least 20 data points.

The complex index of refraction ($\tilde{n} = n + ik$ where n is the refractive index and k is the extinction coefficient) of the substrate, PLA film and NaOH etching solutions were pre-characterized using

models fitting data series recorded over a range of incident illumination angles between 70 and 80°. The best fit model parameters (fitted using Nanofilm Ellipsometry software) are shown in Table 3.3.

3.2 Electrochemical Deposition

Electrodeposition is a low cost and extremely versatile technique for producing thin coatings of pure metals and alloys, ceramic oxides, semiconductors and polymers on conducting or semiconducting substrates [14, 15]. The substrate to be coated forms the ‘working electrode’ when immersed in a liquid electrolyte containing dissolved precursor species of the material component(s) to be deposited forming part of an electrochemical cell (Figure 3.7). Two further electrodes, the ‘reference’ and counter’ electrode are connected to the substrate ‘working electrode’ via a potentiostat able to control relative voltage or current flow in the system.

In essence, electrodeposition occurs by introducing an additional thermodynamic driving force for a reaction in the close vicinity of the working electrode by controlling its potential relative to the solution. Charges transferred across the electrode-electrolyte interface cause oxidation (at the anode) or reduction (at the cathode) to occur. The role of the reference electrode is to provide a reliable reference potential for the working electrode in the cell. The potential measured by the potentiostat between the working and reference electrodes is equal to the potential drop across the electrode-

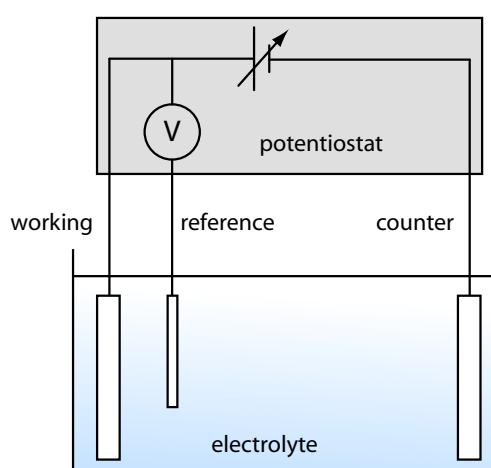


Figure 3.7: **Standard 3-electrode electrochemical cell showing working, reference and counter electrodes immersed in a liquid electrolyte**

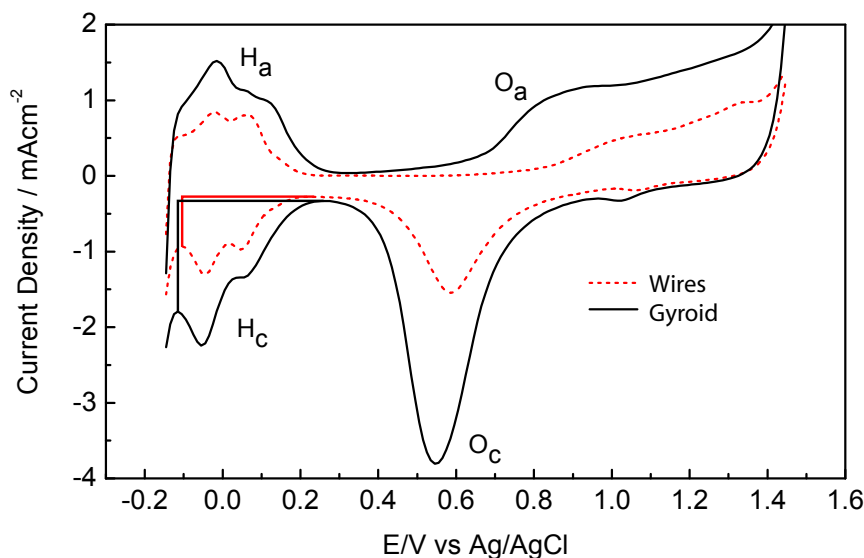
electrolyte interface plus a constant. In ‘potentiostatic’ deposition the potential difference between working and counter electrode is adjusted until the set-point voltage between working and reference is obtained. In ‘galvanostatic’ (or constant current) mode the applied potential is adjusted until a set-point current flows between working and counter electrodes, with simultaneous measurement of potential relative to the reference. Electrodeposition is an extremely useful technique for filling nanostructured templates since the deposited material grows preferentially from the underlying conducting substrate wherever the electrolyte is able to penetrate the pore structure.

3.2.1 Electrochemical Surface Area Measurements

The surface area of certain transition metal electrodes showing hydrogen adsorption in potential regions prior to massive H_2 evolution may be measured using cyclic voltammetry [16]. The most common use of this method is for platinum electrodes, a particularly convenient choice in this study for its straightforward deposition protocol and high conductivity for structural characterization using SEM. The charge under the voltammetric peak for hydrogen adsorption (corrected for capacitive charging of the double layer) is assumed to correspond to adsorption of one hydrogen atom on each metal atom at the exposed surface (H_C). The distribution of platinum atoms at the surface is well defined for a perfect single crystal face, while an average over low-index faces is taken for polycrystalline samples. This value provides an estimate of the expected charge per unit area for a one-to-one correspondence of hydrogen to surface metal atoms (Q_0). The generally accepted value of $Q_0 = 210 \mu C cm^{-2}$ corresponds to a surface density of platinum atoms of $1.31 \times 10^{15} cm^{-2}$. The actual surface area is then given by $A = H_C/Q_0$.

The assumptions of this method are (I) that a point for complete hydrogen adsorption can be identified before the onset of H_2 gas evolution, (II) there is a quantitative relation between the measured charge and the amount of substance deposited, and (III) there is no alteration of the surface upon adsorption.

Surface areas of nanostructured platinum networks were determined by measuring the charge associated with hydrogen adsorption in a 0.1 M $H_2SO_{4(aq)}$ solution with a potential scan rate of $50 mV s^{-1}$ and a Ag/AgCl reference electrode. The working electrode area was defined to be $0.36 cm^2$ using Kapton masking tape. The scan limits at positive potentials are at $\sim 1.4 V$ (oxygen evolu-



	Wires	Gyroid
Integrated Charge /mCcm ⁻²	3.94	8.01
Array Thickness /nm	360	290
Roughness Factor	60	130

Figure 3.8: **Electrochemical measurement of surface area using hydrogen adsorption.** The cyclic voltammogram was recorded for cylindrical wires and gyroid nanostructured platinum electrodes in 0.1 M H₂SO_{4(aq)} solution with a potential scan rate of 50 mV s⁻¹. H_C: formation of adsorbed hydrogen, H_A: oxidation of adsorbed hydrogen, O_A formation of adsorbed oxygen, O_C: reduction of oxide layer. The table shows the measured hydrogen adsorption charge, the thickness of the array, and therefore the calculated surface area multiplicity (over the flat projected substrate) of the array surface per micron of thickness ('roughness factor').

tion) while hydrogen evolution is seen at -0.15 V. The surface of the array was first electrochemically cleaned by holding the voltage at the onset of oxygen evolution for 30 sec followed by hydrogen evolution for 30 sec. The voltage was then swept between oxygen and hydrogen evolution 100 times at 10 V s⁻¹.

The cyclic voltammograms recorded for two different platinum nanostructured electrodes are shown in Figure 3.8 along with the corresponding measured charge H_C. The area is expressed as the multiplicity over the projected flat substrate area for every micron of thickness.

3.3 Photovoltaic Device Characterization

3.3.1 Photovoltaic Performance: Definitions

The following section describes the common performance measures used to evaluate solar cell devices. The experimental conditions used to evaluate solar cells are described in Chapter 4.

Short circuit current (J_{sc}): Cell current density measured under illumination at zero volts applied potential (short circuit). The sign convention used in discussing solar cell characteristics is such that the photocurrent is positive [17].

Open circuit voltage (V_{oc}): Applied voltage bias at which the cell current is zero. Forward bias corresponds to applying a negative potential to the n-type (electron accepting) material relative to the p-type (electron donor) material. The operating regime of a solar cell lies in forward bias between 0 and V_{oc} . Forward bias above V_{oc} is the operating regime of light emitting diodes (the device consumes

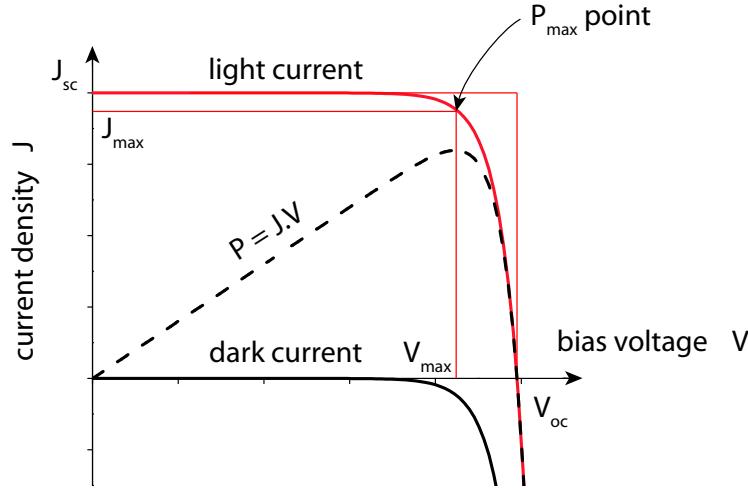


Figure 3.9: **Schematic current-voltage characteristics of an ideal solar cell.** The current under illumination (light current, red) is shifted positive by the short circuit current density J_{sc} relative to the dark current (black). As the bias increases from short circuit the dark current increases until it exactly balances the short circuit current at V_{oc} . The power density (black dashed line) increases from short circuit to a maximum at (J_{max}, V_{max}) before falling to zero at V_{oc} . The fill factor FF is given by the ratio of the inner rectangle enclosed by the max power point P_{max} and the outer rectangle defined by $J_{sc} \times V_{oc}$.

power and emits light). In reverse bias ($V < 0$), the device would act as a photodetector, consuming power to deliver a positive current dependent on illumination intensity but independent of applied potential.

Maximum power output ($P_{\max}$): At any given applied voltage the power output (P) of a solar cell per unit area is the product of the current density and voltage ($P = J_{\text{sc}} \times V_{\text{oc}}$). As the voltage is increased from zero (short circuit) the power output increases to a maximum before falling to zero at open circuit (V_{oc}). The co-ordinates $V_{\max}$ and $J_{\max}$ correspond visually to the largest rectangle contained by the current-voltage curve (Figure 3.9).

Fill factor (FF): Measures the deviation of the current-voltage characteristic from a square curve: the fill factor is the ratio in the areas of a rectangle formed by the max power co-ordinates ($P_{\max}$) and that formed by $J_{\text{sc}} \cdot V_{\text{oc}}$.

$$FF = \frac{J_{\max} V_{\max}}{J_{\text{sc}} V_{\text{oc}}} = \frac{P_{\max}}{J_{\text{sc}} V_{\text{oc}}} \quad (3.4)$$

Efficiency(η): the power conversion efficiency is the ratio of electrical power delivered per unit cell area to the incident illumination irradiance (P_{in} in mW cm^{-2}).

$$\eta = \frac{P_{\max}}{P_{\text{in}}} = \frac{J_{\text{sc}} V_{\text{oc}} FF}{P_{\text{in}}} \quad (3.5)$$

Maximizing power conversion efficiency is achieved by optimizing the three parameters V_{oc} , J_{sc} , and FF of the cell. The efficiency of a real cell is in general dependent on incident power flux and spectral distribution which should therefore be stated whenever the efficiency is quoted.

External quantum efficiency(EQE): Also known as incident-photon-to-electron conversion efficiency (IPCE), the EQE defines the ratio of electrons delivered to the external circuit to the total number of photons incident on the active device area (Equation 3.6). The EQE is usually measured as

a function of incident photon wavelength using monochromatic illumination under short-circuit conditions. In practice, the incident photon flux is measured using a calibrated silicon diode illuminated in tandem with the test cell.

$$\text{EQE} = \frac{n_{\text{electrons}}(\lambda)}{n_{\text{photons}}(\lambda)} = \frac{J(\lambda)hc}{P_{\text{in}}e\lambda} \quad (3.6)$$

Air Mass 1.5 Illumination (AM 1.5): The sun emits a radiation spectrum characteristic of a black body at 5760 K. The emission is strongest at visible wavelengths (300 to 800 nm) and peaks in the blue-green region. Outside the earth's atmosphere the extraterrestrial solar irradiance (AM 0) is 135.5 mW cm^{-2} . Absorption and scattering during passage through the atmosphere causes attenuation of the solar spectrum which is quantified by the Air Mass factor n_{AM}

$$n_{\text{AM}} = \frac{\text{optical pathlength}}{\text{optical pathlength when sun is directly overhead}} \quad (3.7)$$

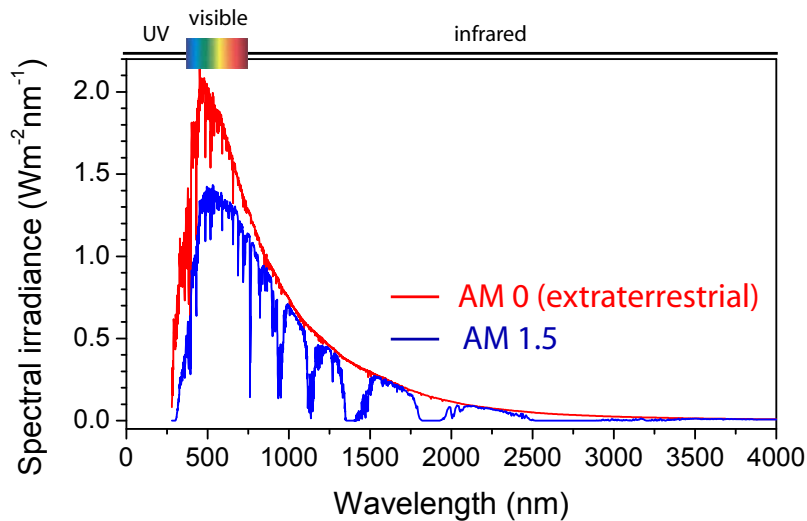


Figure 3.10: **AM 0 (extraterrestrial) and AM 1.5 terrestrial spectra.** Source: American Society for Testing and Materials (ASTM G173-03).

Air Mass 1.5 refers to the terrestrial illumination spectrum with the sun at 42° above the horizon, and corresponds to passage through 1.5 atmospheres if the sun were always directly overhead. Meaningful comparison of solar cell device performance representative of that under real operating conditions demands a single common reference test. The standard testing conditions (STC) for solar cells adopted by the photovoltaic community consists of a temperature of 25°C and an AM 1.5 illumination spectrum with irradiance 100 mW cm^{-2} . The AM 1.5 spectrum is shown in Figure 3.10.

Spectral mismatch: The spectral distribution of artificial light sources inevitably differs to some degree from the ideal reference AM 1.5 solar spectrum. This difference must be accounted for with a mismatch factor when characterizing solar cell devices under simulated solar illumination. The calculated mismatch factor is strongly dependent on the spectral sensitivity of the device in question since this defines which areas of the simulated spectrum are most critical to the cell performance (i.e. it is relatively unimportant if an illumination spectral range is poorly simulated if the cell in question is not sensitive to this radiation). A reference cell (R) is calibrated under AM 1.5, 100 mW cm^{-2} conditions and the value of the short circuit current $J_{\text{AM1.5}}^{\text{R}}$ recorded. The reference cell is used in tandem with the test cell (T) in order to calibrate the simulated light source using the spectral mismatch following the method of Seaman [18]. This allows us to determine what the test cell current would be under true AM1.5 illumination $J_{\text{AM1.5}}^{\text{T}}$. With reference to Figure 3.11 the corrections M^{T} and M^{R} for the test and reference cells respectively can be written as

$$M^{\text{T}} = \frac{J_{\text{AM1.5}}^{\text{T}}}{J_{\text{SIM}}^{\text{T}}} \text{ and } M^{\text{R}} = \frac{J_{\text{AM1.5}}^{\text{R}}}{J_{\text{SIM}}^{\text{R}}} \quad (3.8)$$

The spectral mismatch for this combination of cells is calculated according to:

$$M = \frac{M^{\text{R}}}{M^{\text{T}}} = \frac{\int S_{\text{AM1.5}}^{\text{R}}(\lambda) EQE^{\text{R}}(\lambda) \cdot d\lambda}{\int S_{\text{SIM}}^{\text{R}}(\lambda) EQE^{\text{R}}(\lambda) \cdot d\lambda} \cdot \frac{\int S_{\text{SIM}}^{\text{T}}(\lambda) EQE^{\text{T}}(\lambda) \cdot d\lambda}{\int S_{\text{AM1.5}}^{\text{T}}(\lambda) EQE^{\text{T}}(\lambda) \cdot d\lambda} \quad (3.9)$$

where $S_{\text{SIM}}^{\text{R}}(\lambda)$ and $S_{\text{AM1.5}}^{\text{R}}(\lambda)$ are the two spectral illumination distributions. The current of the test

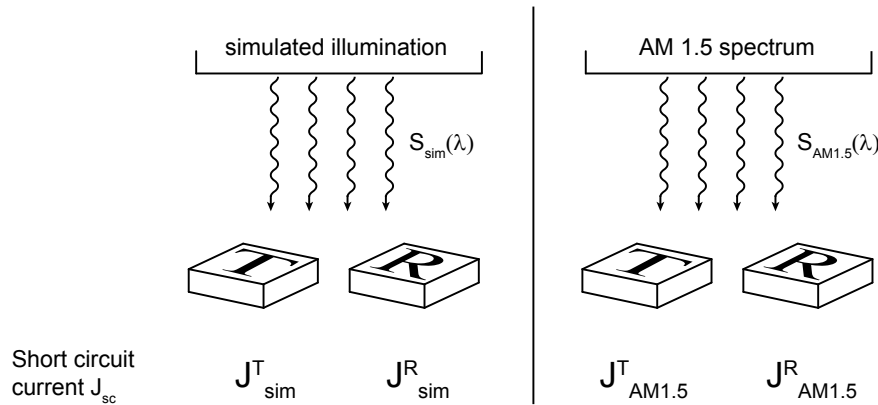


Figure 3.11: **Reference and test cell short circuit current response under simulated and true AM1.5 solar illumination**

cell under AM 1.5 illumination is:

$$J_{AM1.5}^T = \left(\frac{J_{AM1.5}^R}{J_{SIM}^R} \right) \cdot (M)^{-1} \cdot J_{SIM}^T \quad (3.10)$$

Once the mismatch factor M is calculated using Equation 3.9, the simulated source intensity is adjusted until $\left(\frac{J_{AM1.5}^R}{J_{SIM}^R} \right) \cdot (M)^{-1} = 1$ so that, according to Equation 3.10, $J_{SIM}^T = J_{AM1.5}^T$. The current-voltage curve for the test cell recorded under these illumination conditions is equal to that which would be observed under true AM 1.5.

3.3.2 Transport and Recombination

The electron transport and recombination properties of dye-sensitized solar may be probed using transient photocurrent and photovoltage spectroscopy [19]. A red light bias illumination is used to establish a steady-state carrier density at short-circuit or open-circuit which is perturbed by superposition of a weak square-wave red probe pulse (Figure 3.12a). A single red (630 nm peak) LED focused onto the device is used as both the bias and pulse source.

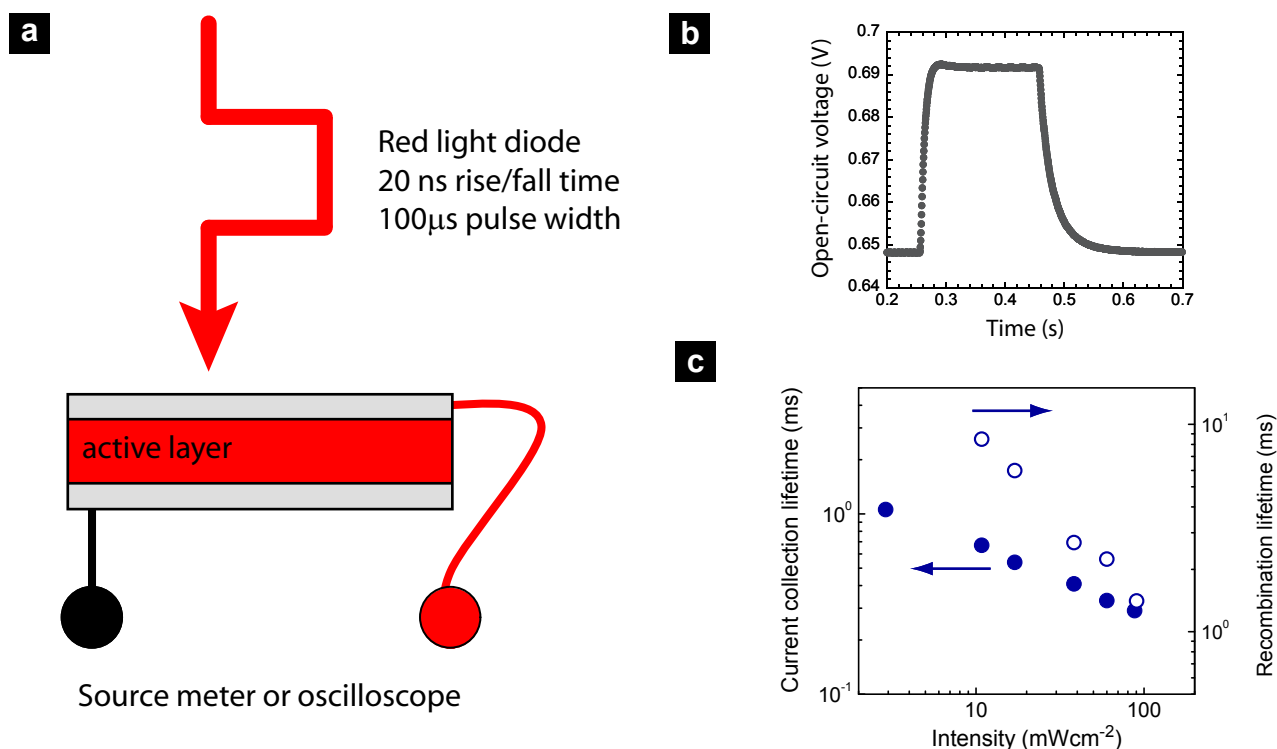


Figure 3.12: **Transient photocurrent and photovoltage spectroscopy of dye-sensitized solar cells.** (a) Schematic of bias and pulse illumination using a red light diode. (b) Typical voltage rise and decay at open circuit in response to the illumination pulse. (c) Transport and recombination times for a nanoparticle DSSC as a function of illumination intensity.

Transport

The photocurrent decay at short-circuit is characteristic of the time for electron transport out of the device. Since the photo-induced charge density is assumed to be uniformly generated throughout the layer, this is in essence a spatially integrated diffusive time-of-flight experiment. The current decay is fitted to a single exponential form and the time constant recorded for a range of background illumination intensities.

Recombination

Charge recombination rates are determined in the same devices via open-circuit voltage decay measurements following a similar procedure to the current collection, however here the device is connected across a high impedance port of an oscilloscope. The open-circuit potential increases as

photo-induced electrons build up in the TiO_2 film and thus raise the quasi-Fermi level. In this instance no charge can leave the cell and the rate of decay of the voltage perturbation is proportional to the rate of charge recombination in the solar cell [20]. Figure 3.12b shows a typical voltage rise and decay back to steady state under the bias illumination. The charge collection time and recombination times for a liquid electrolyte DSSC made using sintered TiO_2 nanoparticles is shown in Figure 3.12c.

3.3.3 Photovoltaic set-up: device testing

Solar cell device construction and characterization was done in collaboration with Dr Henry Snaith of the optoelectronics group, Cavendish laboratories, Cambridge.

Voltage and current decay rates for transient photocurrent and photovoltage spectroscopy were recorded on an Agilent Technologies oscilloscope through the low ($50\ \Omega$) and high ($1\ \text{M}\Omega$) impedance ports, respectively. For voltage perturbation a Kiethley 237 sourcemeter was connected in series with the cell in order to hold the current constant following the perturbation light pulse [20].

To determine the spectral response of the photocurrent, a halogen lamp (spectrally resolved by a monochromator) illuminated the solar cells from the FTO side, at an intensity of order $0.1\ \text{mWcm}^{-2}$ at each wavelength interval. The illumination spot size was approximately $1\ \text{mm}^2$, and the photocurrent was measured by a Kiethley 237 source meter interfaced with a computer. The spectral dependence of the power incident on the devices was calibrated with a reference Si photodiode. The simulated AM 1.5 solar illumination was generated by a 300 W Oriel solar simulator with the corresponding AM 0 and AM 1.5 filters. The intensity of the solar simulator was calibrated using a Si calibration diode purchased from and calibrated at the Fraunhofer Institute for Solar Energy Systems (Freiburg, Germany). The spectral mismatch was found to be 22 % when calculated over the entire absorbing region of the test cell and calibration diode. The active area of the liquid electrolyte-based DSSCs was defined to be $0.13\ \text{cm}^2$ by a black optical mask and the area of the solid-state DSSCs was defined to be approximately $0.045\ \text{cm}^2$ by the overlap of the silver cathode with the FTO anode.

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Experimental

4.1 Materials

The following materials were used as received unless otherwise stated.

Chemicals

- Hydrogen hexachloroplatinate(IV) hexahydrate, 99.90 %, Acros Organics.
- Titanium (III) chloride solution, ~10 %_{mass} solution in 20 – 30 %_{mass} hydrochloric acid (Sigma-Aldrich).
- Toluene (THF), Spectrophotometric grade, 99.5 %, Aldrich.
- 4-Fluorostyrene 99 %, Sigma Aldrich.
- Sodium carbonate, ACS reagent grade, ≥ 99.5 %,Sigma-Aldrich.
- Sodium hydroxide, ACS reagent grade, ≥ 97.0 %,Sigma-Aldrich.
- Ruthenium(III) chloride hydrate, 99.98 % (metals basis),Sigma-Aldrich.
- Spiro-MeOTAD - 2,2',7,7'-tetrakis(N,N-di-methoxypheny-amine)- 9,9' -spirobifluorene, Merck Chemicals.

- Li[CF₃SO₂]₂N, Aldrich.
- Tert.-butylpyridine, Aldrich.

Solar Cell Dye Sensitizers

The following dye molecules, received from École Polytechnique Fédérale de Lausanne (EPFL) were used as sensitizers in dye-sensitized solar cells

- **Z 907** - cis-di(thiocyanato)-(2,2'-bipyridyl-4,4'-dicarboxylic acid)(4,4'-dinonyl-2,2'-bipyridyl)-ruthenium(II).
- **N 719** - cis-di(thiocyanato)-bis(2,2'-bipyridyl-4-carboxylate-4'-carboxylic acid)-ruthenium(II).
- **D 149** - Indolene dye.

Liquid Electrolyte

Electrolyte for the liquid electrolyte dye-sensitized solar cell has the following components:

- Propyl-Methyl-Imidazolium-Iodide (0.8 M), synthesized at the EPFL Laboratory, Lausanne.
- M Iodine (0.15M), Aldrich.
- N-Methylbenzimidazole (0.5 M), Aldrich, recrystallized in Diethyl Ether before use.
- Guanidine Thiocynate (0.1 M), Fluka.

4.2 Block Copolymers

The two copolymers used in this study: poly(4-fluorostyrene)-*b*-poly(D,L-lactide) (PFS-*b*-PLA) and poly(styryltriarylamine)-*b*-poly(D,L-lactide) (PSTA-*b*-PLA) were synthesized using a combination of ring-opening and Reversible Addition Fragmentation chain Transfer (RAFT) polymerization [1] by

Prof. Marc Hillmyer and Dr Sabine Ludwigs. The styryltriarylamine monomer was provided by Steve Scroggins from the Department of Chemistry, University of Cambridge. An outline of the synthesis procedure is provided in the following section, along with a summary of characterization by ^1H NMR spectroscopy, size exclusion chromatography (SEC), and differential calorimetry (DSC).

4.2.1 Synthesis of Poly(D,L-lactide) [PLA]

The PLA block was first synthesized by the controlled, aluminum-catalyzed ring-opening polymerization of D,L-lactide using a mixture of benzyl alcohol and triethyl aluminum as the initiating system (Figure 4.1). The polymerization was carried out in toluene at 90°C for 5 h and terminated with acidic water. The resulting hydroxy terminated polylactide was converted to the corresponding trithiocarbonate by reaction with the acid chloride of S-1-Dodecyl-S'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate using an established procedure [2].

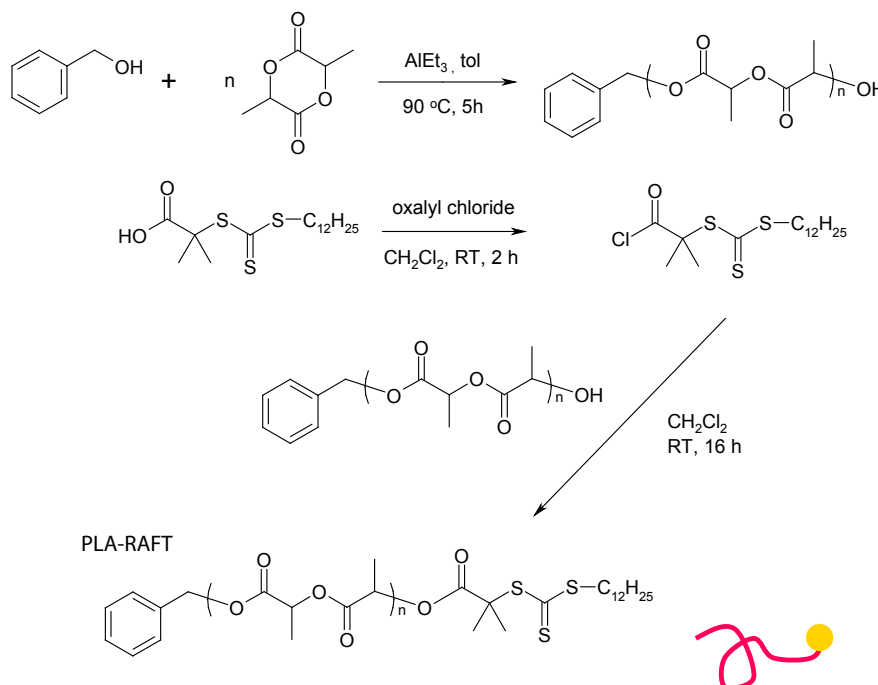


Figure 4.1: Synthesis of poly(D,L-lactide)

4.2.2 Synthesis of Poly(4-fluorostyrene)-*b*-poly(D,L-lactide) [PFS-*b*-PLA]

The controlled reversible addition fragmentation transfer (RAFT) polymerization of 4-fluorostyrene (Figure 4.2) was carried out by first dissolving a 0.4 g portion of the trithiocarbonate functionalized PLA in 1.6 g of 4-fluorostyrene (purified by passage through an alumina column). The solution was degassed and then heated in a sealed flask to 120 °C for 6.3 h. Autoinitiation of the 4-fluorostyrene was the likely source of initiating free radicals. The resulting solid was dissolved in methylene chloride, precipitated in methanol, and the white powder was dried under reduced pressure at 75 °C.

Characterization of molecular weight was made by ^1H NMR spectroscopy and polydispersity was determined using size exclusion chromatography (SEC). Four principle batches of PFS-*b*-PLA were used in this study, as detailed in Table 4.1. The relative volume fractions were calculated assuming the specific monomer volume for PFS is 1.04 times that of PS (using the known ratio of monomer densities ($\rho_{\text{styrene}} = 0.909 \text{ g cm}^{-3}$ and $\rho_{\text{fluorostyrene}} = 1.024 \text{ g cm}^{-3}$)ⁱ and known molecular weights). Alternatively, assuming a specific monomer volume equal to polystyrene results in an estimated PLA

ⁱwww.sigmaaldrich.com

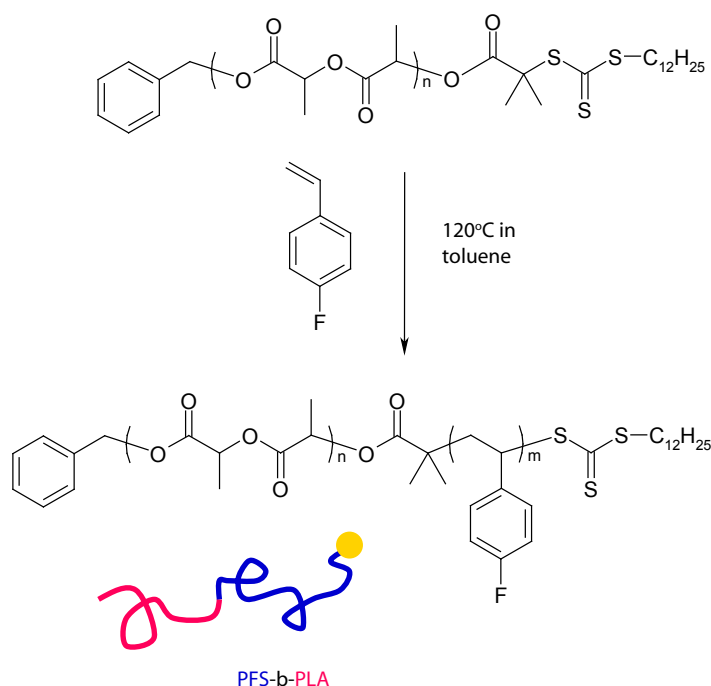


Figure 4.2: Synthesis of poly(4-fluorostyrene)-*b*-poly(D,L-lactide)

volume fraction (f_{PLA}) some 2 – 3 % lower than the calculated values in Table 4.1.

Differential Scanning Calorimetry (DSC) traces on the MHI10 sample of PFS-*b*-PLA showed two glass transition temperatures (T_g) at 103 °C and 57 °C. These are attributable to PFS (value from literature $T_g = 95^\circ\text{C}$)ⁱⁱ and PLA respectivelyⁱⁱⁱ.

Table 4.1: Summary of PFS-*b*-PLA copolymers used in this study

Sample	M_n (kg/mol) PFS	M_n (kg/mol) PLA	N_{PFS}	N_{TOT}	f_{PLA} (%) ^a	PDI ($= \frac{M_w}{M_n}$)
MHI10	19.8	10.0	162	301	33	1.17
MHI41	21.7	14.6	177	380	40	1.21
MHI42	26.8	14.6	219	422	35	1.14
MHI43	28.6	14.6	234	437	34	1.15

^a PLA volume fraction $f_{\text{PLA}} = \frac{N_{\text{PLA}}}{\frac{v_{\text{PFS}}}{v_{\text{PLA}}} N_{\text{PFS}} + N_{\text{PLA}}}$, with $v_{\text{PFS/PLA}}$ the respective specific monomer volumes assuming $\rho_{\text{PLA}} = 1.18 \text{ g cm}^{-3}$ [3] and $\rho_{\text{PFS}} = 1.17 \text{ g cm}^{-3}$.

4.2.3 Synthesis of Poly(styryltriarylamine)-*b*-poly(D,L-lactide) [PSTA-*b*-PLA]

The RAFT polymerization of poly(styryltriarylamine)-*b*-poly(D,L-lactide) is shown in Figure 4.3.

4.3 Substrate preparation

Substrates

The silicon substrates used in this work were polished <100> cleaved p-doped silicon purchased from Si-Mat Silicon wafers (Silicon Materials, Landsberg am Lech, Germany); thickness $675 \pm 25 \mu\text{m}$, surface roughness < 5 nm and conductivity of $4\text{--}7 \Omega \text{ cm}^{-2}$.

The transparent conducting substrates used for solar cell devices were fluorine doped 400 nm tin oxide glass (referred to in the text as FTO) kindly donated by Nippon Sheet Glass with conductivity of $13 \Omega \text{ cm}^{-2}$.

ⁱⁱ www.sigmaaldrich.com

ⁱⁱⁱ Polymer Handbook, 4th Edition, J. Brandrup (Ed)

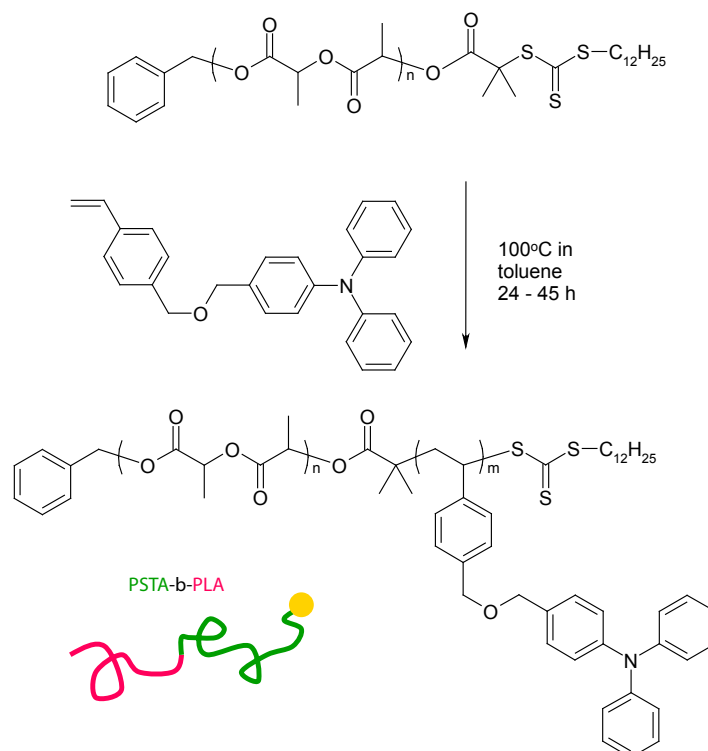


Figure 4.3: **Synthesis of poly(styryltriarylamine)-*b*-poly(D,L-lactide)**

Substrate Cleaning

A jet of carbon dioxide crystals ('snow-jet') was used to remove dust and organic contaminants from the substrates before polymer coating [4]. FTO glass and TiO₂ coated substrates were cleaned by exposure to oxygen plasma (Diener Electronic Femto Plasma System 100 W, 4 kHz) for 5 minutes before snow-jet cleaning.

4.4 Thin film deposition

Spin-coating

The two main techniques used in this work to produce thin polymer films are spin-coating and blade coating (Figure 4.4). In spin-coating (Figure 4.4a) an excess volume of polymer solution is placed onto a substrate held on a vacuum stage which is then accelerated up to a typical rotation speed

of between 500 and 10,000 revolutions per minute. Excess solution is expelled from the edges of the surface by centrifugal forces, while fluid viscous forces control the thinning of the remaining film coating. In the later stages, solvent evaporation dominates the thinning behaviour of the film. The final film thickness can be influenced by the spinning speed and the solution concentration, as well as choice of solvent. Thicknesses ranging from ~ 10 nm to many microns are accessible with this technique, although thicker films require concentrated polymer solutions and as such result in significant material waste in the excess solution thrown from the substrate.

Blade coating

The blade coating technique is shown schematically in Figure. 4.4. A drop of polymer solution is placed at the edge of a strip of cleaned substrate and a blade is drawn across the sample at constant speed producing a layer of solution with thickness determined by the substrate-blade gap. For example, a $10\text{ }\mu\text{m}$ gap and a $10\text{ }\%_{\text{mass}}$ polymer solution was used to produce films approximately $1\text{ }\mu\text{m}$ thick. By using a long and thin sample geometry, no additional lateral confinement is required to produce smooth polymer films. Since almost all the initial polymer solution remains on the substrate in the final film, this method is considerably more material efficient than spin coating.

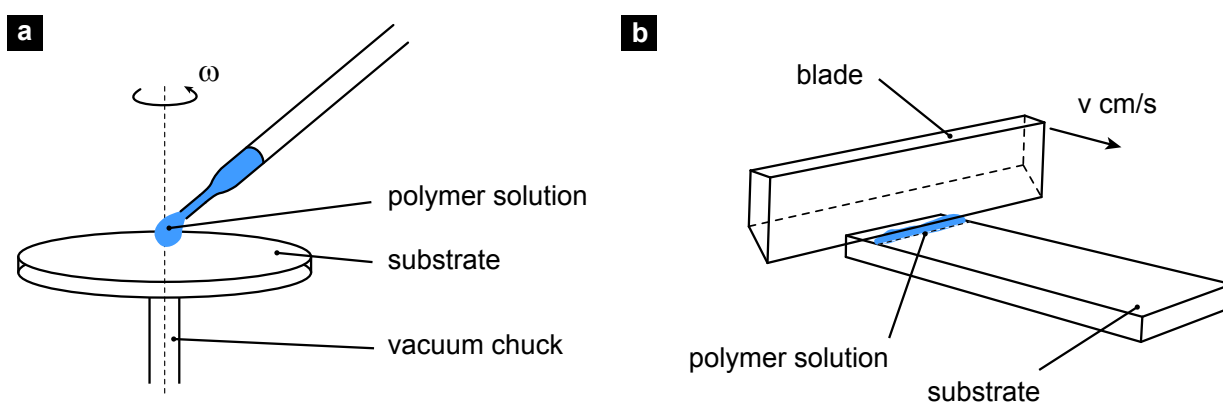


Figure 4.4: **Schematic polymer coating techniques.** (a) Spin coating and (b) blade coating

Thermal evaporation of metals

Thermal evaporation was used to produce metal coatings on silicon substrates or counter electrodes in solar cell devices. The substrate to be coated was mounted in a multiple-source BOC Edwards Auto 306 thermal evaporator with rotating sample holder. For gold coatings, a 2 nm chromium adhesion layer was first deposited at $\sim 0.04 \text{ nm s}^{-1}$ once the chamber pressure was 5×10^{-6} mbar or below. A 40 nm gold layer was then deposited at $\leq 0.15 \text{ nm s}^{-1}$. The chamber was allowed to cool before venting with nitrogen. Deposition rates and accumulated thicknesses were recorded using a water-cooled quartz crystal monitor.

Self Assembled Thiol Monolayers on Au

Gold coated substrates were coated with a self-assembled monolayer of 1-undecanethiol by soaking the freshly cleaned Au (sonication for 10 min in both acetone and ethanol before snow jet cleaning) in a 1 mM solution of 1-undecanethiol in ethanol for 20 h [5]. After soaking, the substrates were immersed in ethanol at 60 °C for 6 h before finally drying and annealing at 100 °C under vacuum for 1 h.

Spray Pyrolysis of compact TiO₂ films

Thin films of TiO₂ can be formed on FTO glass substrates by pyrolysis of an aerosol of titanium-bis(acetylacetonate) (TAA) solution in ethanol [6]. A 0.1 M solution of TAA in ethanol was prepared under nitrogen immediately before use. The substrates were placed on a hotplate and heated to 450 °C. A hand-held atomizing device connected to an oxygen source allowing short bursts of gas flow was directed at approximately 45 °, 20 cm from the hot surface. A series of 30 bursts of aerosol, equally spaced with ~ 5 second pauses was used to spray 2 mL of solution onto a total area of approximately 10 × 10 cm. The spray was directed sequentially from all four directions to ensure a uniform coating thickness of ~ 50 nm. Previous studies have shown this method to produce remarkably reproducible TiO₂ films in terms of morphology and electronic properties despite this seemingly low tech deposition method [7].

Platinized FTO layers

FTO coated glass substrates were platinized by simple spreading of a 50 mM drop of hexachloroplatinic acid in anhydrous isopropanol onto the sample using a glass pipette. The substrates were then placed on a hotplate at 450 °C for 15 minutes followed by slow cooling to room temperature [8]. The films thus formed were transparent with a slight brown sheen.

4.5 Copolymer Electric Field Alignment

The application of a vertical electric field to a copolymer film is achieved in a parallel plate capacitor geometry while the copolymer is heated above the glass transition temperature of both constituent blocks. A copolymer film was first coated on a conducting substrate. Polished silicon substrates were electrically contacted on the reverse side with a 50 nm thermally evaporated gold layer to ensure good contact. FTO glass substrates were contacted using a thin layer of conducting silver paste along and round one edge of the sample. The upper-electrode was a 25 μm thick sheet of Kapton CR (DuPont) with a 50 nm thermally evaporated Au layer on the reverse side. In order to make conformal contact with the polymer layer, a thin layer ($\sim 2 \mu\text{m}$) of poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) was spin-cast on the front side of the Kapton sheet from a 15 %_{wt} solution in chloroform and cross-linked at 80 °C for 10 h. A constant voltage of 3 to 4 kV was applied across the assembled layer throughout the thermal annealing process. The electric field in the copolymer layer depends on the thicknesses (d_i) and relative dielectric constants of the capacitor layers (ϵ_i) and is given by:

$$E_{\text{copolymer}} = \frac{1}{d_{\text{copolymer}} + \sum_i \frac{d_i}{\epsilon_{\text{copolymer}}}} \quad (4.1)$$

The applied field in the copolymer layer is shown in Figure 4.5 calculated using the dielectric constants shown in Table 4.2. An arithmetic mean of the constituent polymer blocks was taken for the effective copolymer dielectric constant.

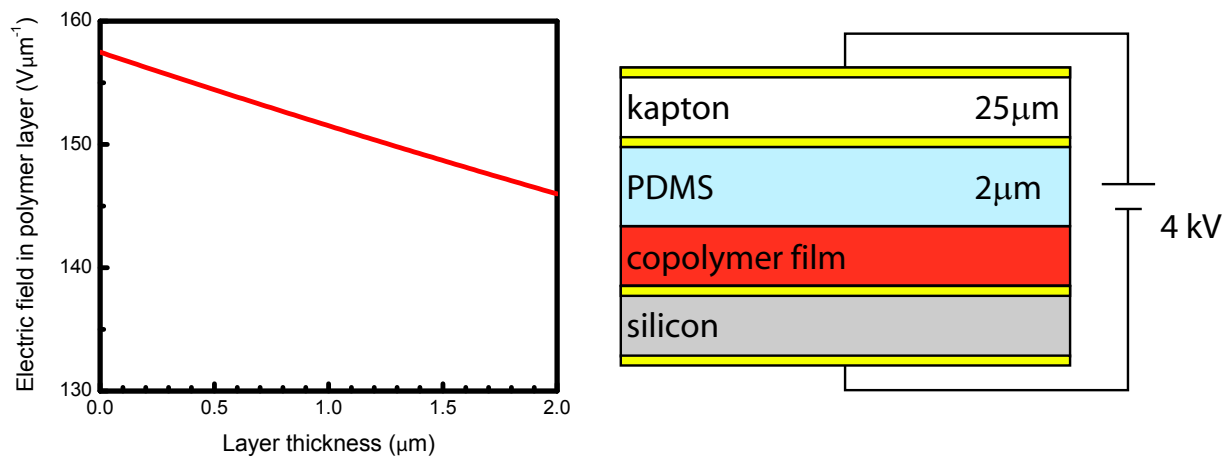


Figure 4.5: **Electric field in a thin copolymer film for a 4 kV applied field** Calculation for a simple parallel plate capacitor geometry from Equation 4.1 and dielectric constants shown in Table 4.2

Table 4.2: Measured dielectric constants at 1 kHz

Polymer	Relative dielectric constant (ϵ_r)
Kapton (CR) ^a	3.3±0.3
poly(dimethylsiloxane) PDMS ^b	2.6±0.2
poly(fluorostyrene) PFS	3.0±0.3
poly(lactic acid) PLA	3.4±0.3
poly(styryltriarylamine) PSTA	3.6±0.4

^a DuPont data sheet value 3.45

^b Dow Corning 100 Hz data sheet value 2.75

Measurements of dielectric constants were made by capacitance measurements of simple parallel plate capacitors defined by crossed electrodes spanning a smooth dielectric film as shown in Figure 4.6. Modelling the device as a simple parallel plate capacitor with area A and spacing d , and assuming linear dielectric material response allows calculation of relative dielectric constant (ϵ_r) according to $\epsilon_r = (Cd)/(A \epsilon_0)$.

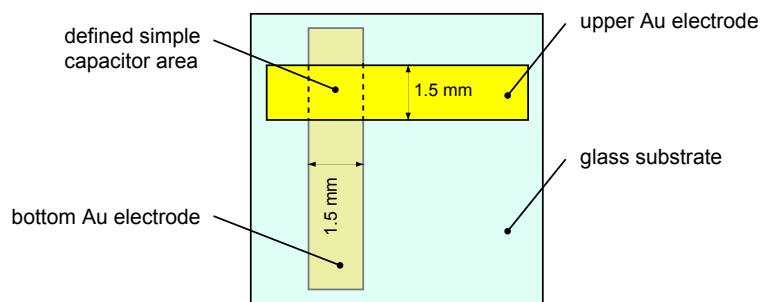


Figure 4.6: **Crossed electrode capacitor design for dielectric measurements of thin films.** The 40 nm thick gold electrodes were deposited on an insulating glass substrate by thermal evaporation through a 3 mm $\times$ 1.5 mm shadow mask using a 2 nm chromium adhesion layer. The material film is deposited on top of the first electrode, followed by evaporation of the top electrode on the film surface at 90° to the underlying electrode. The area defined by the overlap of the two electrodes is 2.25 mm²

4.6 Electrodeposition of Ti(IV)oxide

The protocol for electrodeposition of TiO₂ used in this work was adapted from that developed by Kavan *et al.* for anodic hydrolysis of Ti(III) chloride [9]. The deposition was performed from a 0.2 M aqueous TiCl₃ at pH 2.7, containing 20 %_{vol} methanol (Laboratory reagent grade $\geq$ 99.5 %). The electrolyte was prepared from $\sim$ 10 %_{mass} titanium (III) chloride solution in HCl (Sigma-Aldrich) by drop-wise addition of a 20 %_{mass} Na₂CO₃ aqueous solution. All solutions were continuously purged with nitrogen during preparation and electrochemical deposition at room temperature. The working electrode (anode) was held at 0 V vs Ag/AgCl in a standard three-electrode cell with a platinum wire counter electrode using a CH Instruments potentiostat (Figure 4.7).

In the deposition mechanism proposed by Kavan *et al.* the rate of anodic Ti_(aq)³⁺ oxidation is controlled by a rapid hydrolytic pre-equilibrium (Equation 4.2), followed by the oxidation of thus formed TiOH²⁺ intermediate to Ti(IV) oxide species (Equation 4.3) [10]. The Ti(IV) oxide deposits are likely to consist of partly dehydrated (cross-linked) polymeric Ti(IV) hydroxide, containing both terminal and bridged OH groups (Figure 4.8) [11].



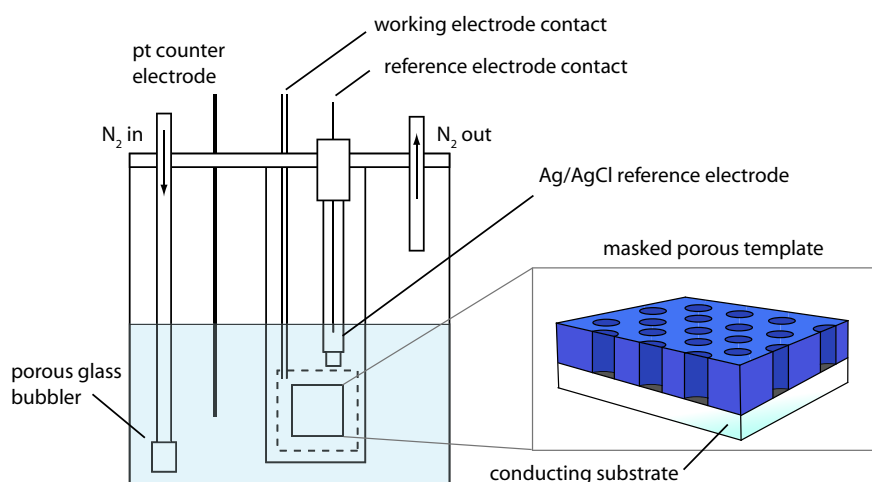


Figure 4.7: **Schematic of a 3-electrode cell used for templated electrochemical deposition of Ti(IV) oxide.** The deposition area was defined by Kapton masking tape.

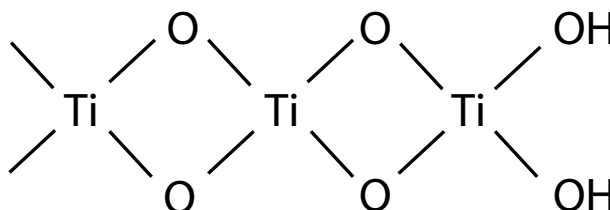
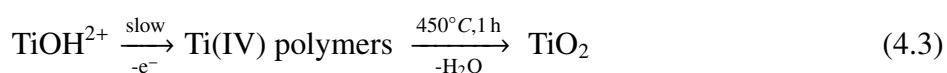


Figure 4.8: **Polymeric Ti(IV) hydroxide deposits from anodic oxidative hydrolysis of Ti(III) chloride solution [9].**



The final stage annealing at 450 °C is required to dry and crystallize the as-deposited amorphous Ti(IV) oxide material into TiO₂. A mass loss of 24 % and a volume reduction of ~ 30 % was reported for the thin film deposits during high temperature treatment. The resulting crystalline TiO₂ adopted the anatase polymorph.

4.7 Electrodeposition of Platinum

Platinum metal was deposited potentiostatically at room temperature with the working electrode at +0.1 V in a standard 3-electrode cell with Ag/AgCl reference and platinum wire counter electrode [12]. The electrolyte was a 20 mM hexachloroplatinic acid solution containing 20 %_(vol) methanol.

4.8 DSSC Device Assembly

4.8.1 TiCl₄ surface treatment

Before construction of solar cell devices, the structured TiO₂ arrays were subjected to a standard surface treatment developed for use in nanoparticulate mesoporous films [13]. A 2 M TiCl₄ aqueous solution was prepared over an ice bath to prevent precipitation of TiO₂. The stock solution was stored in the freezer. The TiO₂ electrodes were immersed in freshly prepared 40 mM TiCl₄ solution and placed on a hot plate at 80 °C for 30 minutes. During this process there is a nucleation of nanometer sized TiO₂ particles on TiO₂ films, increasing the active surface area and material purity of the surface layer [13]. The samples were rinsed with deionized water and annealed on a hot plate at 500 °C for 45 minutes in air.

4.8.2 Solid-state DSSC device assembly

FTO coated glass substrates were used as the transparent electrode for solid-state dye-sensitized solar cells. In order to pre-define the solar cell active area and to facilitate electrical probe contact, strips of the conducting oxide layer were etched away along one edge of each substrate. Firstly, zinc powder was evenly spread over pre-cut FTO strips, covering the edge regions left exposed by a Scotch[®] tape mask (Figure 4.9a). A 4 M HCl solution was then spread over the Zn powder followed by abrasion for ~ 5 s with a cotton tip along the length of the exposed strip. The samples were rinsed with excess DI water and dried in a stream of nitrogen. The patterned substrates were cleaned by sequential sonication in Hellmanex soap (2 % in water), acetone and isopropanol followed by 5 min O₂ plasma etching. A compact TiO₂ layer was deposited over the whole substrate by spray pyrolysis deposition

at 450 °C (Figure 4.9b). Structured titania arrays were subsequently grown electrochemically onto the TiO₂ coated substrates.

After TiO₂ surface treatment the samples were cooled to 80 °C before soaking in 0.5 mM solution of a ruthenium complex sensitizer, termed Z907, overnight or in a 0.5 mM solution of an indolene dye, termed D149, for 10 min. The dyed films were rinsed briefly in acetonitrile and left to dry for several minutes in air. Solid-state dye-sensitized solar cells were fabricated using the organic molecular hole-transporter 2,2',7,7'-tetrakis(N,N-di-methoxyphenyl-amine)-9,9'-spirobi-fluorine (Spiro-MeOTAD) [14, 7]. The material can be infiltrated into, dye-sensitized TiO₂ arrays from a concentrated solution. For example, a 1 cm² sample was covered with 15 μ l of Spiro-MeOTAD solution (100 μ l chlorobenzene, 18 mg Spiro-MeOTAD, 1.75 μ l of tertial-butyl pyridine and 3.75 μ l of Lithium-TFSI ACN solution (170 mg/ml)) for 40 s before spin-coating at 2000 rpm for 30 seconds to remove excess material [15]. Each 12 $\times$ 12 mm substrate was coated with a uniform active layer, with three distinct device pixels defined by 200 nm thick silver counter electrodes deposited by high vacuum thermal evaporation through a shadow mask. A schematic view of the solid-state device construction is shown in Figure 4.10.

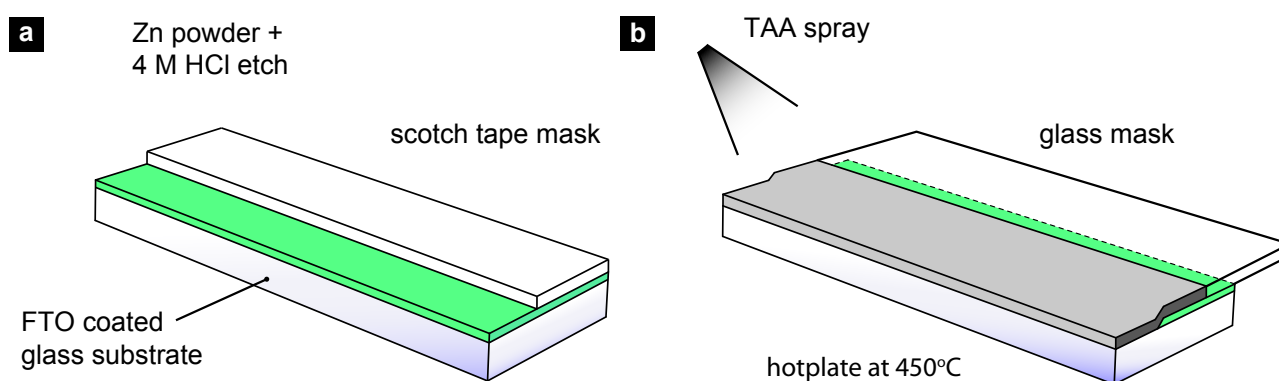


Figure 4.9: **Geometric pre-patterning of solar cell substrates.** (a) Zinc/HCl etching of FTO conducting oxide layer on glass patterned using Scotch[®] tape masks. (b) Spray pyrolysis deposition of $\sim$ 50 nm TiO₂ compact underlayers onto pre-patterned FTO glass substrates. Large substrate plates can be patterned in this way before cutting into the desired single substrate pieces.

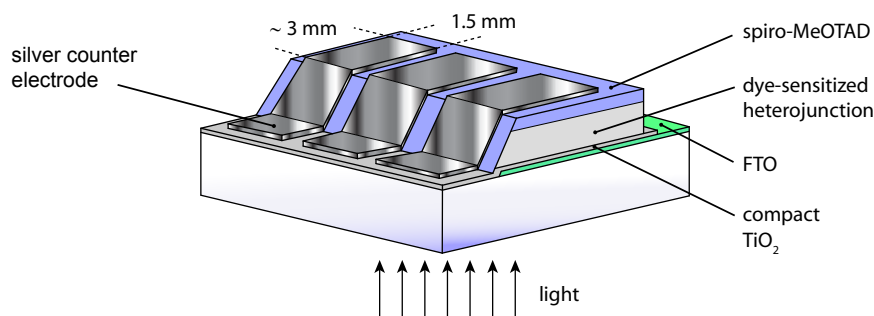


Figure 4.10: **Solid state solar cell device construction schematic.** Each device pixel area is defined by the overlap of silver counter electrode and the non-etched FTO substrate region.

4.8.3 Liquid electrolyte DSSC device assembly

Liquid electrolyte DSSCs were fabricated by first immersing the nanocrystalline titania arrays in an acetonitrile:*tert*-butyl alcohol (1:1 vol:vol) solution of 0.5 mM of N719 ruthenium complex sensitizer overnight. Counter electrodes were fabricated by platinizing pre-drilled FTO substrates with 50 mM hexachloroplatinic acid solution in isopropanol and subsequently heating to 450 °C for 15 minutes. The dyed working electrodes were rinsed briefly in acetonitrile, dried in air for 5 minutes and laminated together with the platinized counter electrodes with a ‘hot-melt’ 50 μm Surlyn^{iv} frame spacer. The assembly was pressed briefly on a hotplate at 100 °C (in a nitrogen atmosphere) in order to seal the cell. A schematic diagram of this construction is shown in Figure 4.11. The two electrodes are made from rectangular substrates crossed at 90° in order to facilitate electrical contact. The cells were filled with an iodide/triiodide based non-volatile liquid electrolyte, termed ‘Robust’ (0.8 M PMII, 0.15 M iodine, 0.1 M GuNCS, and 0.5 M NMBI in 3-methoxypropionitrile) by vacuum back filling [16]. A 10 μl drop of electrolyte is first placed onto the pre-drilled counter electrode hole. An inverted funnel connected to vacuum is then placed over the device causing evacuation of the otherwise sealed inner chamber. On release of the applied vacuum, the electrolyte is drawn into the chamber by the incoming air flow. The hole was sealed with polyimide tape (DuPont). The device area under illumination was defined by a 0.13 cm² square black optical mask.

^{iv}<http://www.dupont.com/industrial-polymers/surlyn>

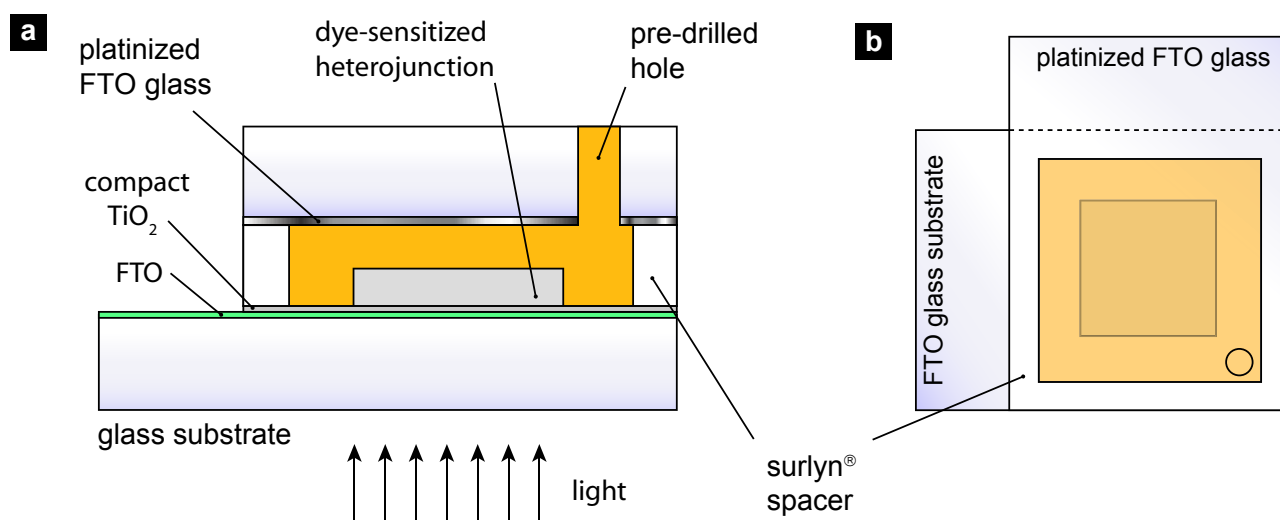


Figure 4.11: **Liquid electrolyte solar cell device construction schematic.** (a) Cross section and (b) top view.

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Nanowire Arrays

The following Chapter describes the successful electric field alignment of poly(4-fluorostyrene)-*b*-poly(D,L-lactide) (PFS-*b*-PLA) films to produce vertical cylindrical PLA microdomains that span the full film thickness to a conducting substrate. Mesoporous PFS templates were formed by mild degradation of the polylactide phase using dilute aqueous base. The templates were used to direct the electrochemical deposition of platinum, TiO₂ and Cu/Cu₂O nanowires. Freestanding nanowire arrays were observed after removal of the template by either simple dissolution of the PFS or by UV ozone etching. The annealing time, the electric field strength used to align the block copolymer films, and the template removal method are shown to influence the freestanding nanowire arrays.

This work is published in the paper ‘Freestanding nanowire arrays from soft-etch block copolymer templates’ in the journal *Soft Matter* [1]. These and additional results are presented below.

5.1 Introduction

In order to create viable copolymer templates for nanowire array templating, it is necessary to form cylindrical microdomains that span the entire film thickness from the underlying substrate to the film surface. To this end, Thurn-Albrecht et al. applied an electric field to a cylinder forming polystyrene-*b*-polymethylmethacrylate (PS-*b*-PMMA) block copolymer film confined in a parallel plate capacitor geometry to align the PMMA cylinders perpendicular to the substrate. The template was subsequently used in the first demonstration of an electrochemically grown nanowire array in a nanoporous block

copolymer template [2].

In the approach described by Thurn-Albrecht *et al.* the minority component PMMA was removed by UV photodegradation. This step has the unavoidable side-effect of crosslinking the surrounding polystyrene matrix phase, creating an insoluble nanoporous membrane. Any aggressive degradation such as this has the drawbacks of (i) limiting the choice of suitable matrix (template) materials and (ii) potentially compromising the integrity of the templated structures upon removal of the template. The following report describes a system amenable to a ‘soft’ chemical etch of the sacrificial component. Specifically, a cylinder forming PFS-*b*-PLA block copolymer in which the minority PLA component is removed by a mild hydrolytic degradation without altering the matrix phase [3, 4, 5]. Thin (~ 50 nm) films of the related polymer PS-*b*-PLA have been used as lithographic etching masks for the underlying substrate [4]. However these films did not have a fully-penetrating pore structure and were limited to an aspect-ratio of around 1. High aspect ratio, standing nanowire arrays can be grown electrochemically in the aligned PFS-*b*-PLA templates and subsequent removal of the template can be accomplished by simple dissolution. Figure 5.1 shows a schematic representation of the template fabrication and nanowire growth procedure.

While the long-term goal is to produce freestanding arrays or specific functional materials such as inorganic semiconductors, the method is first demonstrated with a model electrodeposition system. Platinum is a convenient choice; firstly it is relatively easy to electrodeposit, and secondly its high conductivity make it easy to view with high resolution using SEM imaging. Preliminary results are also presented here using an electrochemical protocol for Cu_2O and TiO_2 , p-type and n-type semiconductors respectively. The electrodeposition of TiO_2 is described in chapter 4 and 9 relating to its application in dye-sensitized solar cells.

5.2 Experimental

The two PFS-*b*-PLA block copolymer samples used in this Chapter are termed MHI10 and MHI42 (synthesis detailed in Chapter 4). The overall molecular weight of MHI10 and MHI42 are 30 kg/mol (PLA volume fraction $f_{\text{PLA}} = 33\%$) and 41 kg/mol ($f_{\text{PLA}} = 35\%$).

Thin films of copolymer (100 nm to 1 μm) were prepared by spin coating from 5-10 %_{wt} solutions

in toluene onto gold coated silicon or TiO_2 coated FTO glass substrates. Selected Au substrates were first coated with a self-assembled monolayer of 1-undecanethiol (see chapter 4). The films were annealed above the glass transition temperatures of each block ($T_g^{\text{PFS}} = 103^\circ\text{C}$ and $T_g^{\text{PLA}} = 57^\circ\text{C}$) under a nitrogen atmosphere for up to 35 h before cooling to room temperature over ~ 3 h. External electric fields of up to $150 \text{ V}\mu\text{m}^{-1}$ could be applied during annealing in the plate capacitor geometry shown schematically in Figure 5.1a. The field was maintained until the sample returned to room temperature.

The PLA minority component of the block copolymer was selectively degraded by immersing the films in $0.05\text{M NaOH}_{(\text{aq})}$ solutions containing 40 %_(vol) methanol. Dry etching of the polymer template was achieved by 15 min exposure to a 172 nm UV source (SUS-128 excimer radiation system, Ushio Europe B.V.) or 5 min exposure to oxygen plasma (Diener Electronic Femto Plasma System 100W, 4kHz). An etching solution of bromine in methanol (80:1 wt bromine : methanol) was used to etch the underlying Au substrate layer to release the film either before or after the PLA degradation. This allowed the imaging of the underside of selected template films.

5.3 Templating of Freestanding Nanowire Arrays

The molecular data for PFS-*b*-PLA in combination with the thin film morphological results presented below are consistent with an ordered block copolymer containing cylinders of PLA in a matrix of PFS.

TappingModeTMSFM was used to view the surface morphology of copolymer films annealed at 180°C in the capacitor sandwich with and without the applied voltage (Figure 5.2a,b), as well as with a free (unconfined) surface (Figure 5.2c). Selective removal of the PLA phase before imaging provides topographic features visible in the SFM height and phase images indicative of the copolymer phase morphology.

The surface of the electric field annealed sample shows an array of hexagonally ordered pits indicative of successful alignment of cylindrical PLA microdomains perpendicular to the substrate ($C_\perp$). Without application of the electric field the surface is featureless, consistent with a wetting layer surface reconstruction of the PFS phase preferentially segregated to the PDMS top electrode.

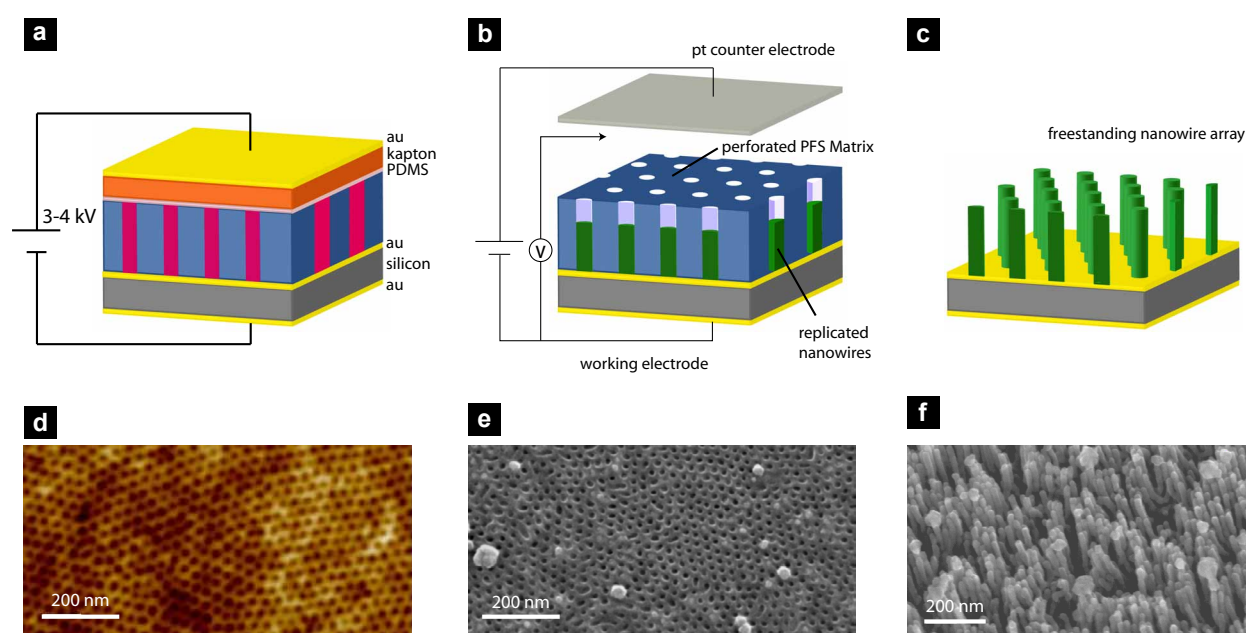


Figure 5.1: Schematic illustration of freestanding nanowire array fabrication from aligned sacrificial cylinder forming block copolymer films. (a) Annealing of PFS-*b*-PLA film above glass transition temperature in a parallel plate capacitor with removable top electrode and an applied electric field of up to $150 \text{ V}\mu\text{m}^{-1}$. The standing cylinder array is frozen in place on cooling to room temperature. (b) voids left by removal of the PLA phase are electrochemically replicated from the underlying conducting substrate. (c) PFS supporting matrix is removed by UV ozone etching to leave a freestanding nanowire array. (d) tapping mode SFM height image of porous PFS template after PLA removal. (e) surface SEM of the electrochemically filled template. (f) freestanding nanowires ($\text{Cu}_2\text{O}/\text{Cu}$ mixed phase) after UV ozone etching of PFS matrix.

The film annealed with a free upper surface showed a ‘terraced’ morphology of discrete islands with step height of 22 nm. These observations, discussed in detail later, are consistent with a PLA cylinders lying parallel to the substrate ($C_{\parallel}$) in the bulk of the film.

The aligned porous PFS templates were used as templates for electrochemical deposition using a protocol for Cu_2O (summarized in figure 5.1)ⁱ. A typical SEM image of a PFS-*b*-PLA film which was aligned at $150 \text{ V}\mu\text{m}^{-1}$ and filled electrochemically after removal of the PLA component is shown in Figure 5.1e. The nanopores in the PFS film are clearly visible and overgrowth of the electroplated material is evident as bright florets in some areas of the film. A freestanding array of nanowires remains after removal of the PFS template by UV ozone etching for 30 minutes (Figure 5.1f).

ⁱWhile the templated nanostructures were successfully replicated using a protocol for crystalline Cu_2O [6], XRD revealed the co-existence of copper (in both structured and non-structured deposits) indicating that the deposition procedure was not optimized from a material perspective. No further functionality was investigated for the Cu_2O arrays.

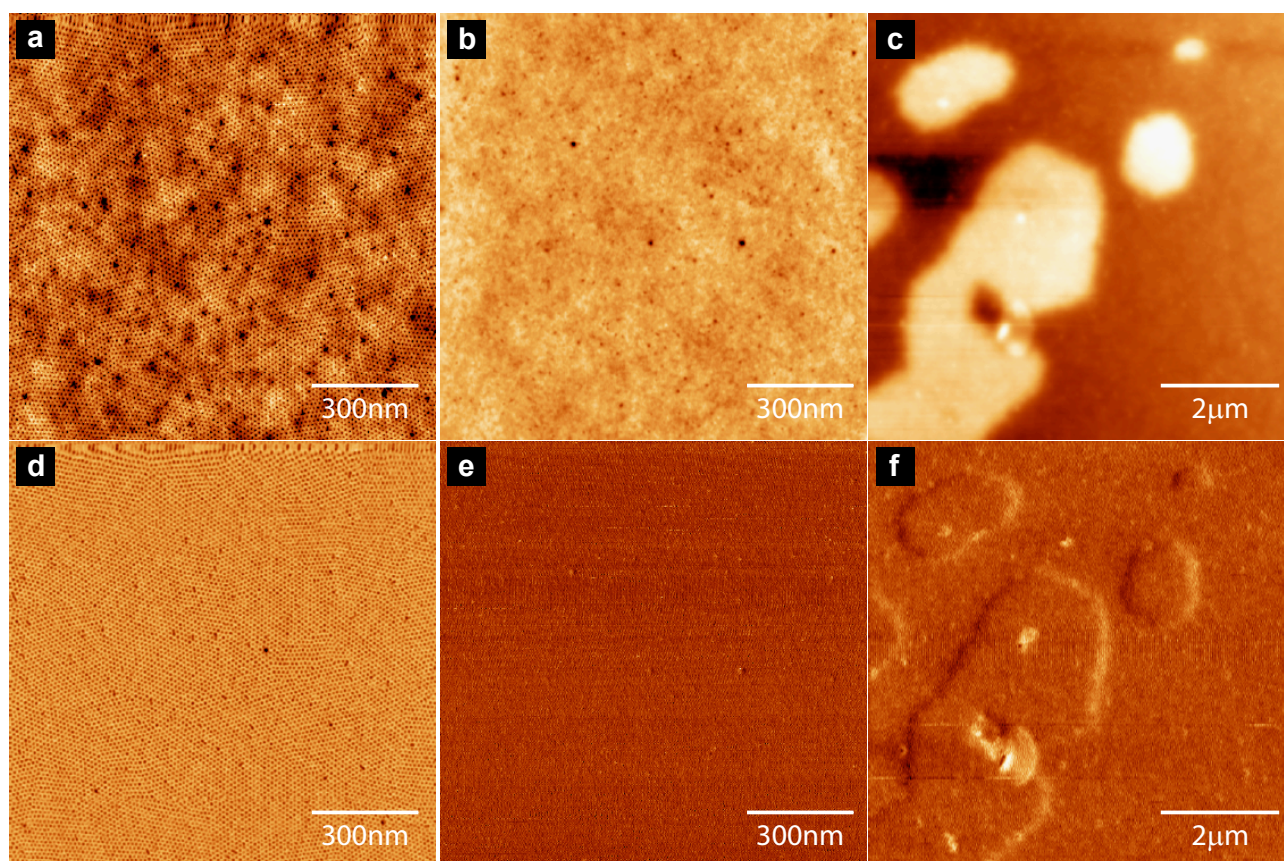


Figure 5.2: **Electric field alignment of cylinder forming PFS-b-PLA copolymer films (a,c)** TappingModeTMSFM height and phase images of a porous PFS template annealed at 180 °C for 35 h with $120 \text{ V } \mu\text{m}^{-1}$ applied electric field after removal of PLA phase. **(b,e)** Equivalent images for an identical film annealed in the same parallel plate capacitor set-up without the applied electric field. **(c,f)** lower magnification view of terrace formation of an identical film annealed with a free surface, terrace height $22 \pm 2 \text{ nm}$. Film thickness 240 nm in all cases.

Figure 5.3 shows a detailed analysis of the PFS template surface after electric field alignment. The image processing software ImageJⁱⁱ was used to analyse the average pore size of MHI42 visible in a surface SEM image. A threshold grey value was used to define the pore shape over the visible area which was used to measure the pore area distribution. An average diameter of $12 \pm 1 \text{ nm}$ was calculated assuming a circular pore. A Fourier transform was used to determine a centre-to-centre distance of $21 \pm 3 \text{ nm}$.

Figure 5.4 shows the detailed surface morphology of a $\sim 70 \text{ nm}$ film annealed at 180 °C for 35 h with no applied field. There is a clear wetting layer of PFS at the Au substrate contact, which results

ⁱⁱ Available free online at <http://rsb.info.nih.gov/ij/>

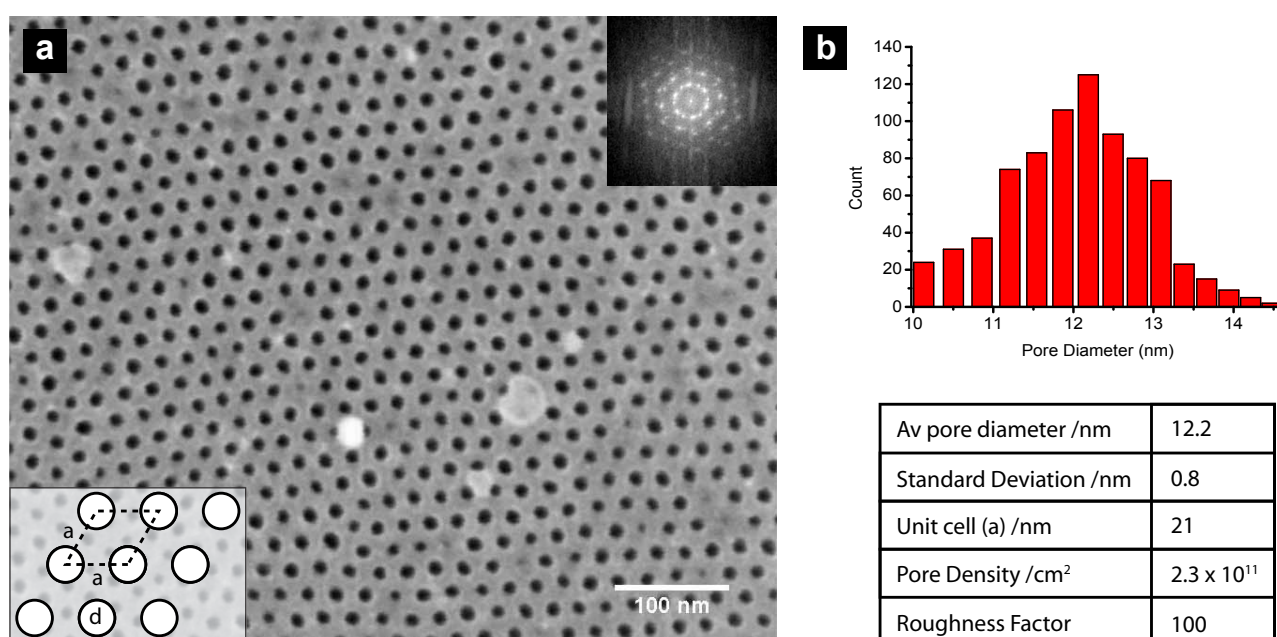


Figure 5.3: Pore size analysis (a) Surface SEM of porous PFS template aligned with a $120 \text{ V } \mu\text{m}^{-1}$ electric field applied at 180°C for 35h after removal of PLA phase. The inset diagrams show the expected HEX unit cell for viewing end-on cylinders, and a Fourier transform of a single domain in order to extract centre-to-centre spacing of $21 \pm 3 \text{ nm}$. The surface density of pores (assuming perfect HEX order is $2.3 \times 10^{11} \text{ cm}^{-2}$) (b) Histogram and summary of pore diameters analyzed using ImageJ software show an average pore diameter (d) of 12.2 nm with standard deviation (fitting to Gaussian distribution) of 0.8 nm . The roughness factor is the calculated enhancement in exposed polymer surface per micron in template thickness compared to the flat substrate (assuming the pores penetrate to the substrate). The polymer film was imaged without additional conductive coating.

in a ($C_{||}$) lying cylinder morphology throughout the film. The strength of the electric field is sufficient to overcome this surface field that generally favours microdomain alignment parallel to the substrate [7]. The relatively low dielectric contrast between PFS ($\epsilon_{\text{PLA}} = 3.1$) and PLA ($\epsilon_{\text{PLA}} = 3.4$) means that high strength electric fields are required to achieve full alignment.

Further detail of the copolymer morphology in the region of the Au substrate contact can be obtained by imaging the underside of a film released from the substrate and turned over. The release is achieved by under-etching Au substrate in a bromine:methanol etching solution. Once again, removal of the PLA phase after release provides topographic features indicative of the copolymer phase which can be seen in SEM and SFM height images (Figure 5.5). After under-etching of the Au substrate layer, the upper surface (Figure 5.5b,d) shows the expected hexagonal array of pores in both SEM

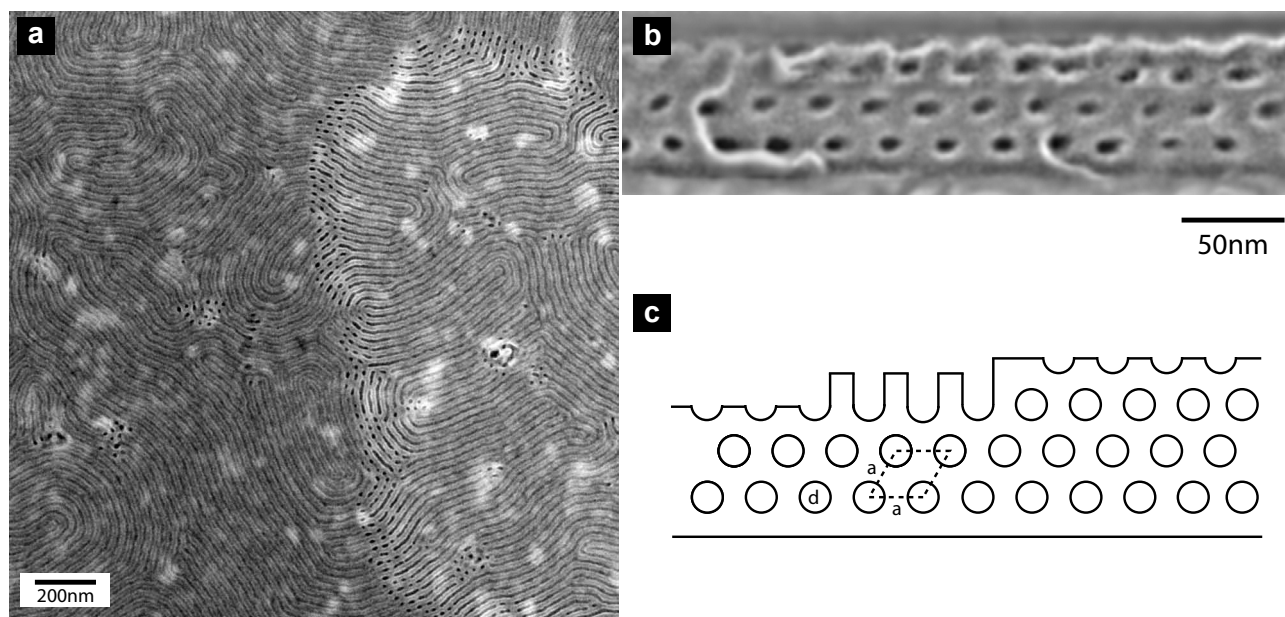


Figure 5.4: **Terracing in thin cylinder-forming films.** (a) Surface SEM of a PFS template annealed at 180 °C for 35 h with no applied field after removal of PLA phase. Open cylinders are visible on the upper surface indicative of a $C_{||}$ morphology (b) Cross sectional SEM of the same cryo-fractured film showing side-on view of $C_{||}$. (c) possible schematic representation of film cross section in the vicinity of a terrace step.

and SFM images, indicating that the electric field overwhelms the apparently weaker surface field at the PDMS contact. The etching solution clearly does not damage the polymer microstructure. The film underside (Figure 5.5a,c) has a degree of surface roughness making it difficult to determine the structure by SFM. However the SEM image shows more clearly a somewhat mixed morphology ($C_{||}$ and $C_{\perp}$) with open pores penetrating into the film bulk.

The morphology of the substrate contact layer apparent by direct imaging of the template can also be probed indirectly by imaging the electrochemically replicated pore structure after etching of the surrounding PFS. Figure 5.6a,b shows cross sectional images of electrochemically filled templates (with the PFS matrix still in place) in which the vertically aligned cylinders appear to penetrate the full thickness. If the PFS template is rinsed away by dissolution in toluene (Figure 5.6d) however, some of the (platinum) nanowires become detached from the substrate allowing imaging of the base structure. The standing wire sections are connected by a single horizontal wire, representative of a template with a single $C_{||}$ layer fully connected to the $C_{\perp}$ morphology in the layer bulk.

Films annealed for a relatively short period (14 h, compared to 35 h) at 150 °C have a mixed ($C_{||}$

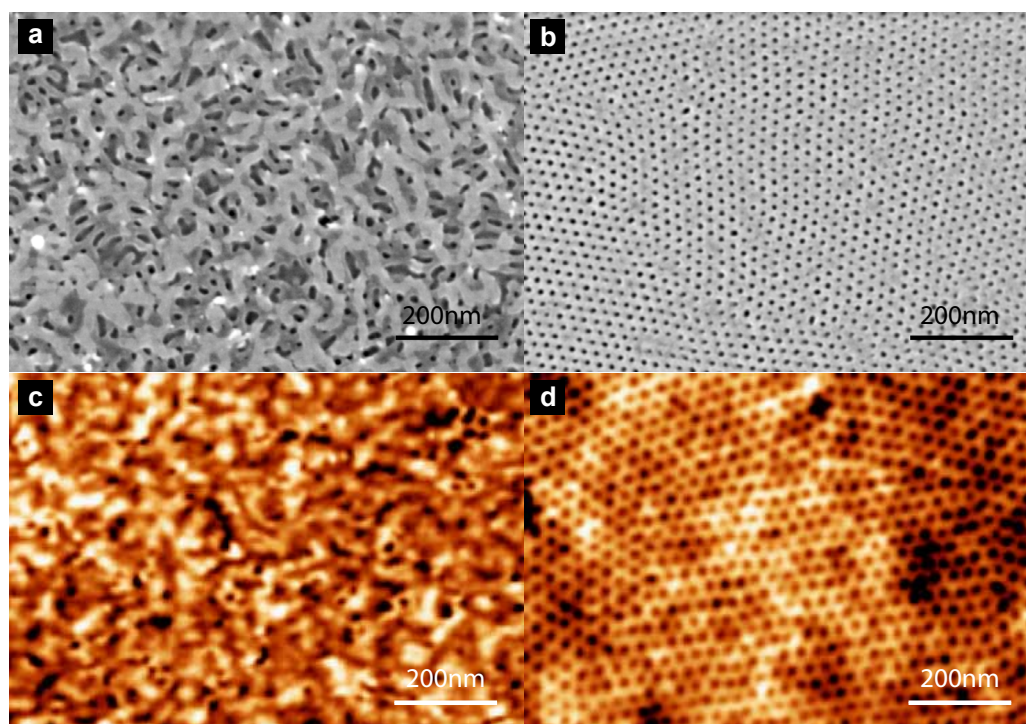


Figure 5.5: Underside and surface template morphologies after electric field alignment. (a) SEM of film underside morphology revealing a degree of $C_{\parallel}$ and $C_{\perp}$ alignment superposed with a degree of surface roughness. Pores can be seen penetrating into the bulk of the film. (b) Hexagonally ordered upper surface morphology indicating $C_{\perp}$ in the upper portion of the film. (c,d) equivalent films imaged with TappingMode™ SFM (height data shown). While the smooth upper surface in (d) can be imaged well the surface roughness and tip convolution make it difficult to resolve the underside morphology. 200 nm thick films were annealed for 35 h at 180 °C with an applied field of $120 \text{ V } \mu\text{m}^{-1}$, then were removed from Au substrates by under-etching with bromine:methanol (1:80 vol:vol) etch. The PLA component was removed in 0.05 M NaOH solution.

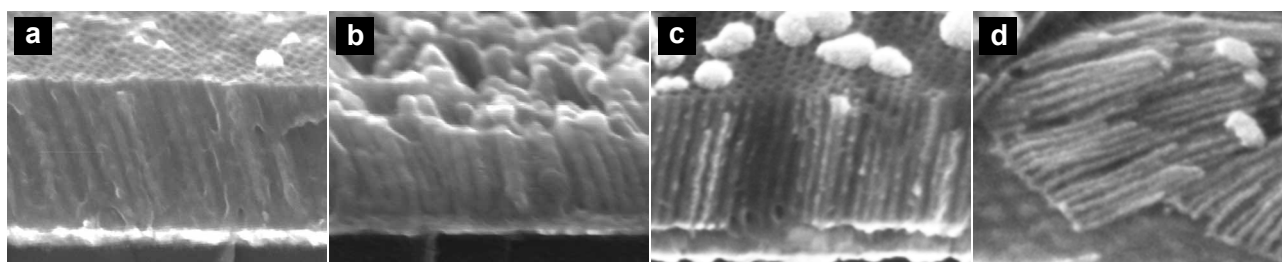


Figure 5.6: Thin film vertical alignment and replication. (a) After 35 h at 150 °C under a $150 \text{ V } \mu\text{m}^{-1}$ applied field the template is well aligned throughout the cross section bulk. (b) UV ozone removal of the template exposes freestanding Cu_2O wires (PFS removal is incomplete in this case). (c,d) equivalent images for replication in platinum. Here, the PFS template was removed by rinsing in toluene, causing many wires to detach from the Au substrate. Many wires are connected by a single parallel cylinder layer at the substrate. Viewing angle 45 °, image width 500 nm.

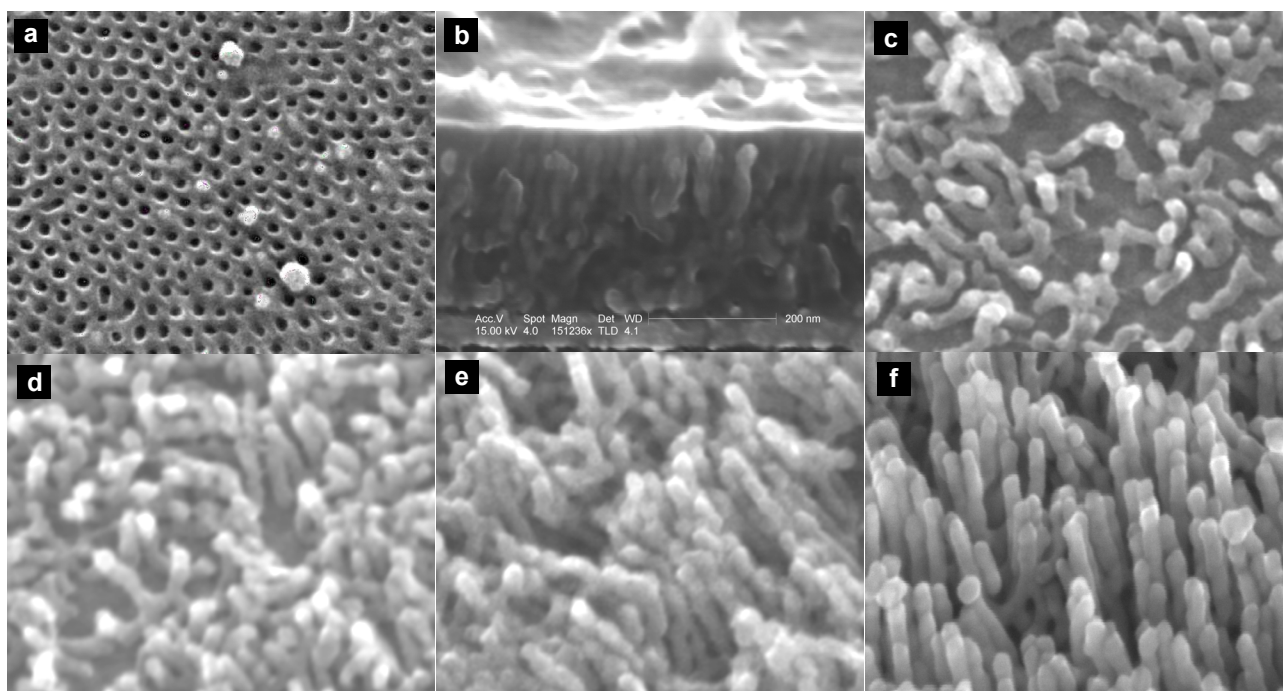


Figure 5.7: SEM study of Cu_2O nanowire growth progression in a partially aligned template. (a) Surface SEM of a 200 nm porous template annealed for 14 h at 150°C under a $150\text{ V}\mu\text{m}^{-1}$ applied field. The template is electrochemically filled with Cu_2O which can be seen growing out of the pores in places. (b) Cyro-fracture cross section revealing vertical alignment and order only in the upper region of the film while the lower half in contact with the substrate remains unaligned. After removing the PFS template by UV ozone etching, the initial deposition (c,d) is apparently disordered; many of the cylinders lie parallel to the Au substrate and have multiply branched structures. Further growth (e,f) reveals connectivity into the upper portion of the template with vertically aligned and ordered pores. This sequence arises from a deposition gradient across the unmasked template area in the electrochemical cell. Image width 500 nm.

and $C_\perp$) morphology that persists further into the layer from the substrate. Figure 5.7a,b shows a surface and cross sectional SEM view of such a film showing HEX pores on the upper surface, but a $C_\perp$ only in the upper portion of the layer. The apparently tangled structure in the lower portion of the film is fully porous, and may be electrochemically replicated - a process shown in gradual stages in Figure 5.7c-f. A branched and tangled structure at the wire base evolves through the film thickness into the fully aligned $C_\perp$ structure found in the upper region of the film.

The tangled branch structure persists further into the layer under weaker electric fields. While a $150\text{ V}\mu\text{m}^{-1}$ field applied for 14 hours produces well aligned $C_\perp$ structures in the upper portion of the film (Figure 5.7b), identical annealing with only $80\text{ V}\mu\text{m}^{-1}$ produces branched structures shown in

Figure 5.8 throughout the film. In this instance only the very top part of the film showed the hexagonal ordered pores consistent with a $C_{\perp}$ aligned morphology.

The branched and tangled structures visible after relatively short annealing times are unsurprising when we consider the initial microphase morphology of the spin coated film. Figure 5.9a shows an SEM image of a porous PFS film spin-coated from a 10 % toluene solution, followed by selective etching of the PLA component (identical features were observed in films with an additional drying stage for 1 h at 60 °C). The mixture of $C_{\parallel}$ and $C_{\perp}$ indicates that the copolymer is well phase separated after the solvent drying process (complete after several seconds). The density of $C_{\perp}$ pores in Figure 5.9a is $1010\mu\text{m}^{-2}$, compared to $1990\mu\text{m}^{-2}$ seen at the surface of the electric field aligned template shown in Figure 5.3a. Therefore roughly half of the PLA domains meet the surface in a perpendicular orientation. There is no long-range ordering of the cylindrical microdomains, with grains extending over some 3 to 5 centre-to-centre spacings. Asymmetric affinity of the PFS to the substrate does not have time to orient the microphase-separated morphology parallel to the layer. A cryo-fractured SEM cross section of the film (Figure 5.9b) shows that the pore structure penetrates into the film bulk with no preferential direction. The pore structure can be electrochemically replicated in platinum (Figure 5.9c) confirming a continuous porosity through to the underlying Au substrate. Detail of the substrate contact morphology can be seen in the Pt replicated structures in Figure 5.10. This negative replica of

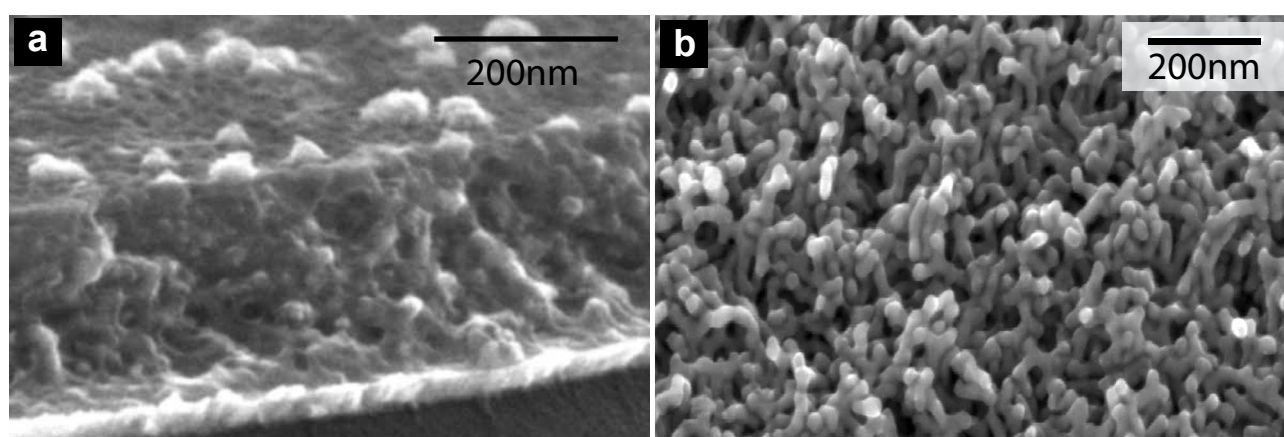


Figure 5.8: Porous templates after annealing for short times under an electric field. (a) Cross sectional SEM image of a porous template annealed for 14 h at 150 °C under an $80\text{ V}\mu\text{m}^{-1}$ applied field. The template is electrochemically filled with Cu_2O which can be seen growing out of the pores in places. The upper surface of the film has a hexagonally ordered pore structure (not shown) (b) tangled growth consistent with unaligned cylinder phase throughout the film layer in (a).

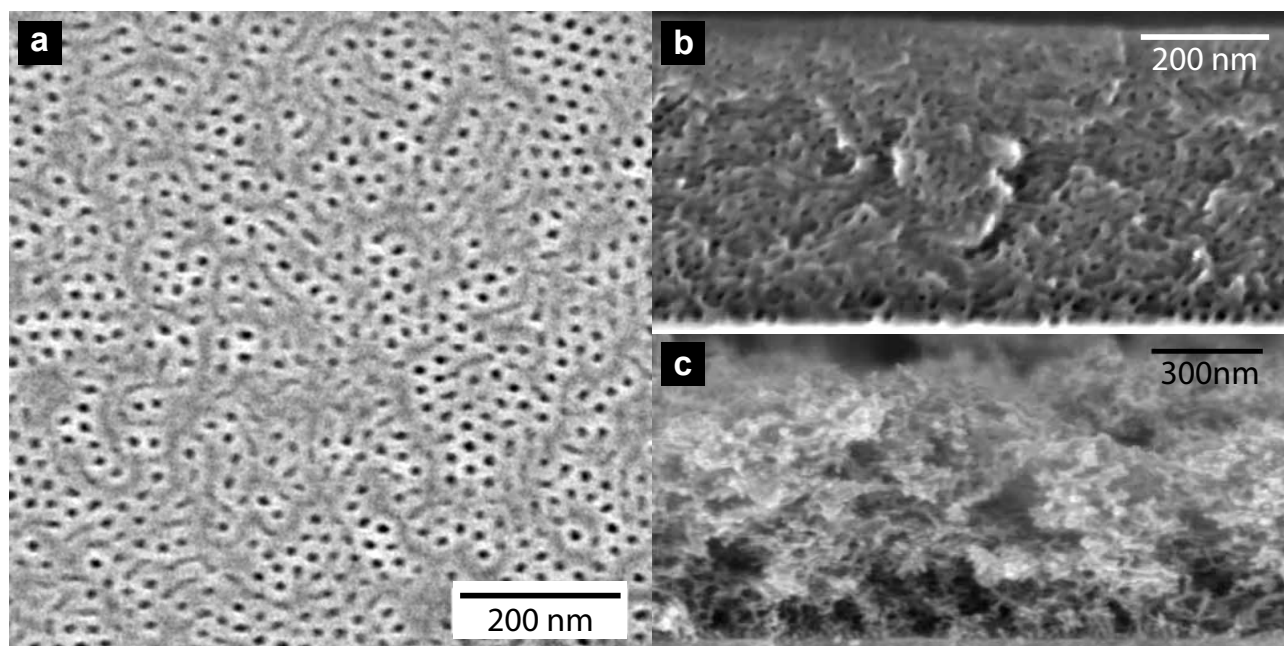


Figure 5.9: **PFS-*b*-PLA film morphology after spin-coating.** (a) Surface SEM of a porous PFS film seen after spin coating from a 10 % solution in toluene (the PLA component has been removed). A mixture of hexagonally packed pores and lying cylinders are apparent at the free surface. (b) cryo-fractured cross section shows a ‘tangled’ pore structure in the bulk of the film. (c) electrochemical replication in Pt and dissolution of the PFS matrix in toluene.

the PFS structure implies that the morphology at the substrate is similar to that seen at the free surface in Figure 5.9a.

These results suggest that the mechanism of electric field alignment is such that cylinders near the upper surface (where the surface field is presumably weaker) are first to align with the electric field. In the region of the substrate, the domains are affected by both competing surface and electric fields. Only with time does the electric field dominate complete $C_{\perp}$ alignment in all but the surface contact layer.

5.4 Templating of thick nanowire arrays

The electric field alignment of thicker PFS-*b*-PLA films (> 500 nm) on Au at 180 °C (35 h) resulted in ordered cylinders which were tilted with respect to the vertical electric field vector, shown. The surface morphology is again a hexagonally ordered array of pores. Figure 5.11 reveals that the cylinders

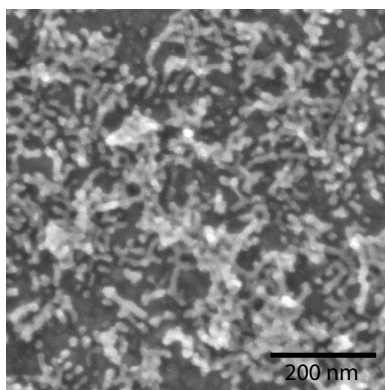


Figure 5.10: **Substrate contact layer of PFS-b-PLA template replicated in Pt.** Sonication in toluene of the platinum growth in Figure 5.9c causes all but the base layers of the nanostructures to fracture from the Au substrate. The morphology of the remaining Pt deposits seen in this surface SEM reveal the pore structure at the substrate contact. There are ‘dots’ and cylinders of replicated material, which show branching into a quasi-continuous pore structure seen in the full replication.

are tilted away from the vertical at an increasing angle as the substrate layer is approached ($\sim 40^\circ$ in the bulk to as much as 70° in the substrate layer).

The highest degrees of vertical alignment was achieved on substrates pre-treated with a self-assembled layer of undecanethiol. The water contact angle on these surfaces is 105° . Figure 5.12 shows a 800 nm thick template aligned on such a surface-treated substrate with and without the supporting PFS template, removed by UV ozone etching. The pores and platinum nanowire replicates are extremely well aligned with the vertical electric field vector throughout the layer. The underside of the wire array (Figure 5.13c) indicate only a single contacting $C_{\parallel}$ layer connecting the wires at the substrate. Xu *et al.* studied the progression of cylindrical alignment under electric fields in thin films using small-angle neutron scattering and 3D TEM tomography in a PS-*b*-PMMA copolymer and also observed either vertical or tilted alignment depending on the degree of microphase separation and order in the starting film [8]. They suggested that starting from a ‘poorly ordered’ state (that is, phase separated but not organized), local domain orientation is biased by a surface field that initially drove $C_{\parallel}$ orientation in the vicinity of the substrate. With further annealing, the electric field distorts and rearranges individual microdomains in relatively small grains parallel to the applied field direction and results in $C_{\perp}$ throughout the layer. Where an initial $C_{\parallel}$ state exists over larger ordered grains, the cylinders were observed to break up into spherical microdomains. With time the spheres deformed

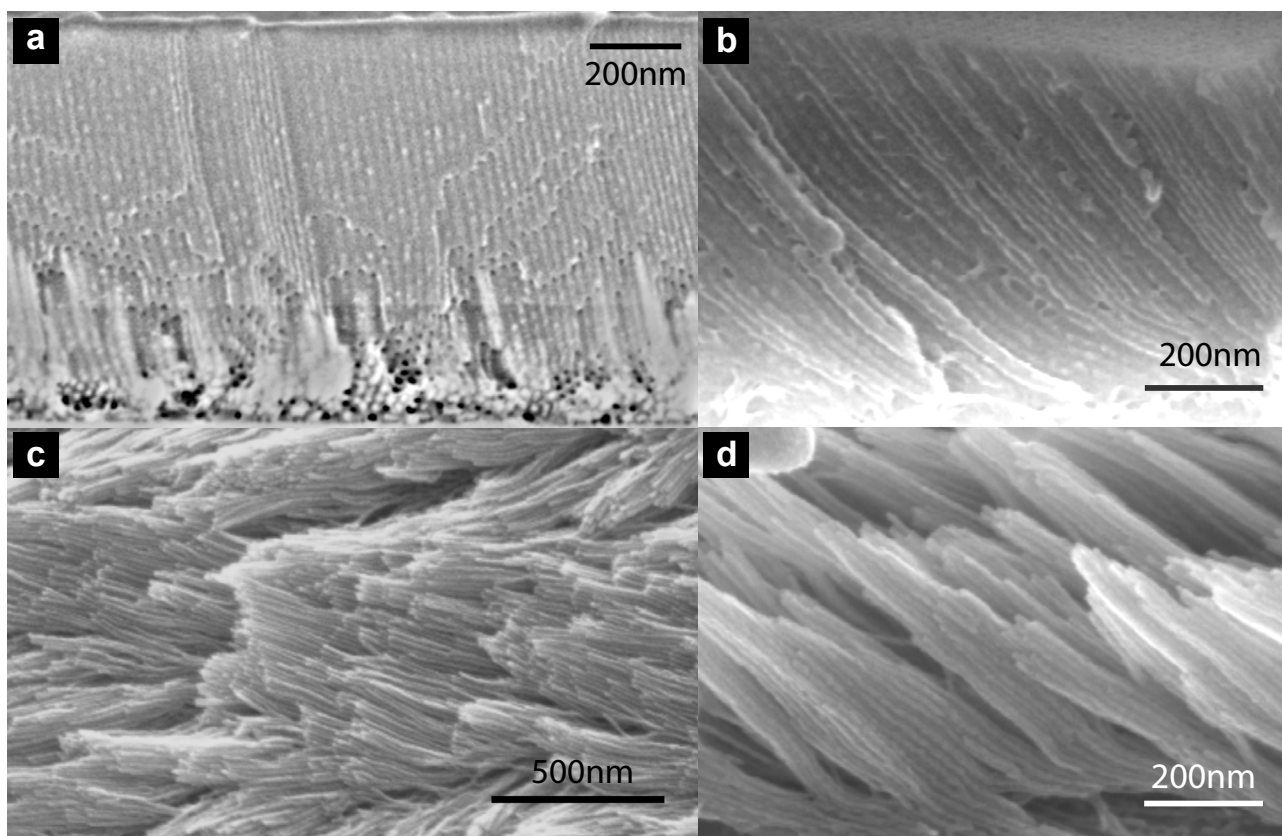


Figure 5.11: **Alignment and replication of thick templates on Au substrates (SEM).** (a,b) Two cross sections of a 800 nm porous template prepared after 35 h at 180 °C with an applied field of $120 \text{ V } \mu\text{m}^{-1}$. In (b) the cylinders are well ordered and aligned at 40° with respect to the surface normal in the upper portion of the film. In (a) the cylinders are tilted away from the viewer and a transition of lying to standing cylinders can be seen at the base of the film. (c) top view and (d) 45° cross section of large area replication of the tilted nanowires after UV ozone removal of PFS template.

into ellipsoids that reconnect into cylindrical domains oriented at $\sim 45^\circ$ to the vertical throughout the film. Only after very long times (and not in the timescale of their experiment) do the tilted cylinders reorient with the vertical. In our system, the degree of vertical alignment is greatest when the surface fields are weak. Why a tilted alignment should occur only in the thicker layers in the PFS-*b*-PLA system is left undetermined but may stem from a difference in the degree of initial order in the thick and thin films.

Importantly, experimentally accessible field strengths are sufficient to compete effectively with surface fields and produce *lm-spanning* PLA microdomains in thick films even without surface modification.

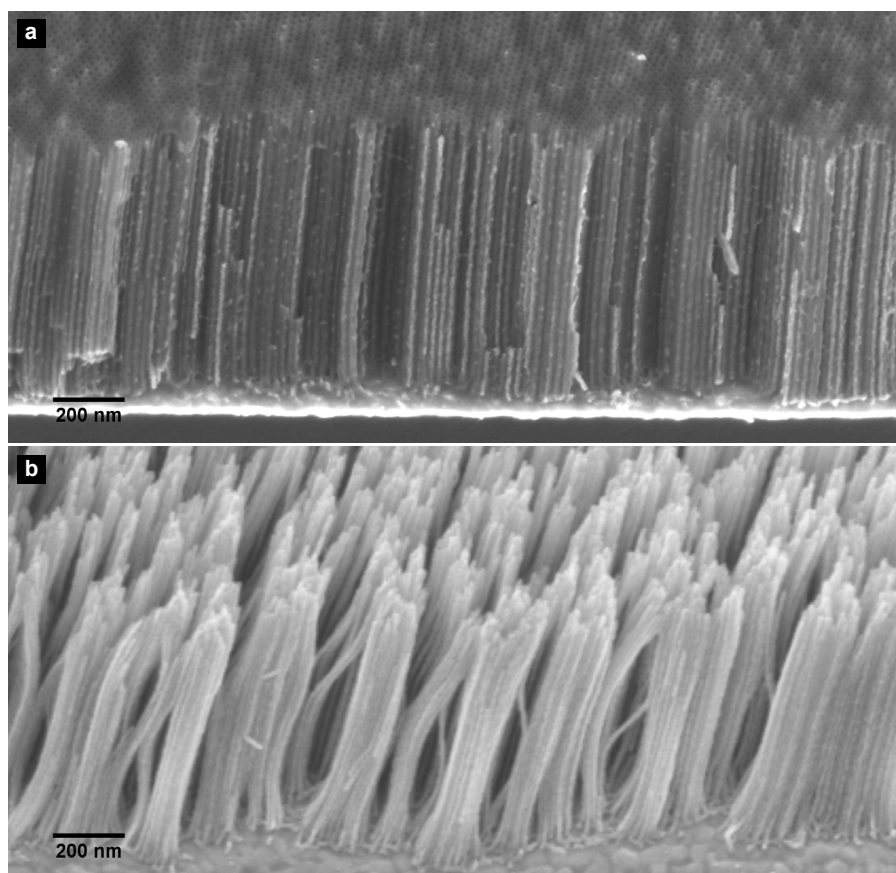


Figure 5.12: **Preparation of free-standing platinum nanowires.** (a) Cross sectional view of a platinum filled template. The copolymer template was annealed at 180 °C for 35 h with an applied field of $130 \text{ V}\mu\text{m}^{-1}$. (b) free-standing platinum nanowires after UV-ozone etching of supporting PFS template. There is partial buckling of individual wires and some degree of aggregation of neighbouring wires after removal of the support. Viewing angle is 45 °.

Removal of the PFS template by dissolution in toluene can result in collapse of high aspect ratio (> 60) structures. Figure 5.13 compares the collapse of the array when rinsed vigorously in toluene and blown dry in a stream of nitrogen gas, with the stable array seen from the same viewpoint after a ‘dry’ etch of the PFS template.

Templates as thick as 1700 nm were made using films spin-coated from chloroform solutions onto TiO_2 coated FTO substrates. After electric field alignment at 180 °C (35 h with a $120 \text{ V}\mu\text{m}^{-1}$ field), cross sectional images revealed in places ‘zig-zag’ morphologies in the otherwise perfectly standing cylindrical arrays (Figure 5.14). In this case the structures were replicated using an electrochemical protocol for TiO_2 described in Chapter 4. The cylindrical domains in the thick layer experience con-

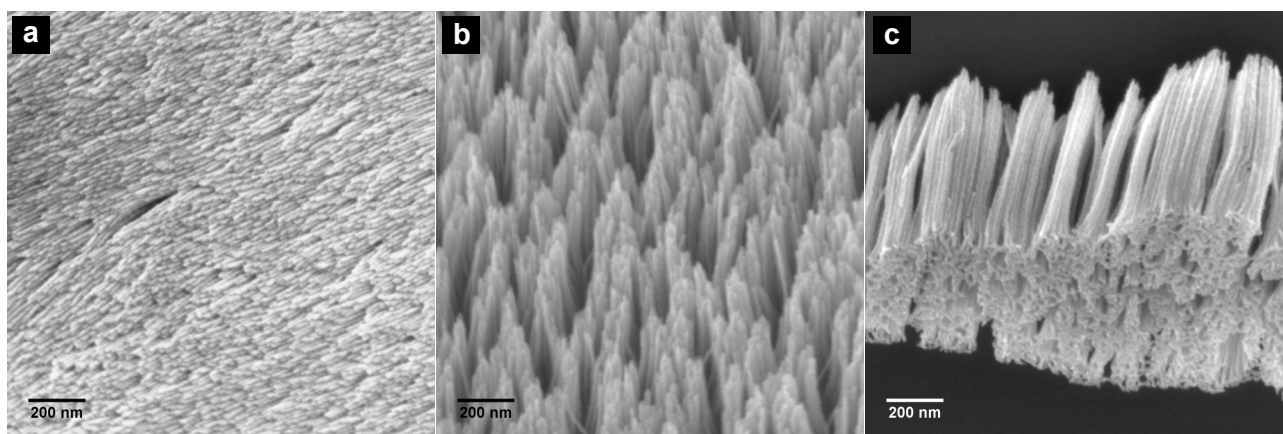


Figure 5.13: Effect of template degradation processing on Pt nanowire stability. (a) Removal by rinsing in organic solvent and drying can lead to complete collapse of the nanowire array. (b) Dry etching by UV-ozone or O₂ plasma etching leaves the wires standing. (c) A clump of nanowires detached from the gold substrate during cryo-fracture. The bases of the wires are interconnected indicating a single layer of lying cylinders in contact with the substrate which is replicated by electrodeposition. Nevertheless, a large fraction of the standing cylinders are in electrical contact with the substrate. Viewing angle in (a,b) is 45°.

ditions considerably closer to those found in bulk than in sub micron films. The ‘zig-zag’ structures in thick films resemble the ‘kink-band’ defects found at grain boundaries in bulk aligned samples of lamellae forming copolymers [9]. Both migration of grain boundaries and grain rotation result in characteristic kink band grain boundaries.

5.5 Summary

A new cylinder forming PFS-*b*-PLA block copolymer with sufficient dielectric contrast for electric field alignment and a sacrificial minority block (PLA) that can be removed under mild conditions is useful as a template for the electrochemical growth of freestanding nanowire arrays. The electric field strength and duration play an important role in the degree of order in both the PFS templates and resulting nanowire arrays. Electric fields that are too low or that are not applied for long enough times lead to either pores that do not span the entire film thickness or a disorganized, branched mesoporous structure that is nonetheless amenable to nanowire deposition. Asymmetric surface interactions with the substrate compete with the electric field in determining the detailed copolymer morphology in the vicinity of external surfaces. The electric field is dominant in the case of a weakly asymmetric surface

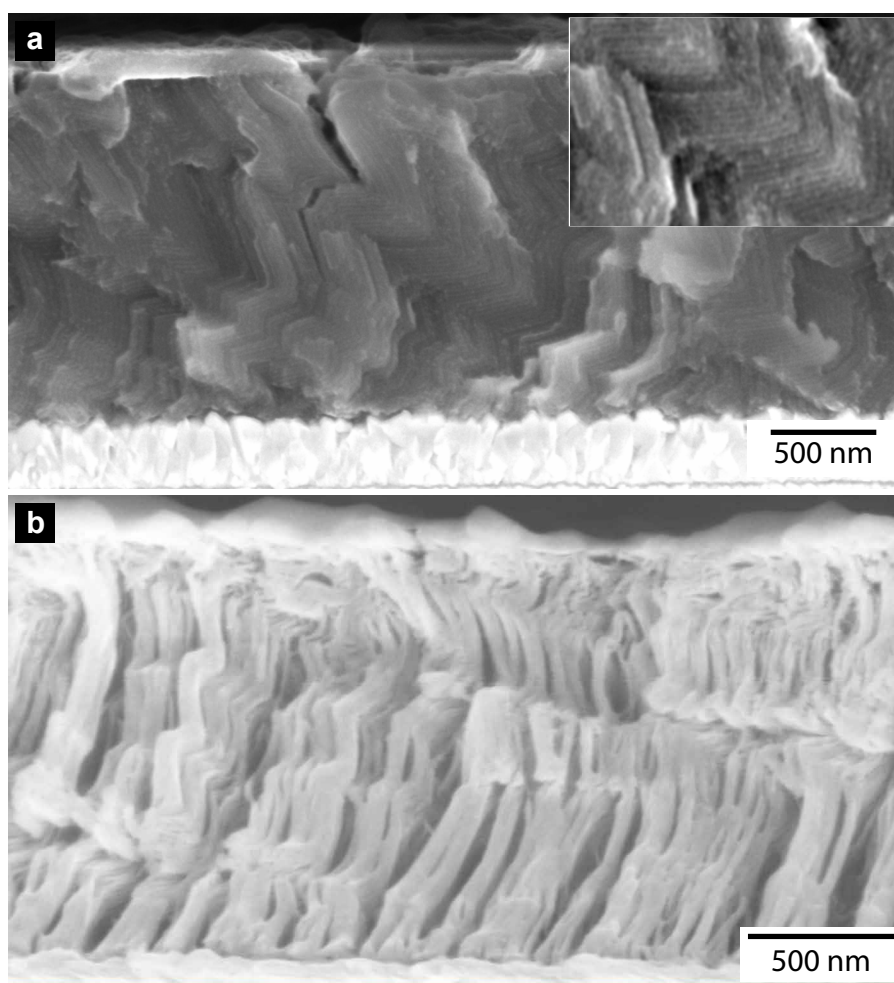


Figure 5.14: **Zig-zag morphologies in thick wire templates.** (a) Cross sectional SEM of a ~ 1700 nm electrochemically filled and fractured template aligned at $120 \text{ V}\mu\text{m}^{-1}$, 180°C for 35 h. The inset shows an enlarged view of the morphology. (b) Removal of the PFS matrix by O_2 plasma etching shows that the domains are fully connected to the substrate.

field. In thick films ($\sim 1.7\mu\text{m}$) kink-band defects were observed between vertically aligned grains. The cylindrical domains are continuous throughout the film and were electrochemically replicated to produce standing wires with kinks.

These results show that it is possible to produce films with 10 nm scale ordered and film-spanning porosity using mild selective etching chemistry. Application of this ‘soft-etch’ technology to functional copolymer materials could permit patterning of self-assembled conjugated polymers for photovoltaic applications.

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In Situ Measurements of PLA Etching in Block Copolymer Templates

This chapter presents a simple in-situ electrochemical probe for monitoring the degradation of poly(lactide) (PLA) thin films on conducting substrates in aqueous base. The method is used to track the selective etching of PLA in poly(4-fluorostyrene)-*b*-poly(D,L-lactide) (PFS-*b*-PLA) cylinder-forming block copolymer films, where it provides an indicator of film porosity and the time taken to completely remove the minority domains. An etching rate of $0.85 \pm 0.05 \text{ nm s}^{-1}$ is found for electric-field aligned standing PLA cylinders, 12 nm in diameter, that span the entire film thickness. The experimental work in this chapter was done in collaboration with Pedro Cunha who made an equal contribution to the author towards electrochemical measurements and sample preparation.

6.1 Introduction

Copolymers of poly(lactide) are particularly attractive materials for fabricating mesoporous materials because PLA is susceptible to ‘mild’ chemical etching by hydrolysis in dilute acid or base [1, 2]. Mesoporous functional materials (such as conjugated semiconducting polymers) which are easily damaged by aggressive processing steps such as exposure to UV radiation [3] or ozone [4] can be patterned via copolymerization with PLA [5].

Successful application of a block copolymer film as a mesoporous template or membrane depends on two factors: (1) selective removal of one phase and (2) presence of a fully film-spanning, contin-

uous pore structure with access to the underlying substrate. Various alignment techniques such as electric fields described in Chapter 5 exist to address aspect (2). After film formation, a number of ex situ spectroscopic [6], gravimetric [7] or calorimetric [8] techniques provide suitable probes for selective polymer degradation. Zalusky *et al.* for example used size exclusion chromatography and ^1H NMR spectroscopy to confirm complete removal of PLA domains from a bulk sample of PS-*b*-PLA [1]. These methods are not necessarily well suited to thin film samples with very small material volumes. Complete knowledge of the nature and alignment of BCP morphology relies on a combination of imaging (cross sectional electron microscopy, atomic force microscopy) and scattering techniques. This chapter presents a simple in-situ electrochemical measurement for simultaneously monitoring the selective etching of a minority PLA copolymer phase and probing for film-spanning porosity in a cylinder forming PFS-*b*-PLA copolymer film. Optimization of the etching procedure is important since excessive degradation can result in cracking or delamination of the film from the substrate.

The copolymer film to be probed is coated on a conducting substrate and immersed in an aqueous base etching solution for PLA which plays the role of both PLA etchant and a probe electrolyte in a 3-electrode electrochemical cell. By applying a fixed potential to the substrate and measuring the electrochemical current flow with a platinum counter electrode we probe the access of the electrolyte to the underlying substrate through the film pore structure. Etching of the PLA domains begins from the exposed film surface and proceeds down towards the substrate. While the PLA remains intact it is an effective insulating layer in the cell and the electrochemical current flow is negligible. Complete PLA removal allows contact of the electrolyte with the substrate and is signified by a characteristic onset of current flow in the cell. On the other hand, if the PLA cylinders do not span the entire film, the electrolyte remains insulated from the working electrode and no current onset is seen. The breakthrough time, once calibrated, also is a measure of film thickness - important for calibrating subsequent functional material deposition.

A full electrochemical characterization of the nature and overall degree of film porosity would require the rigour of electrochemical impedance spectroscopy [9]. Indeed, cyclic voltammetry was recently used as an ex situ probe of PMMA removal from PS-*b*-PMMA films by UV exposure and to further investigate details of the pore wall surface chemistry [10]. We do not attempt to achieve such

thorough characterization with this method; rather we look only to identify a simple binary indicator of film porosity, and the processing time required to achieve this. These results are the first example of direct electrochemical measurements made during the copolymer etching procedure itself. We are able to identify fully penetrating pore networks even in the absence of an ordered, aligned copolymer morphology, something not possible with imaging and scattering techniques. The measurement is simple, in situ, and requires no additional equipment, complex analysis or processing steps.

6.2 Experimental

The PFS-*b*-PLA block copolymer used in this chapter is termed MHI42 (synthesis detailed in Chapter 4). Silicon substrates coated with 40 nm Au by thermal evaporation were used as the conducting substrates. Selected substrates were first coated with a self-assembled monolayer of 1-undecanethiol. Copolymer films with thicknesses up to 800 nm were spin-cast from 10 %_{wt} solutions in toluene before drying at 60 °C for 2 hours to remove residual solvent. To produce ordered standing arrays of PLA cylinders, films were annealed at 180 °C under nitrogen atmosphere in the presence of a 120 V μm^{-1} DC electric field for 35 h, as detailed in Chapter 5.

For comparative measurement of PLA degradation, PLA homopolymer (*h*-PLA) was taken from the precursor polymer used to synthesize the block copolymer. This material had a molecular weight of 10 kg mol⁻¹ and a PDI of 1.12. Electrochemical measurements were made using a CH Instruments potentiostat in a standard three electrode setup. The Au substrate supporting the copolymer film was the working electrode, a platinum wire acted as counter electrode and a Ag/AgCl (3 M KCl) electrode was the reference. Active areas of 0.07 cm² were defined in the cell using Kapton masking tape (DuPont) with a circular aperture. The standard cell electrolyte was 0.05 M NaOH_(aq) containing 40 % methanol by volume.

Nulling ellipsometry measurements were made using a Nanofilm EP3 spectroscopic ellipsometer with a 532 nm green laser source. *h*-PLA films of ~ 100 nm were spin coated from toluene solutions onto fresh Si substrates. The optical properties of the substrate, *h*-PLA film, and 0.05 M NaOH_(aq) etching solution were pre-characterized as described in Chapter 3. Measurement in the dry state (assuming an extinction coefficient of zero) gave a best-fit PLA refractive index of 1.46 and film

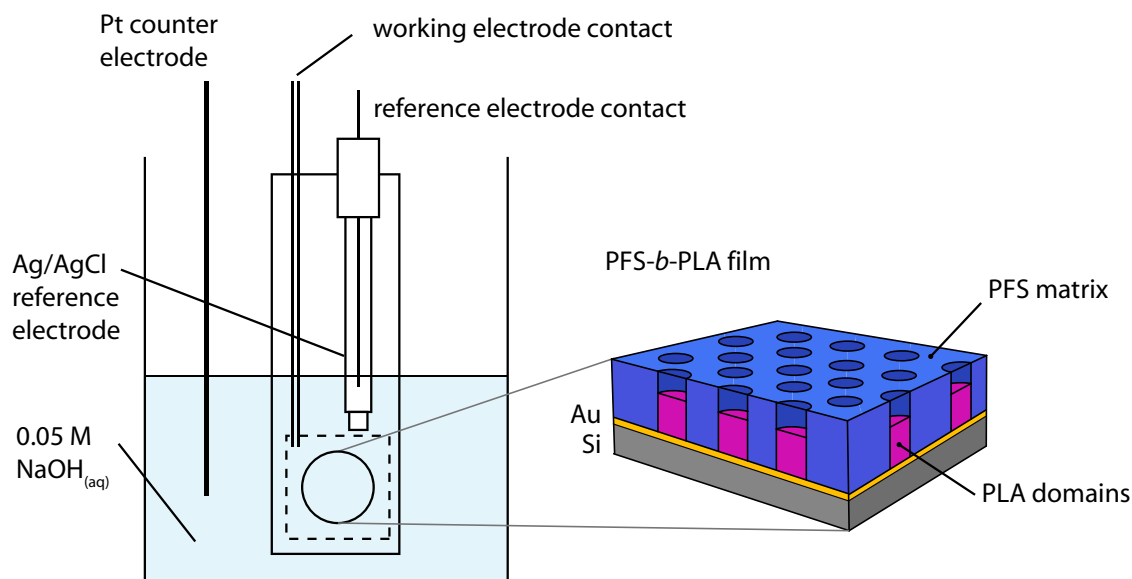


Figure 6.1: **Schematic of a 3-electrode cell probe of a cylinder forming PFS-*b*-PLA copolymer film.**

thickness of 110 nm. In situ etching measurements were recorded in a liquid cell with a 60° angle of incidence. A 1-zone nulling condition was found for each measurement, taking approximately 5 seconds. Ellipsometric data was fitted for the *h*-PLA film thickness assuming no change in the refractive index during etching.

6.3 Results and Discussion

6.3.1 Homopolymer PLA Etching

Figure 6.1 shows a schematic of the 3-electrode cell used to probe the film degradation. We look first at a simple system consisting of a 110 nm thick *h*-PLA film on a Au substrate immersed in a 0.05 M $\text{NaOH}_{(aq)}$ electrolyte. Figure 6.2 shows the (cathodic) current as a function of time with the working electrode held at -50 mV vs Ag/AgCl. After 300 s there is an onset of cathodic current that peaks then decays to a steady state anodic current after 650 s. The final steady-state current is linearly dependent on methanol concentration (Figure 6.3) indicating that methanol oxidation is the likely source, consistent with studies of methanol oxidation at Au substrates at high pH [11]. Alongside the

current trace is shown the thickness of the PLA film as determined by in situ ellipsometric fitting of an identical film on a Si substrate under identical degradation conditions. Close inspection of the current (inset) reveals correspondence of the current onset with the final removal of PLA and breakthrough of the electrolyte to the substrate. The onset of a transient cathodic response (i.e. a positive current peak) reflects the transition from an open circuit (fully insulated working electrode), to electronic contact of the electrolyte with the conducting substrate. The electrochemical origin of the transient response remains undetermined, however PLA degradation products are likely to be released in the vicinity of the substrate which may be electrochemically active. The important result for our purposes is that a characteristic electrochemical signal can be identified that marks the final stages of PLA degradation.

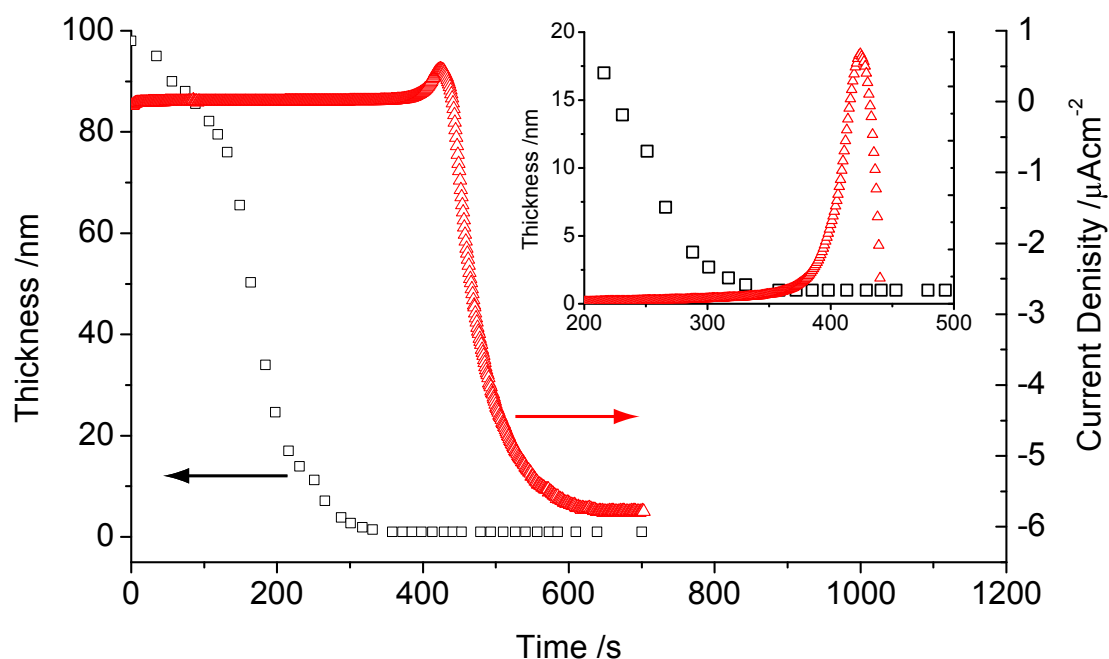


Figure 6.2: ***h*-PLA etching monitored by electrochemical current flow and ellipsometry.** Cathodic current (Δ) as a function of time for a 110 nm thick *h*-PLA film alongside ellipsometric fitting results of the film thickness ($\square$) for an identical film on silicon. An enlarged view of the current onset (inset) shows coincidence of current flow with the final degradation of the *h*-PLA film.

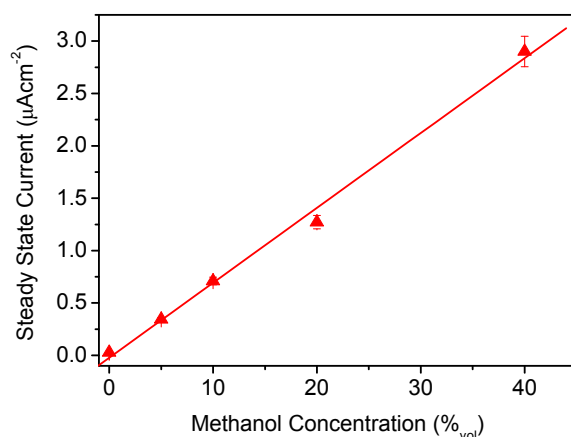


Figure 6.3: **Steady-state anodic current density as a function of methanol concentration by volume.** The working electrode is a clean and non-patterned Au substrate at -50 mV. The steady-state current increases linearly with the methanol concentration.

6.3.2 Etching of PFS-*b*-PLA templates

Equivalent current measurements to those in Figure 6.2 were also made during the etching of PFS-*b*-PLA copolymer films on Au substrates. The PFS-*b*-PLA films were probed either after electric field alignment or immediately after spin-coating and drying (termed ‘as-spun’). The shape of the electrochemical traces was identical to Figure 6.2 for *h*-PLA etching. We therefore attribute the onset of current to the complete etching of PLA domains which fully penetrate the film.

All electric-field aligned and as-spun films showed an onset of current, indicating full penetration of the PLA domains and the corresponding formation of a fully porous PFS template. The etching time is linearly dependent on film thickness for both aligned and as-spun films (Figure 6.4a), indicating that the etching is not limited by diffusion through the pore structure. The etching rates are $0.85 \pm 0.05 \text{ nm s}^{-1}$ for the aligned PFS-*b*-PLA films, $0.35 \pm 0.05 \text{ nm s}^{-1}$ for the as-spun PFS-*b*-PLA films, and $0.36 \pm 0.04 \text{ nm s}^{-1}$ for *h*-PLA films. Copolymer films annealed at 180 °C for 35 h without an electric field showed no onset of current after many hours, indicating that the PLA cylinders do not penetrate the film. Figure 6.5 shows SEM fracture cross sections of the porous PFS films confirming the PLA domain morphologies inferred by the electrochemical measurements.

Figure 6.4b shows how the etching rate of both electric field aligned PFS-*b*-PLA, and *h*-PLA films

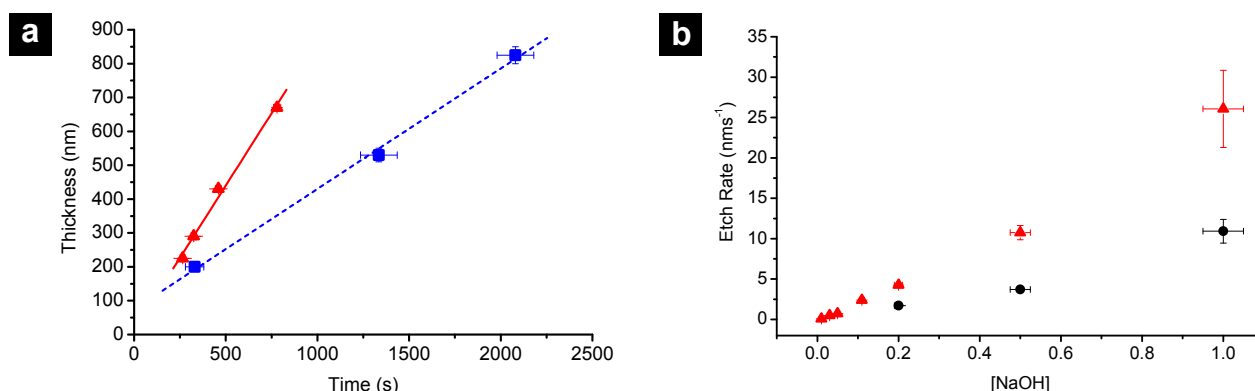


Figure 6.4: **PLA etching rates as a function of film thickness and NaOH concentration.** (a) Time for complete PLA degradation is linearly dependent on film thickness for electric field aligned PFS-*b*-PLA (▲), and as-spun PFS-*b*-PLA (■) films. (b) PLA etching rate as a function of NaOH concentration for electric field aligned PFS-*b*-PLA (▲), and *h*-PLA (●) films.

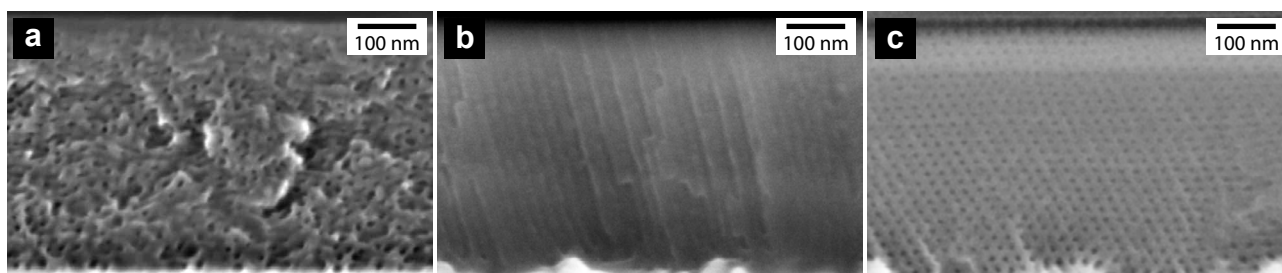


Figure 6.5: **Summary of PFS-*b*-PLA thin film cross section morphologies by SEM imaging.** (a) As-spun template showing a disorganized array of PLA domains, (b) electric field aligned standing cylinders, and (c) non-aligned sample with cylinders parallel to the substrate.

varies linearly with NaOH concentration between 0.01 and 1 M. This linear dependence is consistent with the rate of ester hydrolysis being first order in hydroxide concentration and with a process that is not limited by diffusion through the pore structure in the concentration regime studied.

The etching rate for the electric field aligned films is more than double the rate of as-spun PFS-*b*-PLA films and *h*-PLA films. In both the aligned PFS-*b*-PLA and *h*-PLA film the degradation front advances in a vertical direction. Since the processes appears not to be diffusion limited, one might expect these etching rates to be the same. The increased etching rates observed in the vertical PLA cylindrical microdomains suggests therefore that the degradation reaction proceeds more rapidly in the copolymer domains than in the homopolymer material. The increased degradation rate could

reflect an extended conformation of the PLA chains in the microphase separated domains, enhancing their reactivity to the hydrolysis reaction. The as-spun sample, on the other hand, has an etching rate matching the h-PLA film. There are two possible reasons for this: (1) the polymer chains do not have time to adopt the same degree of chain extension present in the (thermally annealed) aligned sample, or (2) the cylinders could follow a tortuous path through the film such that the actual pathlength to the substrate is greater than the film thickness. If explanation (2) applies then the observed etching rate of the film is a combined result of faster etching through a longer distance. The etching rate of the as-spun film after thermal annealing cannot be measured using this method because the cylindrical pores lie in the plane of the film, giving rise to a porosity that does not span the thickness of the film (Figure 6.5c). It should be noted that some experiments were conducted on 1-undecanethiol modified Au substrates. The measured breakthrough time in thin films was not affected by this additional component.

6.4 Conclusion

These results present a straightforward method of monitoring selective degradation of PLA from PFS-*b*-PLA copolymer films with distinct yet film-spanning porous morphologies on conducting substrates. The etching rate is $0.85 \pm 0.05 \text{ nm s}^{-1}$ for thermally annealed, vertical arrays of cylindrical domains, and $0.35 \pm 0.05 \text{ nm s}^{-1}$ for phase separated films immediately after spin coating with no thermal annealing. At present these measurements provide only a binary indicator of porosity and the etching rate of one copolymer component under a range of solution-based etching conditions. Further development of this technique, for example using a probe redox couple dissolved in the etching solution coupled with impedance spectroscopy might also allow characterization of the morphology of the porous structure (see for example reference [12]) without the need for actual replication and SEM imaging. These techniques are particularly useful where the template lacks well defined order and alignment (such as immediately after coating) where the continuity of the pore structure cannot be determined by imaging alone.

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Templating the Double Gyroid

The following chapter describes the thin film behaviour of a PFS-*b*-PLA copolymer which is found to adopt the bicontinuous gyroid (G) phase in the bulk. The response of the copolymer morphology to applied electric fields in thin films is probed at temperatures where the bulk copolymer adopts either the gyroid or the cylinder (C) phase. At 150 °C the electric field produces standing arrays of cylinders, lamellae, and perforated lamellae, which are electrochemically replicated in platinum after removal of the minority polymer phase. At 180 ° the gyroid phase coexists with a perforated lamellar phase. Surface modification of gold coated silicon substrates using undecanethiol monolayers is found to produce optimal layers for replication of freestanding arrays of the gyroid network phase. The arrays can also be templated uniformly onto FTO substrates which have considerably greater surface roughness than gold coated silicon substrates.

7.1 The gyroid phase in block copolymers

The gyroid phase (G) observed in block copolymers is a microstructure consisting of two interwoven continuous networks of the minority polymer block held in a matrix phase of the majority block. Since *both* minority and majority phases are continuous in all three dimensions the structure is termed ‘bicontinuous’. The G phase was first identified in 1967 by Luzzatti *et al.* as a cubic phase occurring in strontium soap surfactants [1]. An approximation to the copolymer gyroid morphology is based on the

‘Schoen G’ or ‘Gyroid’ surfaceⁱ shown in Figure 7.1a. The gyroid surface is a triply periodic infinitely extending minimal surface (i.e. has zero mean curvature) that divides space into two continuous labyrinthine volumes without intersections.

When the gyroid surface is given a finite thickness by simultaneously expanding two surfaces of uniform thickness on either side, space is effectively divided into three non-intersecting volumes. The ‘central’ volume, centred on the original gyroid surface, forms a matrix through which run two distinct intertwining but non-intersecting networks, each periodic in all three principle directions. The resultant morphology constitutes the constant thickness (CT) model for the G phase [2]. The block copolymer G phase is strictly speaking a *double gyroid*, formed upon segregation of the majority block into the central matrix volume making up roughly 60 % of space, with the minority component making up both of the two network phases. A G phase unit cell with cubic ($Ia\bar{3}d$) symmetry is shown in Figure 7.1b with the matrix phase removed and the two networks shaded blue and red for clarity.

ⁱWeisstein, Eric W. ‘Gyroid.’ From Wolfram Web Resource. <http://mathworld.wolfram.com/Gyroid.html>

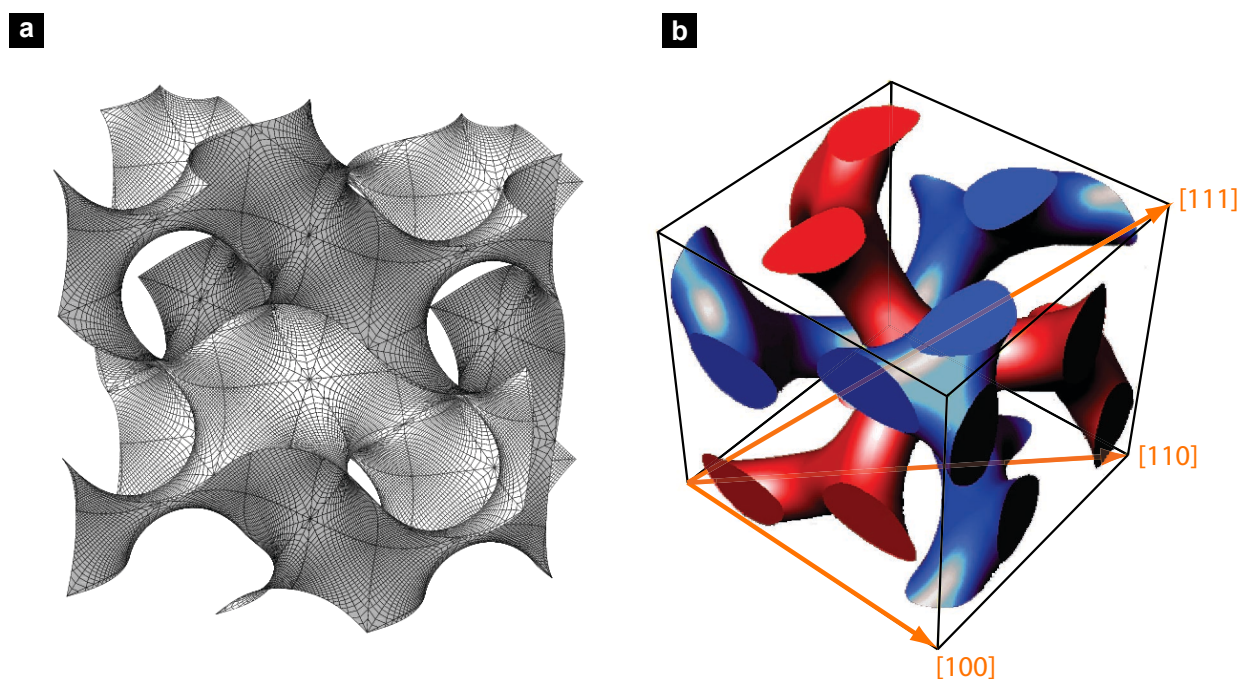


Figure 7.1: **The Gyroid** (a) The triply periodic gyroid minimal surface. (b) the cubic G phase block copolymer network phase unit cell. The matrix phase is removed and the two network phases coloured blue and red.

The gyroid phase was first identified in diblock copolymers by two groups in 1994 [2, 3]. The first consideration of this morphology to explain X-ray diffraction data and cross sectional TEM images highlighted the challenge in unambiguous identification of the complex phases observed in these systems from experimental evidence. Indeed, star-block copolymer microstructures first attributed to a bicontinuous double diamond (OBDD) morphology in 1986 [4] were reevaluated in 1995 by the same group as the gyroid morphology [5]. Following these first investigations the gyroid phase has been observed in AB [6, 7, 8] & ABA [9, 10, 11] diblocks, blends of two AB diblocks [12], and AB diblocks blended with homopolymers [13, 14] or small plasticizing molecules [15].

Order-order transitions between block copolymer phases exhibit certain ‘epitaxial’ relations reflecting low energy pathways connecting local free energy minima of each phase [16]. For example, C to G transitions studied in bulk samples reveal that the [111] G direction is oriented along the original cylinder axis of the C phase [3, 16]. The transition between the hexagonally perforated lamellar (HPL) and G phase shows epitaxy between the HPL layers and the (211) G planes [17]. The thin film orientation behaviour of the G phase was studied by Park and coworkers using sub-micron poly(styrene)-*b*-poly(isoprene) (PS-*b*-PI) copolymer films on silicon and mica substrates [18, 19]. A perfect epitaxy of the HPL sheets (003) and G (211) planes formed parallel to the surface was observed using GISAXS fitting and recently imaged directly with 3D TEM tomography [20]. Thin film order-order transition epitaxies are consistent with the relations reported in bulk samples [3].

7.1.1 Patterning using the gyroid phase

The fascinating bicontinuous topology of the gyroid phase makes it an irresistible target for potential applications ranging from filtration membranes [11], catalytic supports and photonic crystals [21] to photovoltaics and energy technology. A survey of porous gyroid morphologies made from block copolymers found in the literature is shown in Table 7.1, along with the sacrificial phase and etching technique employed.

Hashimoto and coworkers filled the network voids of gyroid forming bulk samples by decorating the exposed internal surfaces with metal nanoparticles [22] and nickel coatings [14]. Thomas *et al.* were able to produce both porous (removal of network phase) and relief (removal of matrix phase) ceramic films from ABA diblocks exhibiting the gyroid phase in which the B block is a Si containing

polymer [23]. Exposure of the phase separated copolymer to an ozone atmosphere and UV radiation led to removal of the A block and conversion of the B block to a silicon oxycarbide ceramic.

Table 7.1: Examples of reported porous gyroid structures from block copolymers

Copolymer	Etching Method	Component Etched	Reference
PS-PLA	0.05 M NaOH _(aq) at RT	PLA	[12]
	Conc HI _(aq)	PLA	[12]
PS-PEO	Conc HI _(aq)	PEO	[24, 12]
PS-PI	Ozonolysis	PI	[25, 26]
	UV Irradiation	PI	[21]
PVP-PI	1,4-diiodobutane + Ozonolysis	PI	[13, 22]
PI-PMDSS-PI	UV irradiation in 2 % Ozone	PI	[23]
PS-PDMS	HF	PDMS	[8]

Where: PS = poly(styrene), PEO = poly(ethyleneoxide), PVP = poly(2-vinylpyridine), PI = poly(isoprene), PMDSS = poly(pentamethyldisilylstyrene), PDMS = poly(dimethylsiloxane).

7.2 Experimental

Synthesis of the PFS-*b*-PLA block copolymer described in this chapter, termed MHI41, is described in detail in Chapter 4. The overall molecular weight was 36 kg/mol and the PLA volume fraction was 40 %. The polydispersity index was 1.21.

Thin films of MHI41 (100 nm to 1 μ m) were prepared by spin coating from 5 to 10 % solutions in toluene onto gold coated silicon substrates. Selected substrates were coated with a self-assembled monolayer of 1-undecanethiol (detailed in Chapter 4). The films were annealed at 150 °C or 180 °C under a nitrogen atmosphere for 35 h before cooling to room temperature over 3 h. External electric fields of up to 120 V μ m⁻¹ were applied using the standard parallel plate capacitor setup detailed in Chapter 4. The field was maintained until the sample reached room temperature.

The PLA minority component of the block copolymer was selectively degraded by immersing the films in 0.05 M NaOH_(aq) solutions containing 40 %_(vol) methanol. Electrochemical deposition of Pt

and TiO₂ are described in Chapter 4. Dry etching of the polymer template was achieved by 15 min exposure to a 172 nm UV source (SUS-128 excimer radiation system, Ushio Europe B.V.) or 5 min exposure to oxygen plasma (Diener Electronic Femto Plasma System 100 W, 4 kHz).

X-ray Scattering

Scattering experiments were performed at the G1 line at Cornell High Energy Synchrotron Source (CHESS) by Marleen Kamperman.

7.2.1 Simulation of the double gyroid phase

A better understanding of the various observed SEM and TEM patterns presented can be obtained by comparison to a simulated gyroid phase based on the gyroid minimal surface. In practice a trigonometric level set function is used as an approximation of the gyroid minimal surface [26, 27]:

$$f(x, y, z) = \sin\left(\frac{2\pi x}{L}\right) \cos\left(\frac{2\pi y}{L}\right) + \sin\left(\frac{2\pi y}{L}\right) \cos\left(\frac{2\pi z}{L}\right) + \sin\left(\frac{2\pi z}{L}\right) \cos\left(\frac{2\pi x}{L}\right) = 0 \quad (7.1)$$

Where L is the cubic unit cell repeat distance. The surface defined by equation 7.1 divides space into two equal volumes. Routines written in Matlab by Dr Gilman Toombesⁱⁱ were used to construct this surface and the two related level set surfaces representing the interfaces with the minority phase (so-called ‘skeletal surfaces’). Once constructed, the cross sectional representations of this structure defined by projections along the desired lattice vectors are computed by intersection of the surfaces with the desired plane. Before presenting the results of this chapter it is instructive to view the schematic form of the gyroid morphology both in 3D rendering and certain cross sections through the structure. A 3D simulated schematic of the cubic gyroid structure generated using the procedure above is shown in Figure 7.2a, with the [211] lattice vector pointing upwards. The two independent networks are coloured in blue and pink, with the central matrix represented schematically by the gyroid surface (green) with a small (finite) thickness for clarity. Figure 7.2b,c, and d show views of the structure viewed down the [0 $\bar{1}$ 1], [$\bar{1}$ 11] and [211] lattice vectors respectively, both with and without the green matrix phase.

ⁱⁱBased on the work of Jim Hoffman <http://www.msri.org/about/sgp/jim/geom/level/skeletal/index.html>

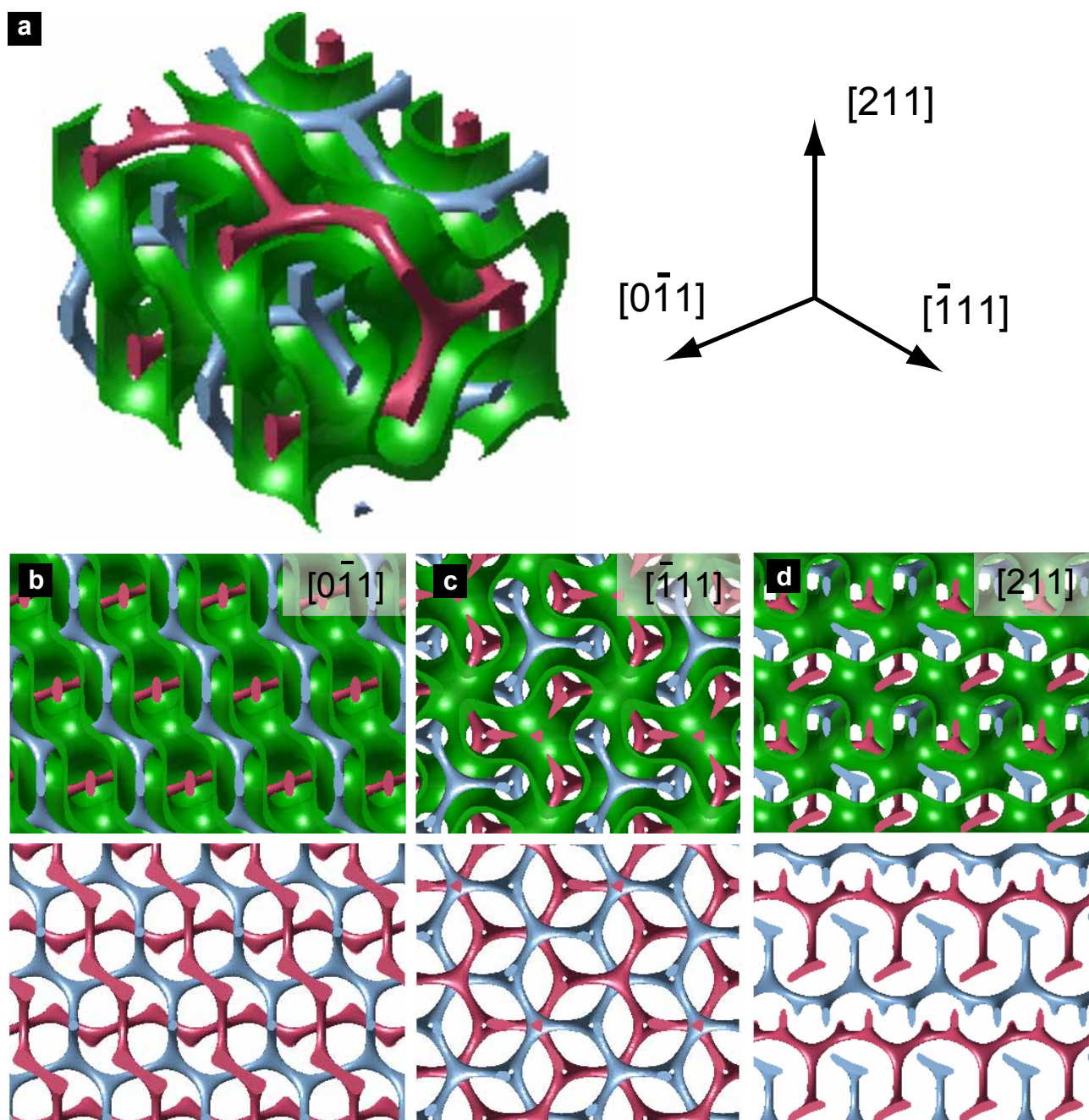


Figure 7.2: **Simulated reconstruction of the gyroid morphology from zero-mean-curvature surfaces.** (a) 3D view of the full structure with (211) cubic lattice planes aligned parallel to the top and bottom layer: green (the gyroid surface), red and blue (interwoven network phases). (b) shallow volume projection view down $[0\bar{1}1]$ lattice vector of the structure in (a) with a depth of half the repeat distance and lateral size twice the repeat distance of the respective lattice vector. (c,d) projections as for (b) down the $[\bar{1}11]$ and $[211]$ lattice vectors. The projections in (b,c,d) are shown with and without the matrix phase (green).

Figure 7.3 shows simulated sections normal to the $[211]$ lattice vector taken at different heights through the unit cell. This face has the ‘double-wave’ pattern characteristic of the gyroid structure. The series in effect views thin slices through the unit cell at various distances along the $[211]$ lattice vector.

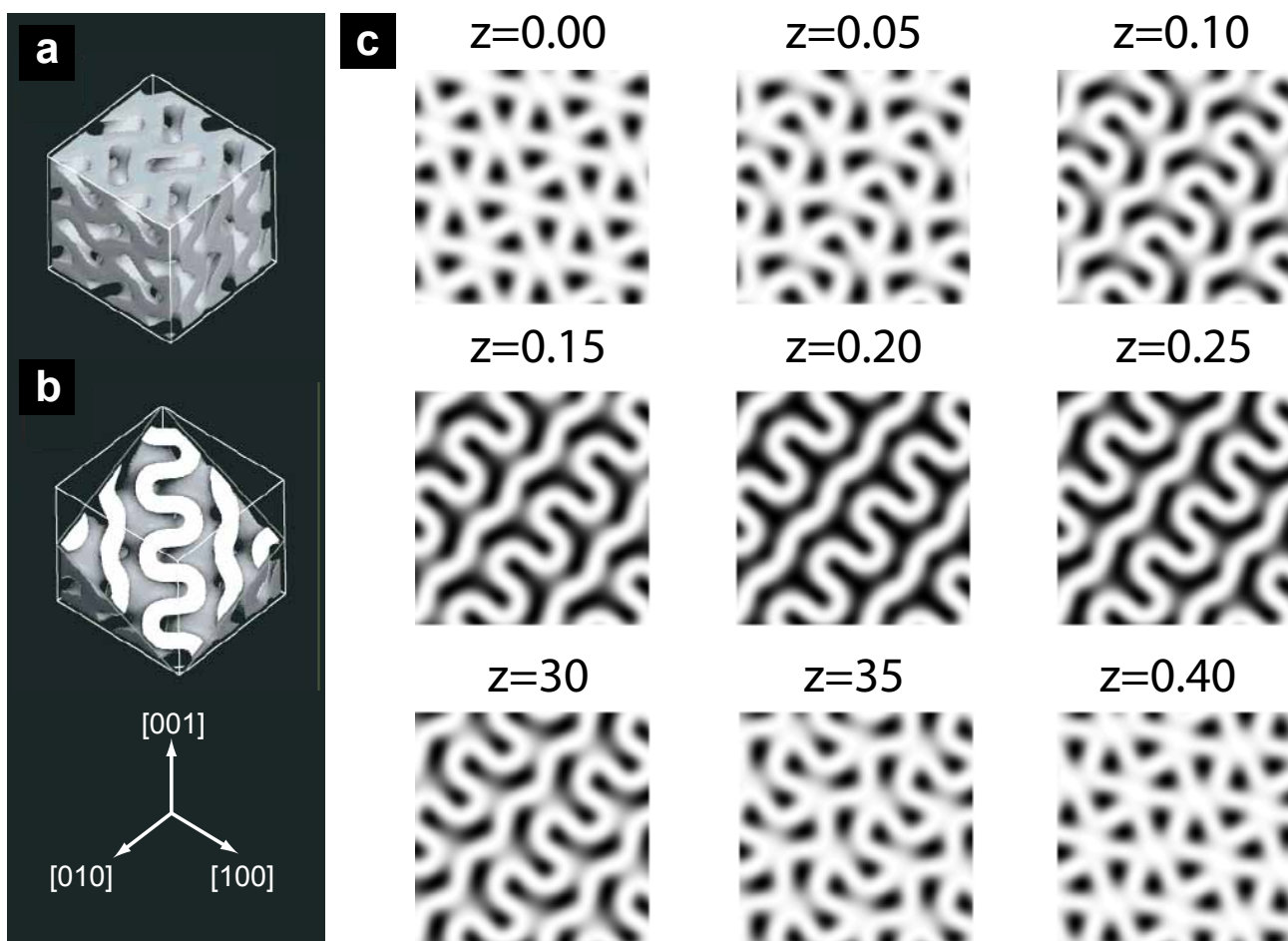


Figure 7.3: **Simulated section views of (211) lattice planes.** (a) A (2×2) standard cubic unit cell of the gyroid structure with the minority phases removed. (b) A section perpendicular to the $[211]$ lattice vector shows the characteristic ‘double wave’ pattern. The $[11\bar{1}]$ direction runs parallel to the waves. (c) simulated cross sections with the matrix phase bright and voids left by removal of the minority phase black. Each section has a thickness of 5% of the repeat distance along $[211]$ and is taken at a height z (as a fraction of the total lattice vector). Images (a) and (b) are reproduced from reference [26].

7.3 Results and discussion

7.3.1 Bulk phase behaviour

Bulk samples of MHI41 were annealed under vacuum for 70 h at either 150 °C or 180 °C before cooling to room temperature at $\sim 10^\circ\text{C}/\text{min}$. The structure is vitrified by cooling the sample below the glass transition temperature of the two phases (103 °C for PFS and 57 °C for PLA). Small-angle X-ray scattering (SAXS) data recorded at room temperature are consistent with a gyroid phase (G) of unit cell length 49 nm after annealing at 180 °C (Figure 7.4). The SAXS trace of the bulk phase after annealing at 150 °C (Figure 7.5) is consistent with a cylindrical HEX (C) phase with a centre-to-centre distance of 23 nm.

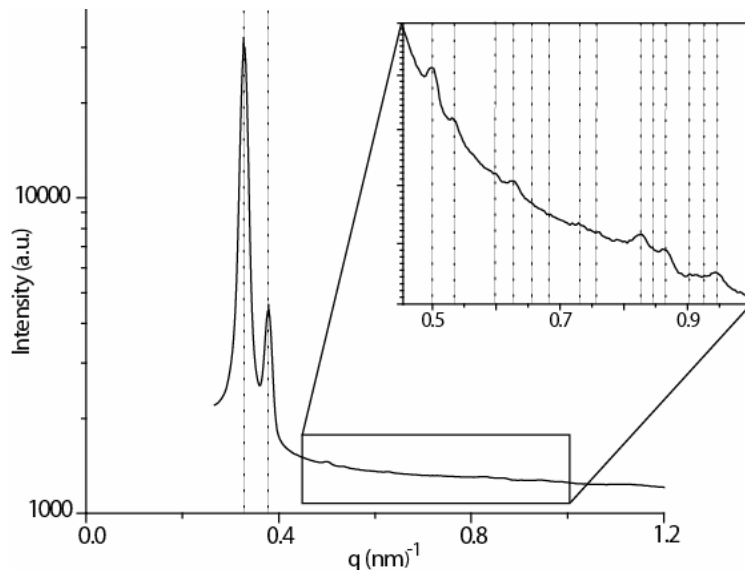


Figure 7.4: **Small angle X-ray scattering (SAXS) pattern for a bulk sample of MHI41 annealed at 180 °C.** Peaks with scattering wave vector $q = 4\pi \sin(\theta)/\lambda$ spacing-ratios of $\sqrt{6}$, $\sqrt{8}$, $\sqrt{14}$, $\sqrt{16}$, $\sqrt{20}$, $\sqrt{22}$, $\sqrt{30}$, $\sqrt{32}$, $\sqrt{38}$, $\sqrt{40}$, $\sqrt{42}$, $\sqrt{46}$, $\sqrt{48}$, $\sqrt{50}$ are discernible, consistent with a gyroid phase with a unit cell of 49 nm. The expected peaks for an $\text{Ia}\bar{3}\text{d}$ cubic lattice are indicated by vertical lines.

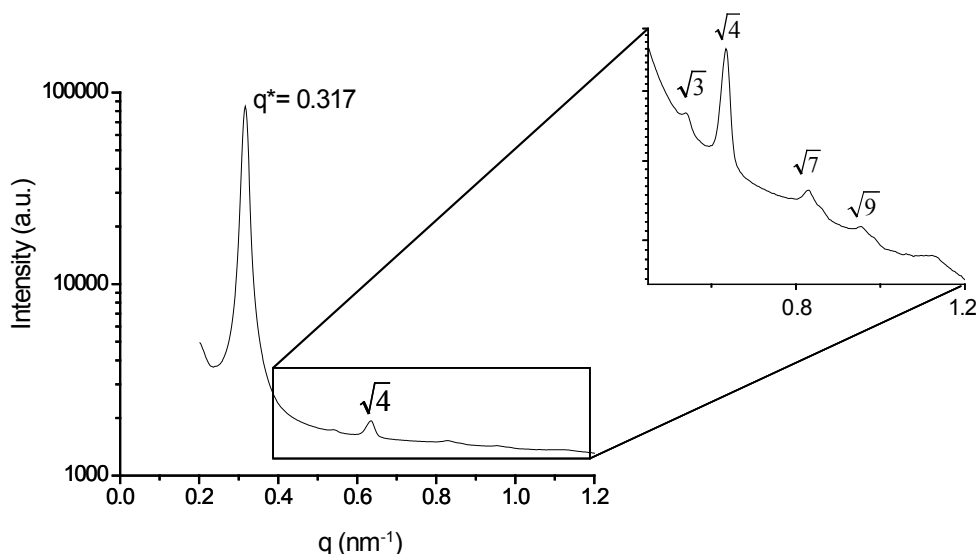


Figure 7.5: **Small angle X-ray scattering (SAXS) pattern for a bulk sample of MHI41 annealed at 150 °C.** Peaks with scattering wave vector $q = 4\pi \sin(\theta)/\lambda$ at $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$ are discernible, consistent with a cylindrical HEX phase with a centre-to-centre distance of 23 nm.

7.3.2 Low temperature thin film behaviour

The ‘low temperature’ behaviour of MHI41 refers to annealing at temperatures at which SAXS indicates a cylindrical morphology in the bulk. While a C phase may dominate in the bulk at 150 °C, the thin film behaviour reveals coexistence of at least two further morphologies. Figure 7.6 shows the free surface of a 250 nm film on a gold substrate after annealing at 150 °C for 35 h followed by removal of the PLA minority phase. The surface shows reconstructions of the (211) gyroid lattice plane coexisting with regions of hexagonally ordered holes. Digital analysis of the HEX pore structure (see Chapter 5), enlarged in Figure 7.6b yields an estimate of the average diameter as 9.5 ± 1.5 nm with centre-to-centre spacing of 19 ± 3 nm. The best fit simulated (211) lattice plane using a unit cell dimension of 47 nm is overlaid in Figure 7.6c.

The underside of the film was studied by under-etching the Au substrate in a bromine methanol solution and imaging by SEM. The underside surface is mostly flat and featureless except for occasional ~ 10 nm holes with an estimated frequency of $\sim 10/\mu\text{m}^2$ (Figure 7.7a). The underside morphology points towards a near-complete wetting layer of the PFS component at the Au substrate interface with occasional penetrating PLA domains. Bright regions are seen on the polymer underside after expo-

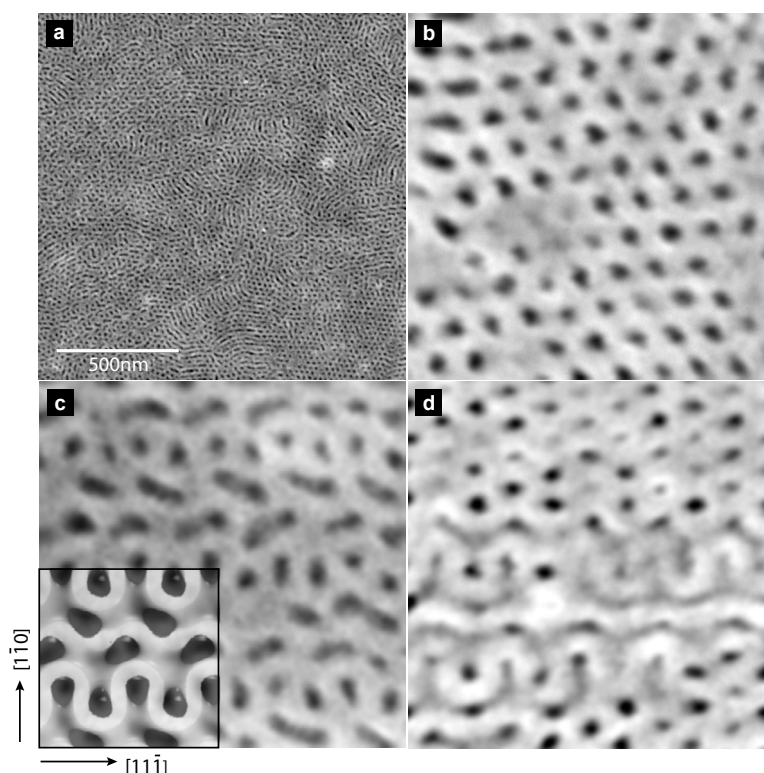


Figure 7.6: **Thin film behaviour of MHI41 after thermal annealing at 150 °C for 35 h.** (a) SEM of the free surface shows a mixture of the (211) gyroid plane and regions of hexagonally packed cylindrical holes with no terrace formation. (b), (c) and (d) show 200 nm × 200 nm enlargements of the coexisting surface morphologies. The inset in (c) is an overlaid (211) gyroid simulation with a 47 nm unit cell.

sure to the Au etching solution. The origin of these features is unknown, however they do not seem to mirror directly any substrate topography (see surface SFM height image in Figure 7.23).

Further details of the film morphology are revealed by electrochemical replication of the voids left by PLA removal. Access to the conducting substrate is blocked in most of the film area by the surface PFS wetting layer. However, sporadic growth of platinum nanostructures is possible, which presumably nucleate through defect sites in the wetting layer (Figure 7.7b). The density of nucleation sites is extremely low, around 1 every $100\mu\text{m}^2$, which leads to isolated patches of growth illustrated in Figure 7.7. After electrochemical growth, the surrounding PFS template is removed by UV ozone etching to enable direct viewing of the replicated Pt nanostructures by SEM, shown in Figure 7.8. The intriguing structures in Figure 7.8a show a region of coexisting lying cylinders ($C_{||}$) and perforated lamellar ($HPL_{||}$) morphologies. Figure 7.8b shows that the growth emerges into a gyroid morphology

in the bulk of the film layer. The replication indicates a $\text{HPL}_{\parallel}$ surface reconstruction which in a perfect structure does not allow access through the PLA phase in a direction normal to the layers. Park *et al.* observed $\text{HPL}_{\parallel}$ on mica substrates in a PS-*b*-PI copolymer with wetting of the majority phase [20]. However in this case where a coexistence with the gyroid was observed, the transition to G begins preferentially at the substrate interface, in contrast to the surface reconstruction apparent in our system. Presumably a stronger asymmetric wetting favours the $\text{HPL}_{\parallel}$ reconstruction over G at the interface.

The application of an electric field during annealing at 150 °C results in a radically different phase behaviour of MHI41 films. Figure 7.9 shows the surface topography imaged by TappingMode™SFM (height) after annealing at 150 °C for 35 h under a $120 \text{ V}\mu\text{m}^{-1}$ applied field. While annealing in a parallel plate capacitor geometry the upper surface is now contacted by a cross-linked PDMS counter electrode. On removal of the electrode, Figure 7.9a reveals what at first appear to be parallel structures in the plane of the substrate delineated by a small height contrast between PLA and PFS domains

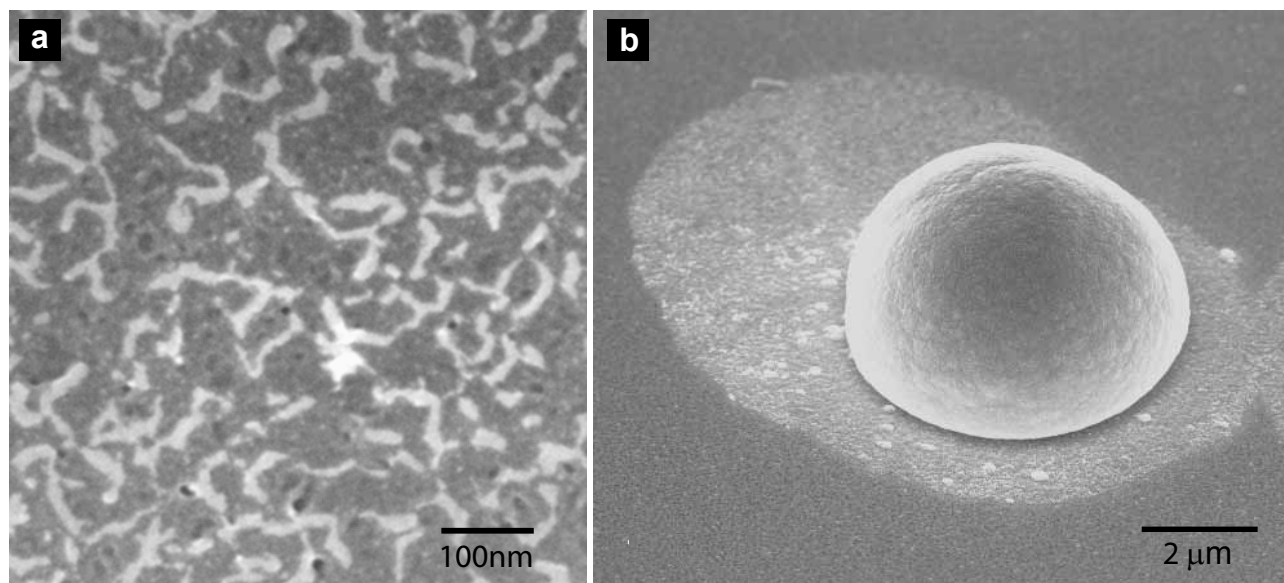


Figure 7.7: **Low density nucleation sites of electrochemical platinum replication through the film template shown in Figure 7.6.** (a) SEM of the underside of the PFS template is topographically featureless except for occasional 10 nm holes (the bright regions are an additional result of etching away the Au substrate). (b) Low magnification SEM of templated Pt electrodeposition after UV ozone etching of the polymer template. The Pt deposition is sporadic with growth site density of approximately 1 per $100 \mu\text{m}^2$, with dome-like overgrowth forming above the template. Viewing angle: 45°.

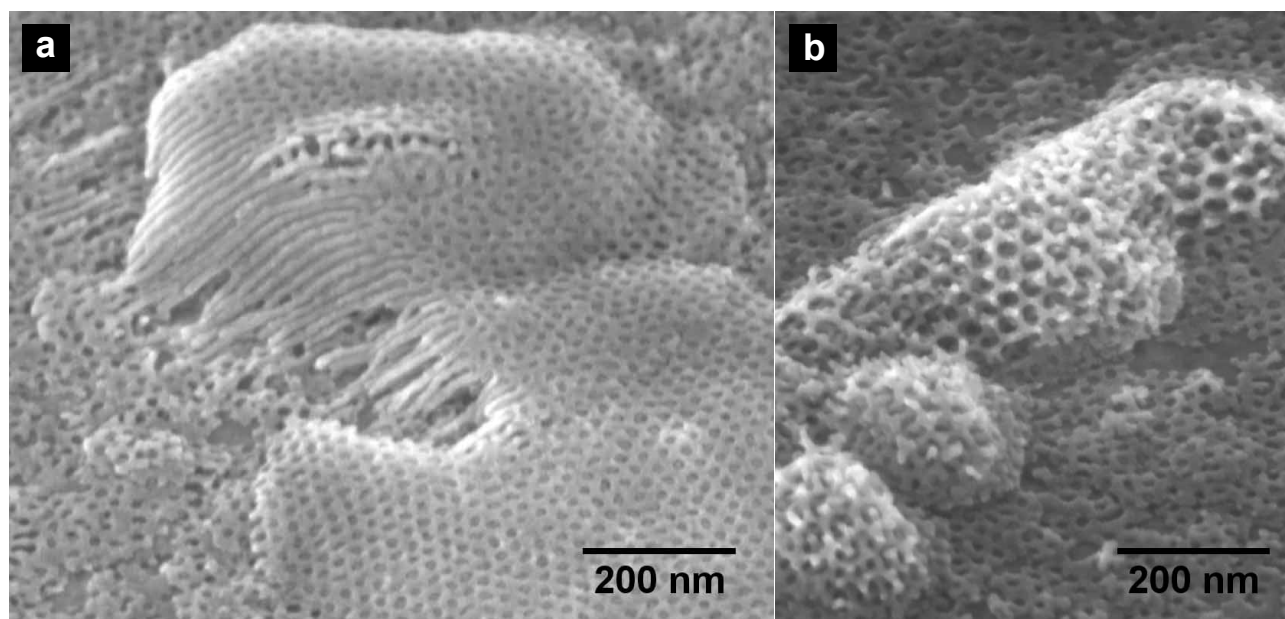


Figure 7.8: **Electrochemical replication of 250 nm thick MHI41 free film templates annealed at 150 °C on gold substrate.** (a) Coexistence of $HPL_{||}$ and $C_{||}$ morphologies. (b) Growth into the bulk of the film replicates the gyroid phase. Viewing angle: 45°.

(~ 2 nm). The characteristic spacing of the parallel structures (determined by Fourier analysis) is 23 ± 2 nm. The film was immersed in a 0.05 M NaOH etching solution for 5 min (with an etch rate of $\sim 1 \text{ nm s}^{-1}$) and the same area was imaged again. In places, the gaps between the structures open where the PLA domains are removed. Indeed, over a larger viewing area, such as shown in Figure 7.10a, there are regions in which complete collapse of adjacent PFS structures occurs, leading to large ‘chasms’ running into the bulk of the film. These observations suggest standing lamellar ($L_{\perp}$) or standing perforated lamellar ($HPL_{\perp}$) morphologies aligned by the applied electric field.

Standing sheet-like structures are expected to be unstable without connecting material supports between adjacent sheets. These interconnections would be present in the case of a $HPL_{\perp}$ morphology, but not for $L_{\perp}$ in which adjacent sheets remain isolated from each other. Indeed, the energetic tendency of lamellar domains to remain parallel rather than curving means that the standing PFS sheets do not gain structural stability by forming ‘S-shaped’ standing structures. The structures in Figure 7.9a indeed remain straight before making abrupt changes of direction in the region of grain boundaries. While sheet collapse points towards a $L_{\perp}$ morphology, the top view in Figure 7.9c does show regions with interconnections between adjacent sheets consistent with $HPL_{\perp}$. Also visible at the

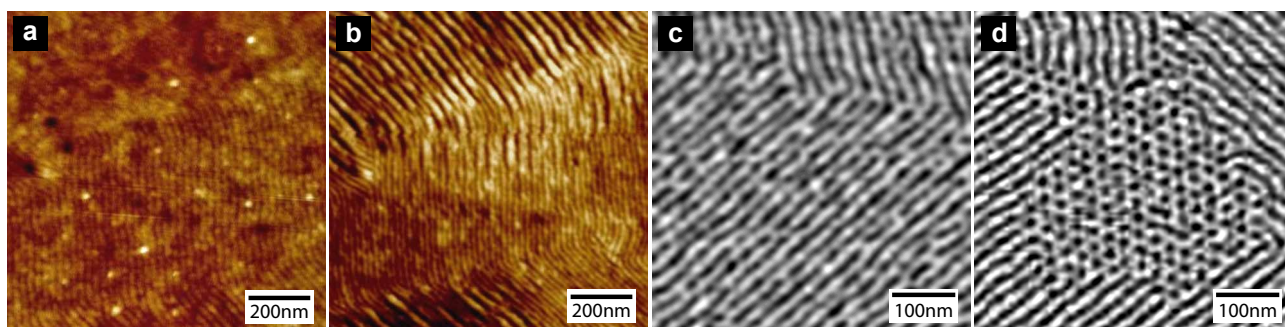


Figure 7.9: **TappingMode™ SFM height images of a 240 nm MHI41 film after annealing at 150 °C under an applied field of 120 V μm⁻¹.** (a) Surface image before removal of the PLA component reveals small height difference in PLA and PFS L_⊥ domains. (b) The same area after 300 s etching in 0.05 M NaOH_(aq) shows how the removal of the PLA component causes adjacent PFS sheets to collapse together, producing chasms in the film. (c) Enlarged region of standing sheet structures that appear to have interconnecting PFS bridges, indicative of the HPL_⊥ phase. (d) C_⊥ domains are located epitaxially within the standing sheets.

surface are regions of hexagonally ordered holes, suggesting a C_⊥ morphology with a centre-to-centre spacing of 21 ± 2 nm. These domains are epitaxially related to the surrounding sheet-like phases with the HEX [10] direction parallel to the sheet direction.

As before, a good deal about the film morphology is revealed by electrochemical replication of the template voids in platinum, followed by UV ozone etching of the PFS matrix, shown in Figures 7.10 and 7.11. The results of this procedure are most easily seen in the cross section of the ~ 600 nm thick replicated template in Figure 7.11. The lower portion of the film is almost exclusively a C_⊥ morphology, which blends into sheet structures consistent in most instances with L_⊥ structures. Some of the replicated sheet structures in Figure 7.11d have perforations indicative of a HPL_⊥ phase template alongside L_⊥.

The morphology at the substrate interface can be seen in areas where either the template, or the replicated structures have peeled away from the Au substrate (Figure 7.12). The C_⊥ morphology in the bulk of the film gives way to a single layer of C_{||} running along the Au surface. Since the electrochemical replication of the template is so uniform and complete, it is reasonable to assume that these C_{||} PLA domains are everywhere in electrical contact with the substrate as opposed to contact only at defect sites in a wetting layer. The electric field is sufficient in this case to overcome surface fields (which otherwise drives a complete wetting layer of PFS) but not enough to induce a perfect

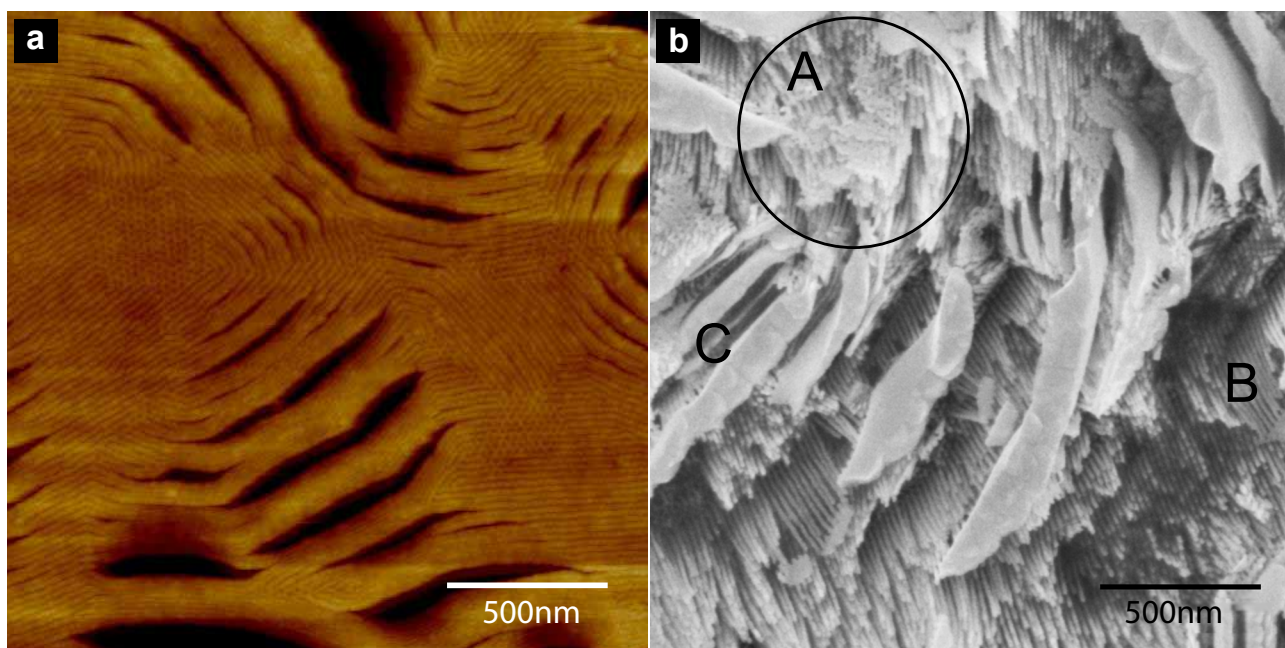


Figure 7.10: **Large area view of a MHI41 surface after $120 \text{ V}\mu\text{m}^{-1}$ electric field alignment at 150°C .** (a) TappingMode™SFM image of template surface after PLA removal. (b) Corresponding SEM top view of Pt replicated nanostructures after ozone removal of PFS template showing (A) $\text{HPL}_\perp$, (B) $\text{C}_\perp$ and (C) $\text{L}_\perp$ morphologies.

$\text{C}_\perp$ phase at the interface.

The evidence presented so far has suggested a morphological transition from gyroid to standing cylinders and sheet structures in thin films under applied electric fields. However we should also consider the additional thin film confinement present in the electric field capacitor geometry introduced by the PDMS counter electrode. Figure 7.13 illustrates the effect of annealing a $\sim 200 \text{ nm}$ film at 150°C with (a) a free surface, (b) confined in the capacitor geometry with no applied field (a ‘blank’ sample), and (c) an applied field of $120 \text{ V}\mu\text{m}^{-1}$. As described previously, the free film shows a clear gyroid phase morphology in cross section. The ‘blank’ sample however shows no surface features and a cross section consistent with $\text{C}_\parallel$ throughout the bulk of the film. The featureless surface is a clear indication of a wetting layer surface reconstruction driven by preferential contact of the PFS component. This reconstruction might be a single $\text{HPL}_\parallel$ layer, although this is not conclusive (Figure 7.13b). The upper wetting layer is an effective barrier for the electrolyte such that this structure cannot be replicated in platinum. The electric field aligned film cross section in 7.13c shows again the standing sheet structures alongside $\text{C}_\perp$ columns.

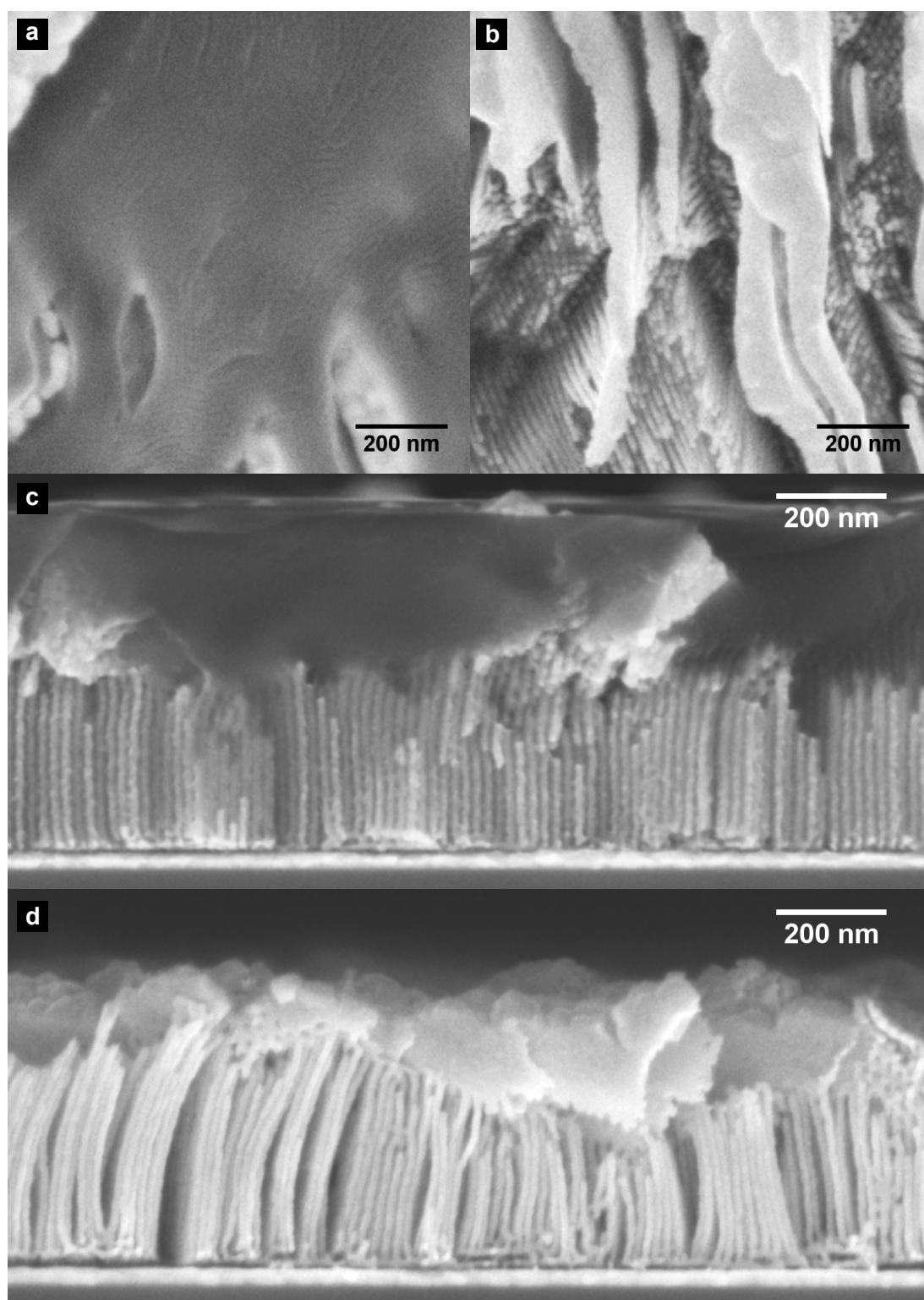


Figure 7.11: **Standing nanowires after electric field alignment at 150 °C.** (a,c) Top and cross sectional SEM images of the aligned polymer template filled with Pt (bright) after removal of the minority PLA phase. (b,d) Corresponding top and cross sectional views of the freestanding platinum arrays after UV ozone etching of the supporting PFS polymer template.

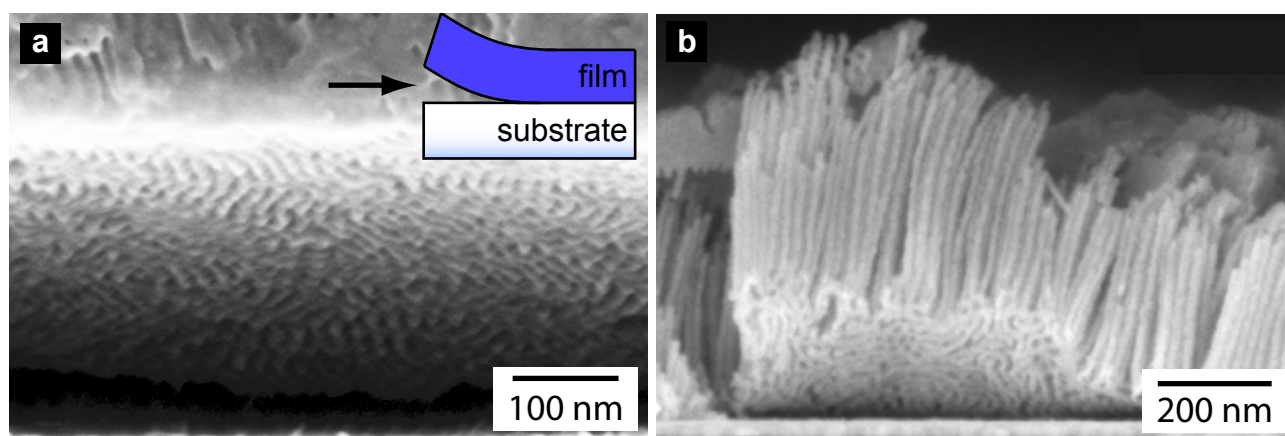


Figure 7.12: **SEM cross sectional view of an electric field aligned (150°C , $120\text{ V}\mu\text{m}^{-1}$) MHI41 template and replicated platinum array underside after partial delamination from the substrate.** (a) PFS template after PLA removal shows a layer of $C_{||}$ at the gold substrate interface. The inset shows the viewing geometry. (b) Electrochemical replication of the template in (a) shows perfect filling of the $C_{||}$ layer, which is everywhere connected to the $C_{\perp}$ region in the bulk of the film.

Further investigation of the confined ‘blank’ sample was conducted using transmission electron tomography reconstructions. The film was removed from the substrate, embedded in epoxy, sectioned by microtome and the PFS phase was stained using ruthenium tetroxide vapours (see Chapter 3). These images are not ideal, most likely because of imperfect staining throughout the sample thickness. However, a snapshot of the section viewed at $\sim 30^{\circ}$ to the section normal, combined with 3D reconstructions of selected regions confirms cylinder channels running in the plane of the film. The resolution of these images is not sufficient to determine the presence or otherwise of HPL or L morphologies in the layer at the film interfaces.

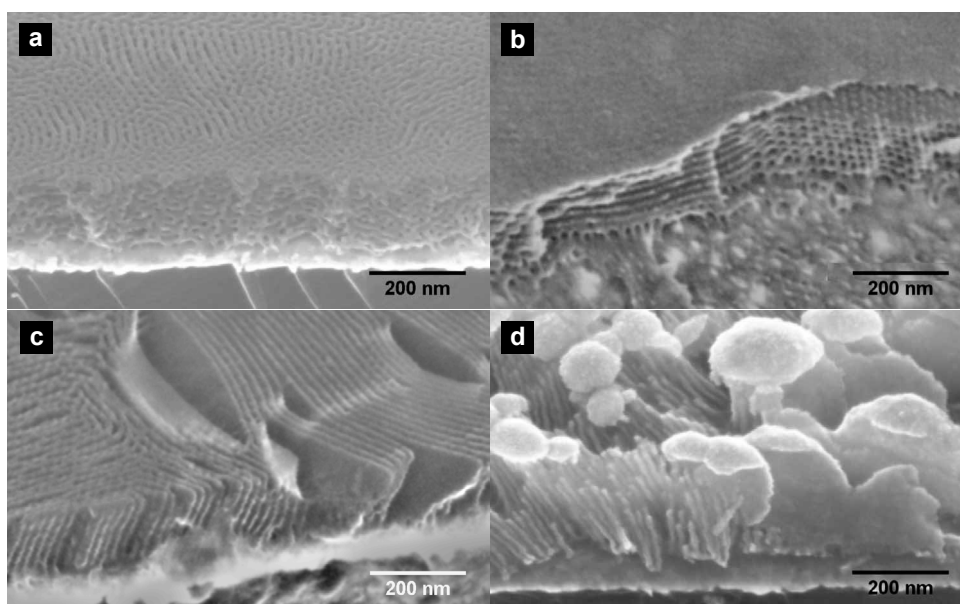


Figure 7.13: **Electric field alignment and electrochemical replication of MHI41 at 150 °C.** (a) SEM cross sections of ~ 250 nm thick films after removal of PLA for a free-surface film showing mixed morphology on the surface with gyroid morphology apparent in cross section. Identical films confined in a parallel plate capacitor geometry during annealing with (b) no applied field or (c) $120 \text{ V}\mu\text{m}^{-1}$. The confined film in (b) shows $C_{\parallel}$ in the film bulk, consistent with TEM tomography, and a PFS wetting layer at the upper surface. The aligned sample (c) shows a mixture of $C_{\perp}$ and $L_{\perp}$ morphologies. (d) Pt replication of (c) producing a mixture of standing nano-sheets and nanowires. The rounded features are electrochemical overgrowth out of the template surface. Viewing angle: 45° .

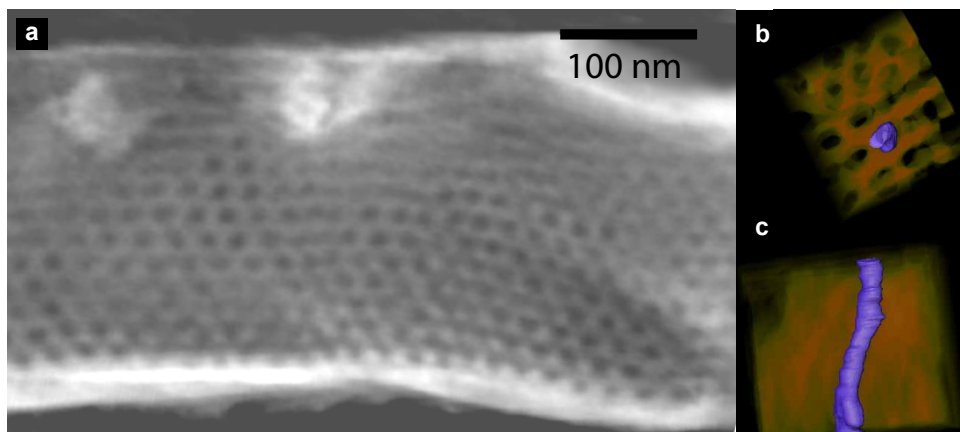


Figure 7.14: **Transmission electron tomography of MHI41 film annealed at 150 °C confined in a capacitor plate geometry with no applied field.** (a) Cross section reconstruction viewed at 30° to the sectioning plane reveals hexagonally packed spanning channels running parallel to the substrate. The bright areas correspond to the PFS matrix phase. (b) small area reconstruction viewing down channels (i.e. parallel to substrate) and (c) perpendicular to channels (viewing down substrate normal) confirming the $C_{\parallel}$ morphology in the confined film.

7.3.3 High temperature thin film behaviour

The bulk phase morphology of MHI41 indicated by SAXS is G at 180 °C. Thin films annealed at 180 °C on Au substrates showed exclusively the gyroid morphology (211) plane at the free surface. Electrochemical replication of these templates in platinum show again sporadic nucleation sites growing into the G network phase, demonstrated in Figure 7.15 a to c. The density of nucleation sites is $2.7 / \mu\text{m}^2$, which is dramatically greater than the $\sim 0.01 / \mu\text{m}^2$ seen for films annealed at 150 °C on the same substrates.

An indication of the surface reconstruction morphology at the Au interface is shown in figure 7.16 where all gyroid type growth is seen to sit above a sheet-like layer with perforations. This layer is consistent with a $\text{HPL}_{\parallel}$ reconstruction with occasional defect site contacts to the substrate as seen for Pt replication of free films annealed at 150 °C (Figure 7.8).

MHI41 films annealed under a $120 \text{ V}\mu\text{m}^{-1}$ electric field at 180 °C remain largely in the G phase,

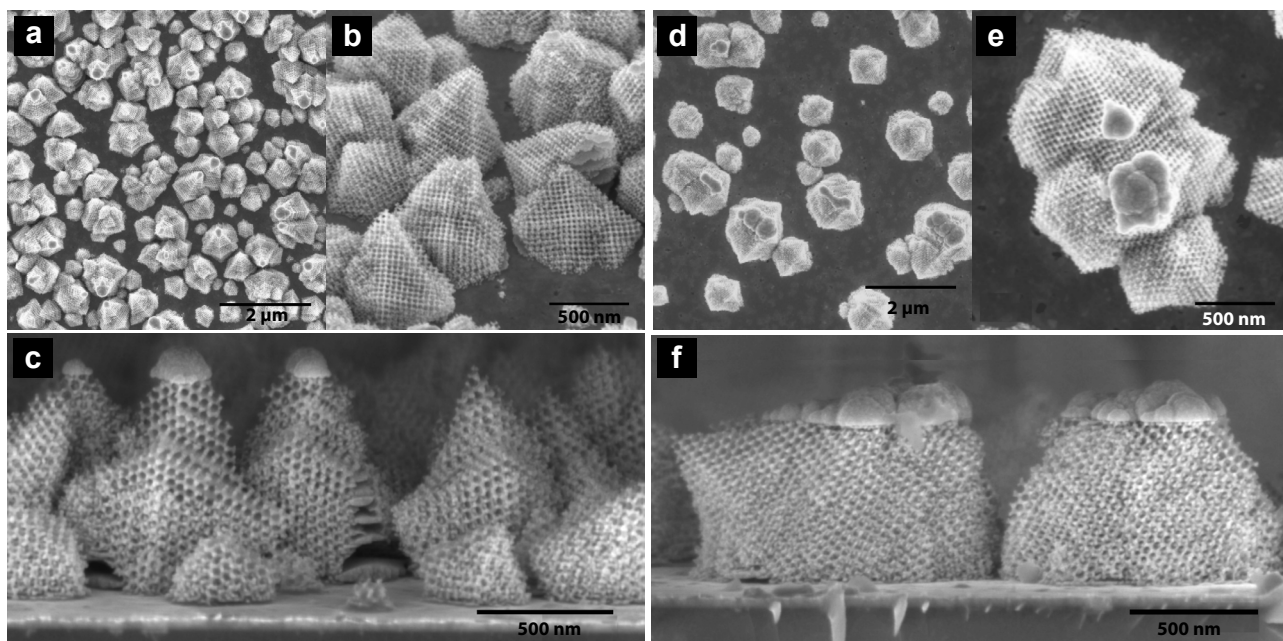


Figure 7.15: **Platinum gyroid replication after annealing at 180 °C unconfined or under a $120 \text{ V}\mu\text{m}^{-1}$ electric field on untreated Au substrates.** (a,b) Top view SEM in low and high magnification and (c), cross section showing nucleation of electrochemical growth sites for platinum (bright) in the gyroid phase. (d,e,f) are equivalent images for films annealed under an electric field. The dome-shaped structures are overgrowth out of the PFS template.

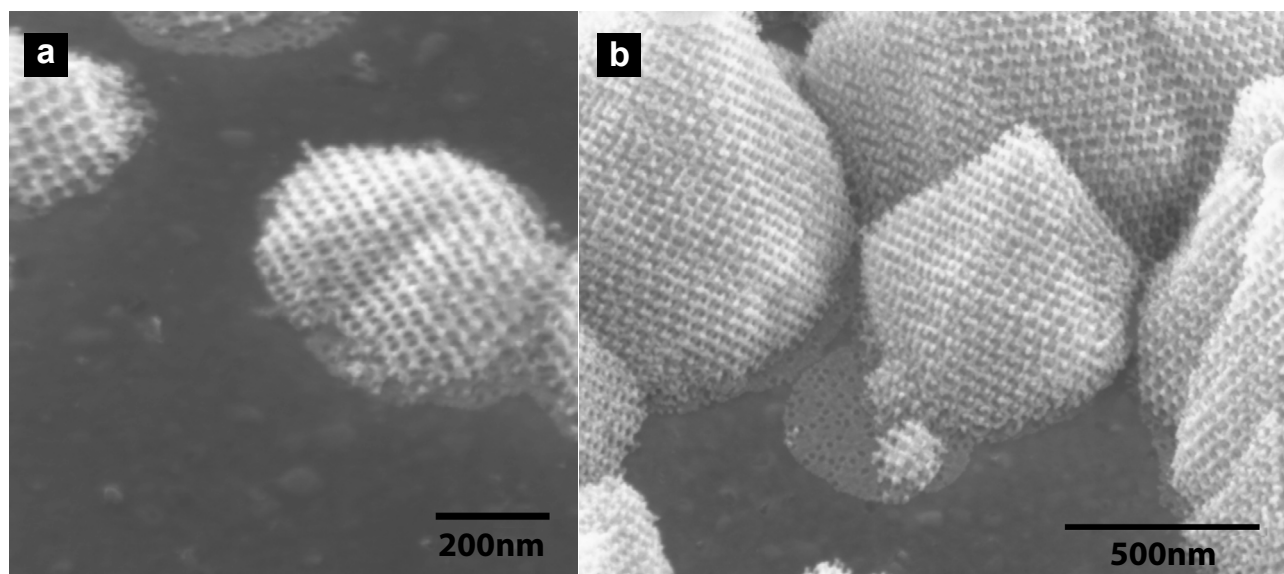


Figure 7.16: **Platinum gyroid replication of free surface films annealed at 180 °C on untreated Au substrates.** (a) Early stage growth and (b) late stage growth both show a sheet-like underlayer with perforations at the Au substrate interface. Viewing angle 45°.

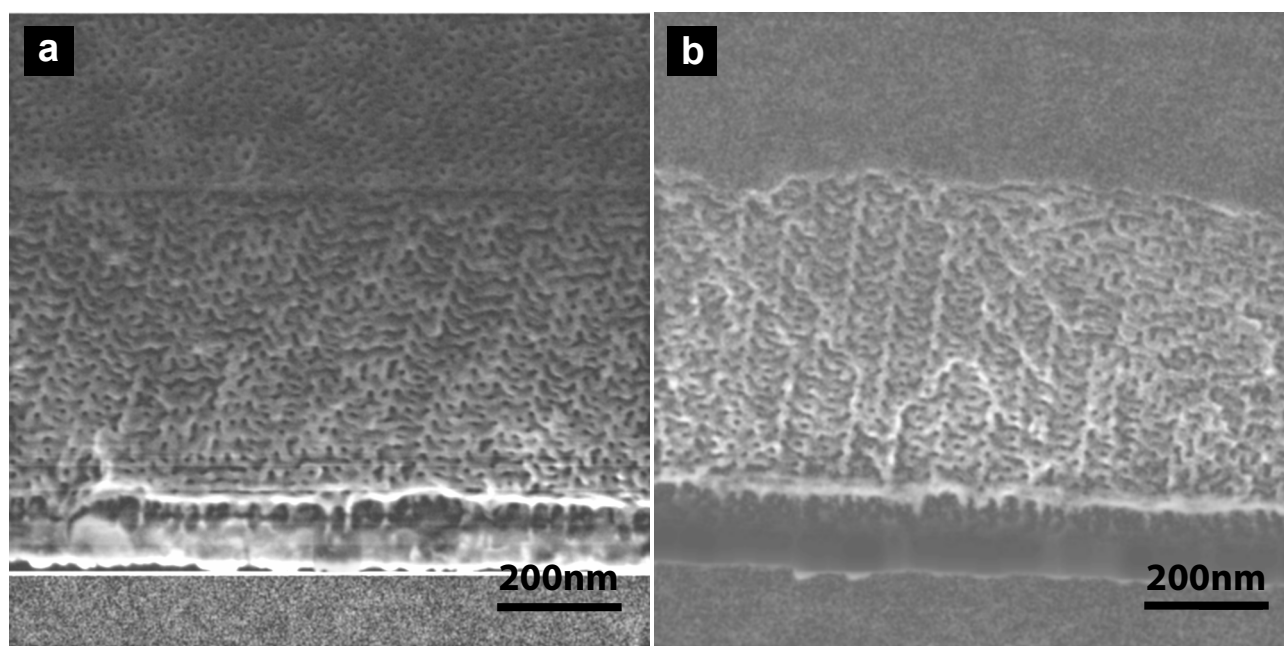


Figure 7.17: **Cross section SEM images of MHI41 films annealed at 180 °C for 35 h with and without a $120 \text{ V}\mu\text{m}^{-1}$ applied electric field.** (a) Under an applied electric field the structure seen in most of the film is characteristic of the gyroid morphology with the (211) face visible at the upper surface. (b) The ‘blank’ sample shows a featureless surface characteristic of a wetting layer reconstruction at the PDMS contact surface, while the bulk of the film exhibits the a gyroid structure. Viewing angle 45°.

as shown in Figure 7.17. Electrochemical platinum deposition into the electric field annealed sample shows nucleated growth into the gyroid phase with a reduced nucleation density of $0.6 - 1.3/\mu\text{m}^2$, summarized in Figure 7.15 d to f. Without an applied field, the contact surface with PDMS counter electrode again results in a wetting layer of PFS making the template impermeable to the electrolyte. Application of the electric field overcomes the surface field at the upper interface to again favour a (211) gyroid reconstruction at the upper surface. The gyroid-to-cylinder transition predicted by Pinna *et al.* [28] was not observed under the experimentally accessible field strengths at 180°C .

The electric field at 180°C does however lead to the coexistence of a $\text{HPL}_\perp$ phase which can be imaged following replication in platinum (Figure 7.18). The nucleation density of electrochemical growth into these structures is the same as for the G phase regions under the electric field ($0.6 - 1.3/\mu\text{m}^2$). Figure 7.18a shows that neighbouring nucleation sites have the same $\text{HPL}_\perp$ orientation, suggesting that in the bulk of the film a $\text{HPL}_\perp$ structure extends over fairly large domain sizes.

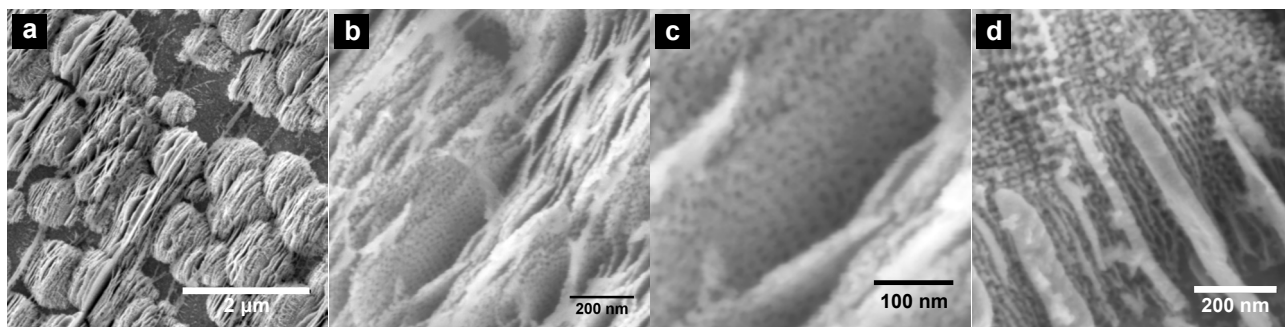


Figure 7.18: Standing perforated lamellae phases replicated in Pt after $120 \text{ V}\mu\text{m}^{-1}$ electric field alignment at 180°C . (a) Low magnification SEM top view of nucleated electrochemical platinum growth into a 900 nm thick aligned MHI41 polymer template after ozone removal of the PFS matrix. Magnified images (b,c) reveal a perforated lamellae microphase $\text{HPL}_\perp$. The $\text{HPL}_\perp$ phase in this template coexists with the G phase in the upper left portion of (d) which covers the majority of the patterning area.

Substrate modification

Electrochemical replication of the gyroid network phase using templates on Au substrates is limited by sporadic nucleation sites for growth determined by the surface reconstruction layers at the substrate. Modification of the surface field can be achieved by forming a self assembled monolayer of undecanethiol on the Au substrate (see chapter4). Substrates modified in this way had a water contact angle of 105° (Table 7.2). Films of MHI41 annealed at 180°C on these modified substrates show a nucleation density of $21/\mu\text{m}^2$ (compared to $2.7/\mu\text{m}^2$ for the equivalent film on an untreated Au substrate). When viewed in cross section (Figure 7.19) growth from adjacent nucleated sites coalesce rapidly to form complete lateral replication of the gyroid network morphology.

The complete replication of thicker gyroid forming templates on SAM modified Au substrates is summarized in Figure 7.21. Details of the surface reconstruction morphology on the modified

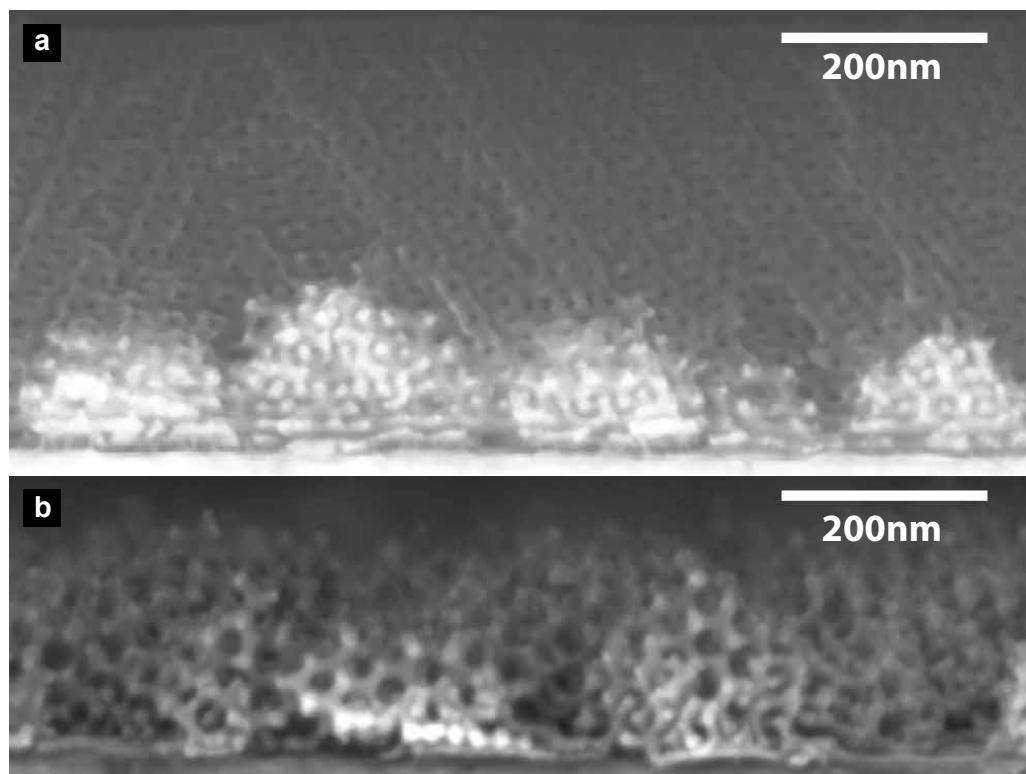


Figure 7.19: **Platinum gyroid replication of free surface films annealed at 180°C on undecanethiol modified Au substrates.** (a) Early stage growth with the PFS template still in place and (b) after UV ozone etching of polymer matrix. The growth layer is relatively uniform with complete lateral coverage from initial nucleation sites after $< 200\text{ nm}$ vertical growth.

substrates are shown in Figure 7.20. Once again the surface layer shows characteristics of a single $\text{HPL}_{\parallel}$ layer underlying the gyroid phase in the film bulk. With the formation of a complete lateral coverage in replication comes the option of under-etching the replicated layer away from the substrate in order to image the array from the underside. This can once again be achieved using a bromine etching solution for the Au substrate, which leaves the platinum array unaffected. Large flakes of the templated array float away from the substrate and were remounted on holey carbon TEM grids. SEM images of these arrays from the side and directly underneath are shown in Figure 7.20b,c. Discernable in the underside view are the characteristic $[111]$ lattice directions contained in the (211) gyroid plane. While it is not possible to see the perforated platelet structures apparent in the original SEM views, there are clearly some regions of the underside which do not appear to be completely open and porous. To illustrate the difference between this structure and that seen for a fully replicated gyroid network, the top view of a filled template is shown in Figure 7.20d. It is possible that in the SEM image we are able to see structures through this thin (~ 10 nm) layer, or indeed that the layer is not well adhered to the bulk of the gyroid growth and becomes detached during the etching removal procedure.

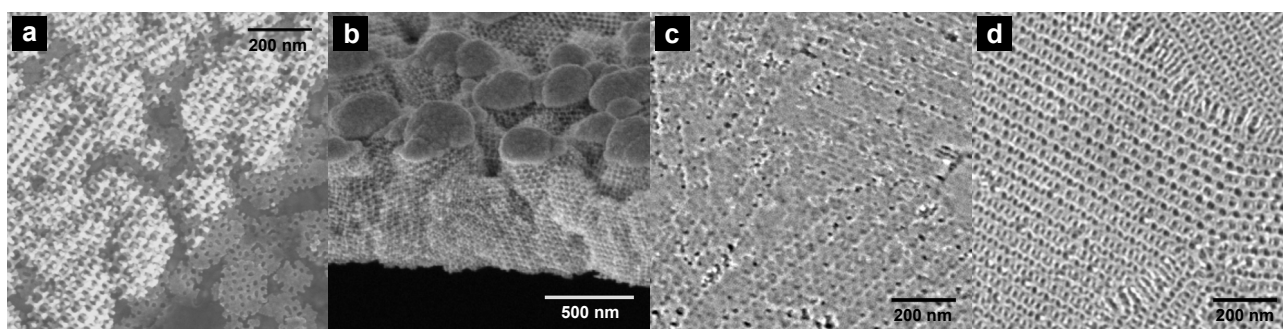


Figure 7.20: Analysis of gyroid template platinum replication on undecanethiol SAM substrates (a) Very early stage growth suggest that the contact morphology is a perforated lamellar layer ($\text{HPL}_{\parallel}$) immediately adjoining the gyroid morphology in the film bulk. (b) On etching the Au substrate layer a thicker platinum gyroid replicate comes away as a single film owing to the lateral connectivity of the structure. (c) Underside of the film in (b), the $[111]$ type wave patterns are visible. (d) Comparison to the free surface morphology seen in a TiO_2 replicate showing ideal porosity between the gyroid network struts into the bulk of the film.

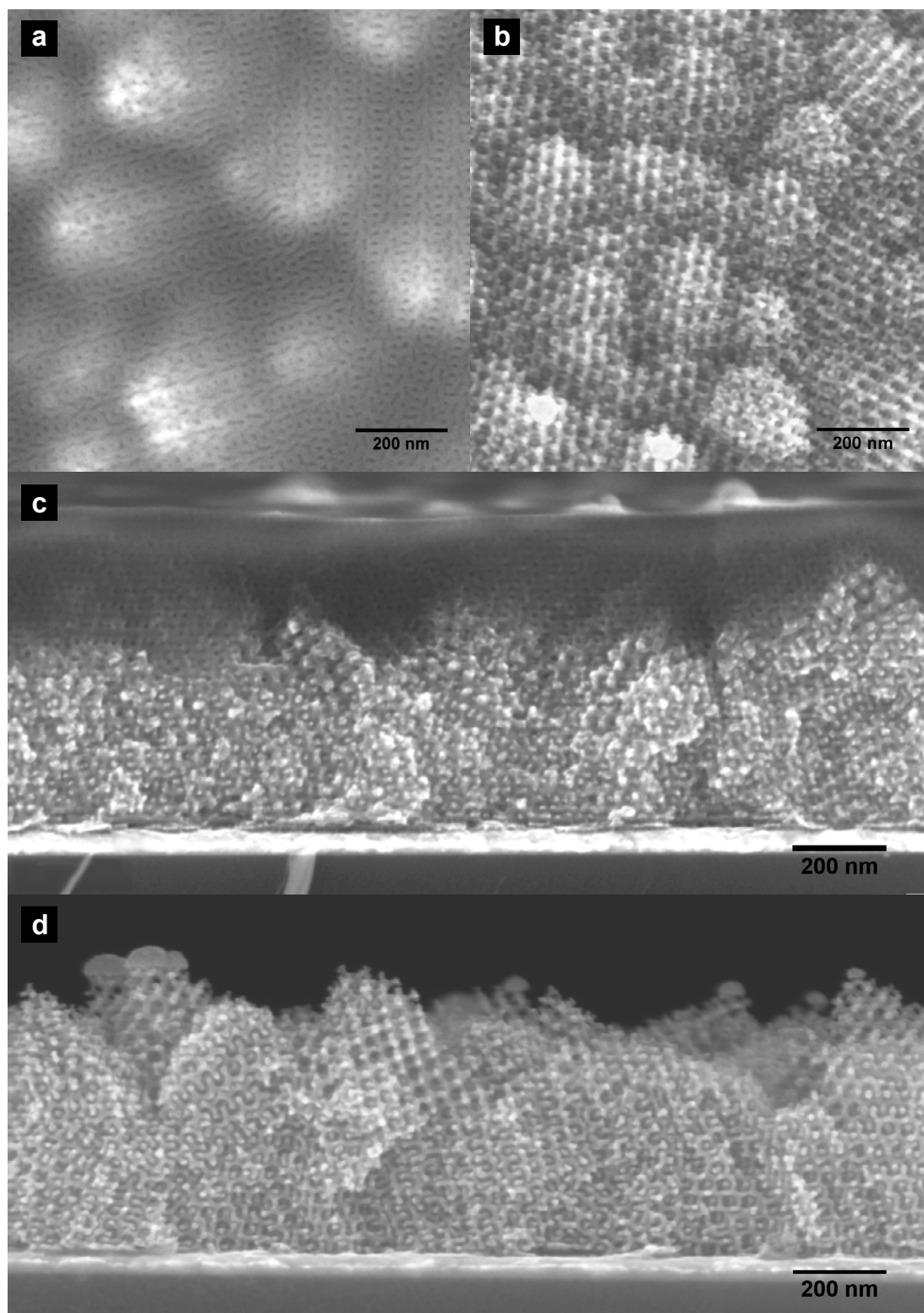


Figure 7.21: **Replication of the gyroid morphology after annealing at 180 °C with no applied field on an Au substrate modified with an undecanethiol SAM. (a,c) Top and cross sectional SEM images of the porous gyroid template filled with platinum. The free surface in (a) shows the 211 lattice projection (b,d) Corresponding top and cross sectional views of the freestanding platinum arrays after UV ozone etching of supporting polymer template.**

The gyroid on FTO substrates

Progress towards functional device structures using templated arrays requires a suitable choice of both structured material and underlying substrate. Photovoltaic devices require at least one transparent window electrode and a suitable choice for the dye-sensitized solar cell is a glass substrate with fluorine doped tin oxide transparent conductive coating, referred to as FTO. The FTO is further coated with a ~ 50 nm layer of TiO_2 by spray pyrolysis deposition (see chapter 4). MHI41 films were prepared on the TiO_2 substrates without further modification except cleaning by exposure to O_2 plasma for 300 s.

After annealing at 180°C and removal of the PLA phase the porous films were used for electrochemical growth of Ti(IV) oxide, the details of which will be discussed in chapter 8. The growth was found to be extremely even over the substrate indicating a uniform porosity of contact with the substrate. The nature of the surface reconstruction was again probed by removing flakes of templated material and viewing the underside of the array by SEM. Arrays removed by sonication in toluene are shown in Figure 7.22. The underside of the gyroid array adopts the large scale structures from the TiO_2 surface roughness (shown alongside). This structure makes it difficult to identify a clear gyroid projection, although a characteristic [111] type lattice direction can be seen in Figure 7.22a, consistent with the (211) planes lying parallel to the substrate. The large roughness of the FTO based substrate compared to the Au layers is highlighted by Figure 7.22d showing typical height profiles determined by TappingModeTMSFM. The feature height of the TiO_2 substrate is comparable to the domain size in the copolymer (~ 10 nm).

The surface roughness was quantified by analysis of height maps obtained from TappingModeTMSFM (Figure 7.23). These data, along with the static water contact angles of the various substrates used are shown in Table 7.2. On the relatively flat Au surface (RMS roughness (R_q) = 1.02 nm) the most porous copolymer reconstruction was observed on undecanethiol SAMs, with a high contact angle (105° , indicating a relatively low energy surface). There is a tendency for lamellar-type surface reconstructions driven by a contact energy asymmetry at flat interfaces. Presumably the SAM layer is energetically more neutral than the bare gold surface.

On the other hand, the TiO_2 substrate has an RMS roughness of 19.7 nm, a peak height of 129 nm

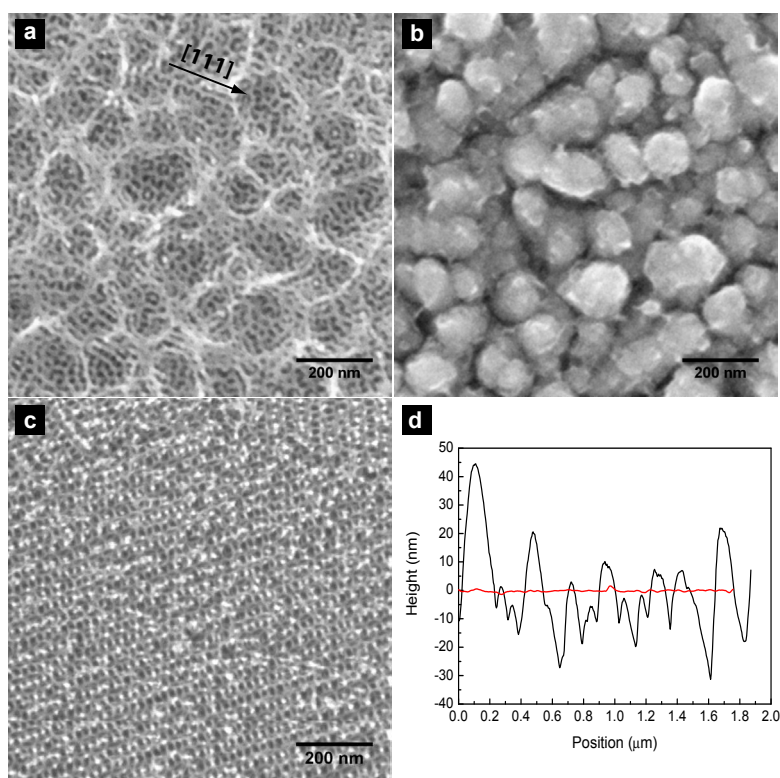


Figure 7.22: **SEM surface images of Ti(IV) oxide replication of gyroid templates on TiO₂ substrates.** (a) Underside of Ti(IV) oxide flakes released from substrate by sonication in organic solvent. (b) TiO₂ substrate morphology. The replicated template underside shows no evidence of surface reconstruction away from bulk gyroid phase. [111] type lattice vectors are highlighted. (c) Corresponding upper surface of a replicated layer illustrating a remarkably uniform layer growth. (d) 2D section height profile taken from TappingModeTMSFM images showing large amplitude roughness of the TiO₂ substrate (black) in comparison to Au coated silicon (red).

and results in no trace of a wetting layer or $\text{HPL}_{\perp}$ reconstruction. The static water contact angle is 0° , indicating a high energy surface. While the static water contact angles are not direct measurements of the respective polymer-substrate interactions they do serve to show that the two surfaces are at least likely to have very different interaction energies. The role of surface roughness may be important in making it energetically unfavourable to reconstruct a lamellae type wetting layer even in the case of asymmetric substrate-polymer interactions. A lamellar domain would have to curve sharply on a length scale not far from the domain size in order to conform to the peaks and troughs in the substrate, which carries an elastic deformation penalty compared to flat interfaces [29]. Sivaniah *et al.* observed similar behaviour using a symmetric PS-*b*-PMMA copolymer on ITO substrates with

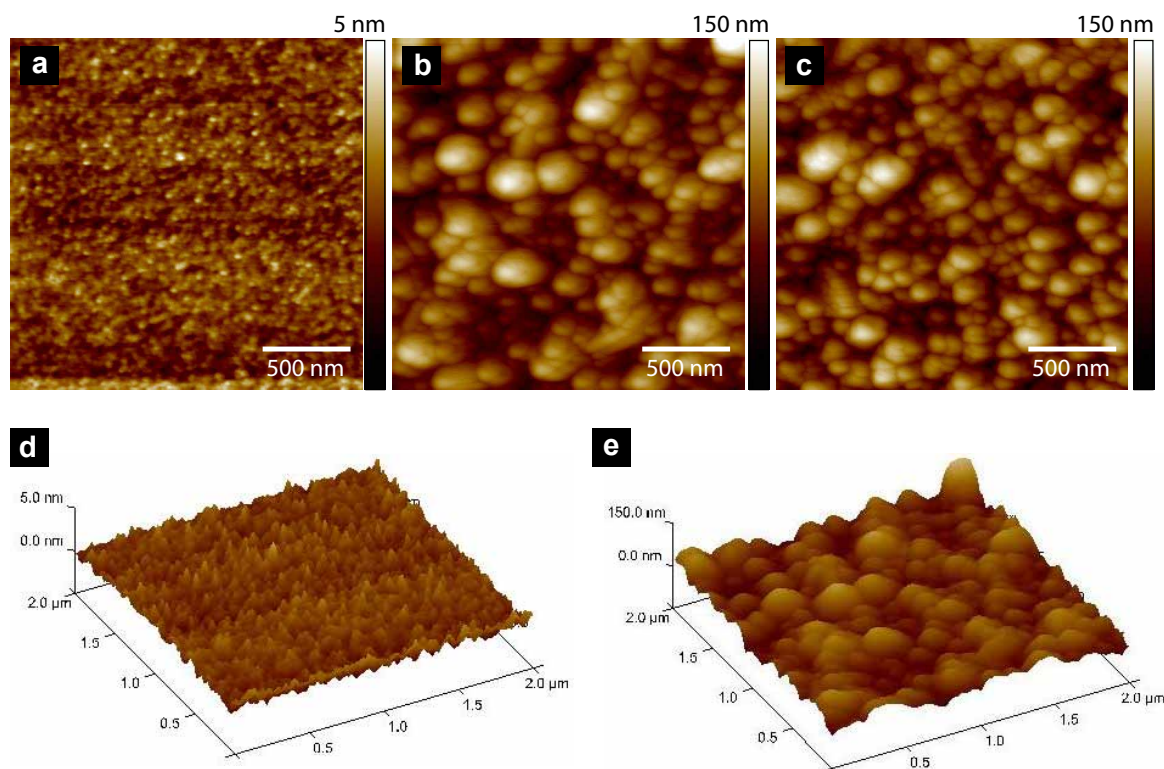


Figure 7.23: **TappingMode™ SFM height images characterizing surface roughness features.** (a) Au (b) FTO and (c) FTO coated with ~ 50 nm TiO_2 layer. The RMS roughnesses are 1.02, 20.5, and 19.7 nm for Au, FTO and TiO_2 respectively (summarized in table 7.2). (d) and (e) are 3D surface projections of Au and TiO_2 , note the difference in height scale.

an RMS roughness of around 15 nm [30]. In this instance, lamellar domains were found to orient perpendicular rather than parallel to the rough substrate. Absolute confirmation of this effect with the gyroid phase reconstruction would require further investigation of the precise energetic asymmetry of these copolymer components to the substrate in question. The observation of a fully uniform porosity on rough surfaces raises the interesting question of whether surface roughness could be employed to produce porous gyroid coatings on a wide range of functional surfaces regardless of their detailed enthalpic polymer-substrate interactions.

Table 7.2: Substrate roughness and water contact angles

Substrate	Cleaning Method	RMS Roughness $R_q = \sqrt{z_i^2}$ (nm)	Peak Height $R_{\max}$ (nm)	Contact Angle (°) ^a
Au	Undecanethiol SAM	-	-	105
	None ^c	-	-	64
	SJ	1.02	4.06	63
	Sonication (acetone) and SJ ^b	-	-	45
FTO	Plasma cleaned	20.5	126	wets
TiO ₂	Plasma cleaned	19.7	129	wets

^a Contact angles given are the average of at least 5 measurements taken over the substrate area

^b Roughness measured for snow-jet (SJ) cleaned Au are assumed to not differ significantly for other cleaning methods

7.4 Summary

The gyroid network phase was electrochemically replicated to produce freestanding arrays with uniform coverage over large areas. The surface reconstruction layer is crucial in determining continuity of the minority phase to the conducting substrate, which is necessary for electrochemical deposition. Electrochemically replicated structures suggest a HPL surface reconstruction with preferential wetting of the PFS majority component. Application of a $120 \text{ V}\mu\text{m}^{-1}$ electric field at 150°C results in standing arrays of L, HPL, and C phases which can also be electrochemically replicated to produce mixed arrays of nanosheets and nanowires. Annealing at higher temperatures (180°C) results in a G morphology with more complete substrate access. Gyroid (211) planes are found at the free surface of the film (further discussion of the G phase alignment is given in chapter 8). Application of an electric field at 180°C results in a mixture of the G and standing HPL phases. The (211) gyroid plane remains parallel to the upper surface of the film under the applied electric field. There are no other reported experiments in the literature investigating the response of the gyroid phase to an external electric field.

In contrast to the behaviour on smooth Au substrates (RMS roughness ~ 1 nm), no HPL surface reconstruction layer is seen for films annealed on TiO_2 coated FTO substrates with an RMS roughness of ~ 20 nm. The G forming films on these substrates allow perfect electrochemical replication of the network structure. These results mark the first example of direct electrochemical replication of the G or HPL phases from block copolymer templates which may prove extremely interesting for patterning of functional materials for device applications.

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The double gyroid solar cell

This chapter describes the fabrication of freestanding TiO_2 semiconductor gyroid network arrays and their application in liquid electrolyte and solid-state dye-sensitized solar cells. These devices are the first example of functioning electronic devices exploiting the gyroid structure. We first focus on complete structural and orientational characterization of the arrays using direct imaging and scattering techniques. The results presented here are contained in the paper ‘The bicontinuous double gyroid dye-sensitized solar cell’ [1].

8.1 Introduction

Self assembly of the bicontinuous gyroid phase provides in principle an ideal route for patterning of mutually interpenetrating functional material junctions such as bulk heterojunction photovoltaics. However, coupling the delicate thermodynamic balance of this bicontinuous self assembly with functional material and in the correct geometry for real applications is extremely challenging. Gyroid morphologies were recently reported in germanium [2], have been replicated by platinum electro-deposition [3], and ionic transport in one domain of the bicontinuous cubic morphology has been demonstrated [4]. However there are no reports of the self assembled gyroid structure exploited in a functioning electronic device of any type. The results presented here describe the first replication of a metal-oxide semiconductor in the gyroid network phase, achieved via electrochemical deposition of anatase TiO_2 into the voided gyroid templates developed in Chapter 7. The arrays are used to construct

liquid electrolyte and solid state DSSCs with excellent power conversion efficiencies under simulated solar illumination.

8.2 Experimental

The characteristics of the G forming poly(4-fluorostyrene)-*b*-poly(D,L-lactide) (PFS-PLA) block copolymer used in this chapter, termed MHI41, are described in detail in Chapter 7. Experimental details of solar cell construction are given in Chapter 4. The graphical simulation methods used to help identify and determine the orientation of the gyroid phase are outlined in Chapter 7.

Substrate and polymer template preparation

FTO glass substrates (Nippon Glass) were cleaned with acetone, isopropanol and exposure to O₂ plasma for 5 minutes and coated with a compact TiO₂ film (~ 50 nm) by spray-pyrolysis deposition as described in Chapter 4 and in references [5, 6]. PFS-*b*-PLA films were prepared by spin coating or blade coating from 10 %_{wt} solutions in toluene. The films were annealed at 180 °C in a N₂ atmosphere for 35 h and allowed to cool to room temperature over 3 hours. The PLA component was selectively removed by immersing the films in 0.05 M NaOH_(aq) containing 40 %_{vol} MeOH at room temperature.

Electrochemical deposition of titania

Electrochemical synthesis of hydrated Ti(IV) oxide mesostructured films was performed from a 0.2 M aqueous TiCl₃ at pH 2.7 using the protocol of Kavan et al. detailed in Chapter 4. The filled templates were annealed on a hotplate at 500 °C for 2 hours under nitrogen, then for a further hour in an oxygen flow in order to form nanocrystalline TiO₂ and to completely burn away the polymer template. The resulting films were transparent and optically smooth.

Material and morphological characterization.

Block copolymer and electrodeposited nanostructures were characterized by scanning electron microscopy (SEM) using a FEI Philips XL30 sFEG at an accelerating voltage of 5 kV with no additional coating. Cross-sectional images were obtained by immersing the sample in liquid nitrogen and frac-

turing the substrate. Electrodeposited Ti(IV) oxide array structures for TEM cross sectional imaging were first embedded in epoxy (Streurs Epoxide) before removal of the entire array from the substrate by immersing the sample in liquid nitrogen. The embedded sections were cut using a microtome and imaged without further staining.

8.3 Freestanding titania gyroid network arrays

8.3.1 Structural characterization

A schematic drawing of the gyroid templating, processing, and solar cell construction procedure is shown in Figure 8.1. Successful template replication can be observed by surface and cross sectional SEM imaging after removal of the PFS matrix by UV ozone etching (Figure 8.2). In order to convert the Ti(IV) oxide material into (nano)crystalline anatase titania, a high temperature annealing stage is required. The Ti(IV) oxide-PFS gyroid composite was annealed on a hotplate at 500 °C for 2 h under argon followed by 1 h under oxygen. This treatment results in complete degradation of the polymer template and the simultaneous crystallization of the electrodeposited material. Profilometry of a series of non-structured Ti(IV) oxide films deposited in this manner revealed a 37 ± 6 % thickness (volume) reduction during temperature processing, as shown in Figure 8.3. In the gyroid arrays this material contraction is again reflected directly in the film thickness which show a 40 ± 12 % contraction during high temperature annealing.

A notable problem encountered with application of the TiO₂ electrodeposition scheme was deposition of insoluble deposits on the walls of the template in the layers above the electrochemical growth front. This unwanted material can block off the template pores, making further deposition impossible. In addition to this, templates not completely filled by the electrodeposition had a covering layer of TiO₂ between 20 and 100 nm thick over the entire upper surface of the film after high temperature annealing, blocking proper access to the templated material network (Figure 8.4). In practice this could be prevented by ensuring complete filling of the template by monitoring the electrochemical cell current under potentiostatic operation as shown in Figure 8.5. Alternatively it was found that briefly dipping the template (before annealing) in strong acid (which did not destroy the polymer

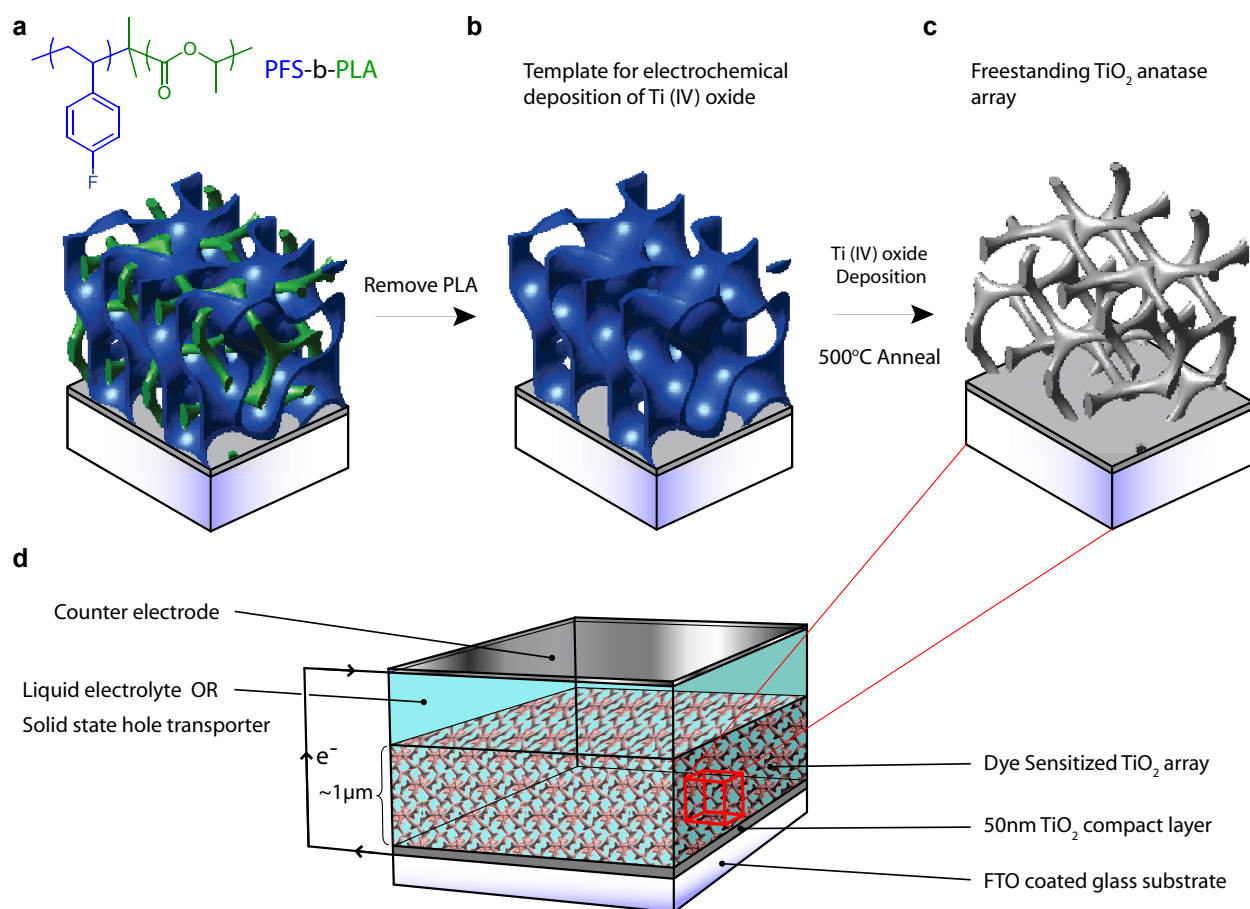


Figure 8.1: Schematic representation of inverse gyroid TiO_2 replication from block copolymer templates and assembly of dye sensitized solar cells. (a) PFS-*b*-PLA gyroid block copolymer film with the (211) plane oriented parallel to the substrate (for clarity only the central gyroid surface of the majority PFS block is shown). (b) Voided PFS gyroid template after selective removal of the minority PLA networks. The networks are electrochemically replicated in hydrated Ti(IV) oxide grown uniformly from the underlying substrate. (c) Freestanding inverse gyroid anatase TiO_2 array after thermal annealing at 500°C which burns away the supporting PFS template and simultaneously crystallizes the electrochemically deposited material. (d) The array, sensitized with a suitable dye, is assembled between a platinum-coated counter electrode and back-filled with a iodide/triiodide electrolyte to form a liquid electrolyte dye-sensitized solar cell. Alternatively, a solid state dye sensitized solar cell is made by backfilling with a solid state molecular hole transporter (Spiro-MeOTAD) and a silver counter electrode.

template) effectively removes the accessible Ti(IV) oxide deposits. An etch rate of electrodeposited Ti(IV) oxide was found to be $\sim 10 \text{ nm s}^{-1}$ in 2 M sulfuric acid measured on non-templated films.

GISAXS was used to study the order and orientation of the films over macroscopic length scales

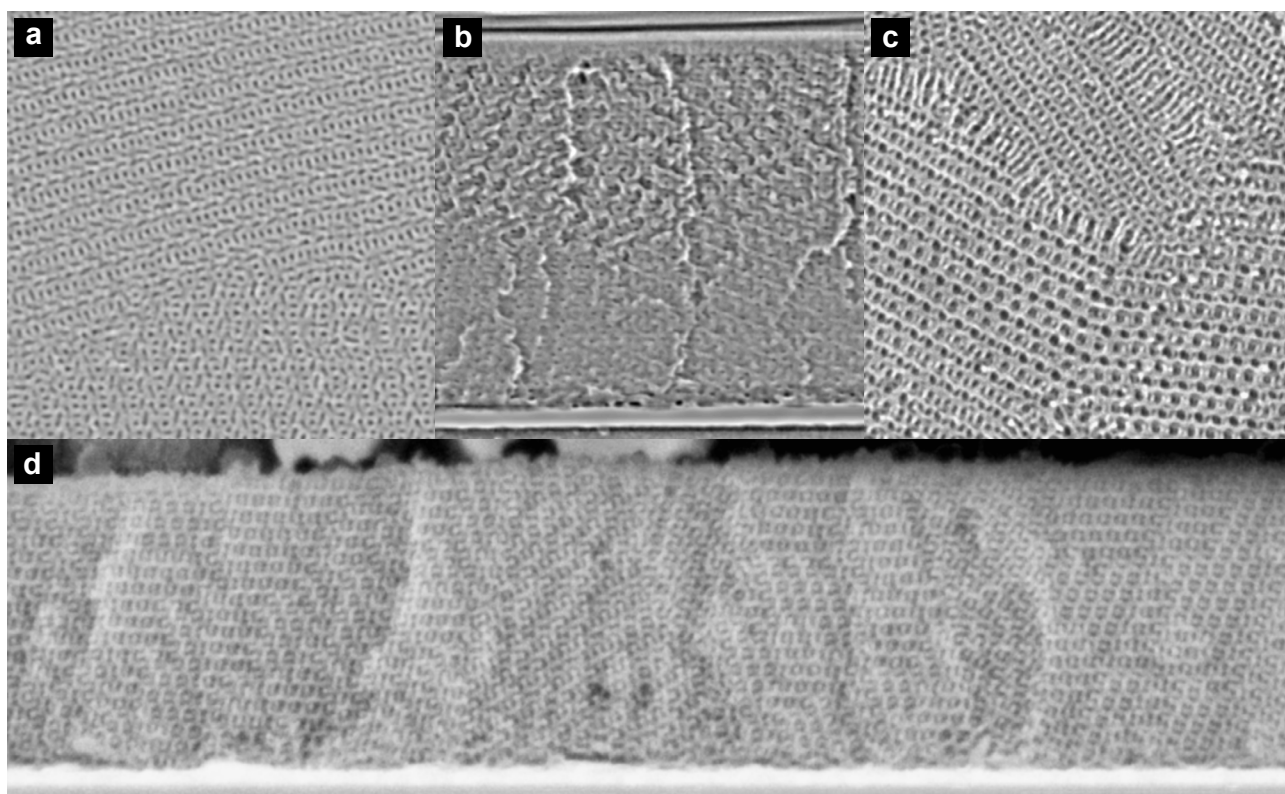


Figure 8.2: **Electrochemical replication of Ti(IV) oxide in porous gyroid templates.** (a) Surface and (b) cross sectional SEM images of porous gyroid PFS templates after removal of the minority PLA component. (c) Surface and (d) cross sectional SEM images of the Ti(IV) oxide inverse gyroid array by uniformly filling the template voids from the conducting substrate by electrochemical deposition and dissolving the surrounding template in organic solvent. (a,b,c) image size $1\mu\text{m}$, (d) image width $3\mu\text{m}$.

($\sim \text{cm}$) for I: the porous polymer template, II: the electrochemically filled template, and III: the heat annealed and contracted array. The assignments of the diffraction peaks of the network arrays were made on the basis of a structure possessing $\text{Ia}\bar{3}\text{d}$ symmetry, whose (211) planes are oriented parallel to the substrate, consistent with the SEM observations and previous GISAXS experiments on gyroid structures reported in the literature [3, 10]. For the mesoporous PFS film (Figure 8.6a), the best match was obtained for a structure with a unit cell of 50.5 nm with a uniaxial compression of 9 % perpendicular to the substrate (Figure 8.6d). For the nanostructured hydrated Ti(IV) oxide-PFS films (Figure 8.6b), a unit cell of 50 nm and a uniaxial compression of 21 % was found (Figure 8.6e). GISAXS patterns confirm that periodic ordering is preserved after TiO_2 crystallization and scattering can be indexed to a cubic unit cell that has been compressed by 52 % (Figure 8.6c,f). These fit

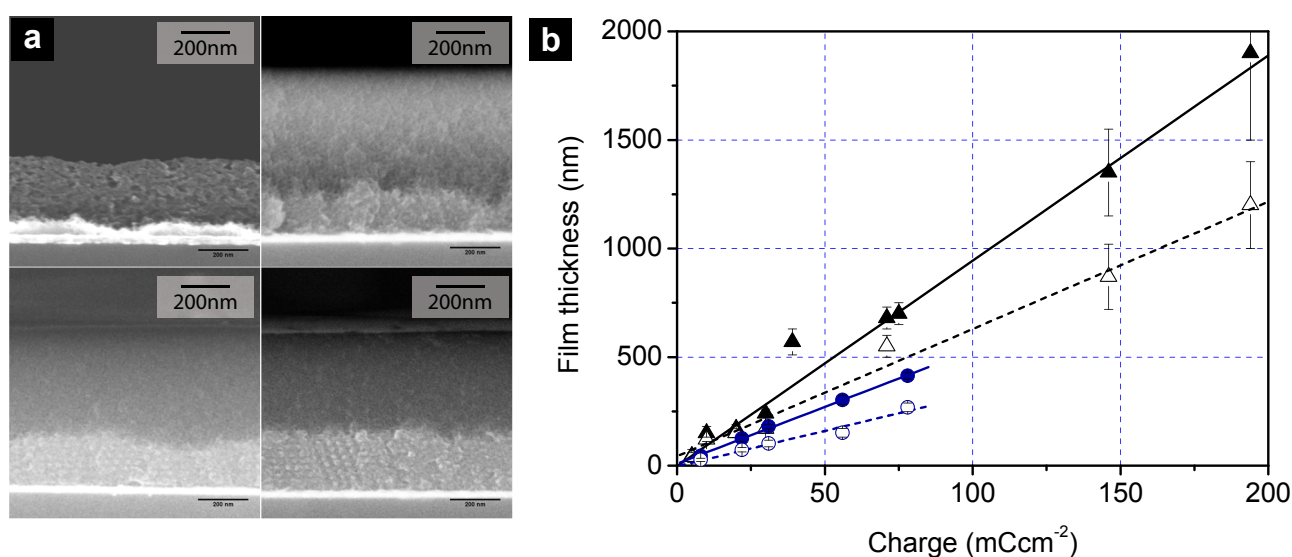


Figure 8.3: **Ti (IV) oxide electrodeposition thickness calibration measurements and film contraction on high temperature annealing.** (a) Example series of cross-sectional SEM images taken of gyroid film replication with 5, 10, 20, 30 mC cm^{-2} charge passed through the porous template in order to calibrate the deposition thickness. The first image is of a film heated to 500°C , showing additional material left from the empty template region. (b) Plot of deposition thickness (d) versus charge (Q) for non-templated deposition before heating ($\bullet$) and after annealing at 500°C ($\circ$). The ‘deposition efficiency’ ($\eta = d/Q$) is $5.2 \pm 0.2 \text{ nm/mCcm}^{-2}$ with a $37 \pm 6 \%$ compression on heating. The equivalent plot for gyroid templated arrays ($\blacktriangle, \triangle$) gives a deposition efficiency of $10 \pm 1 \text{ nm/mCcm}^{-2}$ and a $40 \pm 12 \%$ compression on heating. The straight lines are linear fits to the data.

parameters and a summary of the gyroid structural compression are given in Table 8.1.

Table 8.1: Gyroid structural compression calculated from GISAXS fitting to a uniaxially compressed cubic $\text{Ia}\bar{3}\text{d}$ structure

	Unit cell (nm)	Incremental compression (%)	Accumulated compression (%)
Bulk PFS- <i>b</i> -PLA	49.0	0	0
Voided PFS template film	50.5	9	9
Hydrated Ti(IV) oxide film	49.5	13	21
Anatase titania array	50.5	39	52

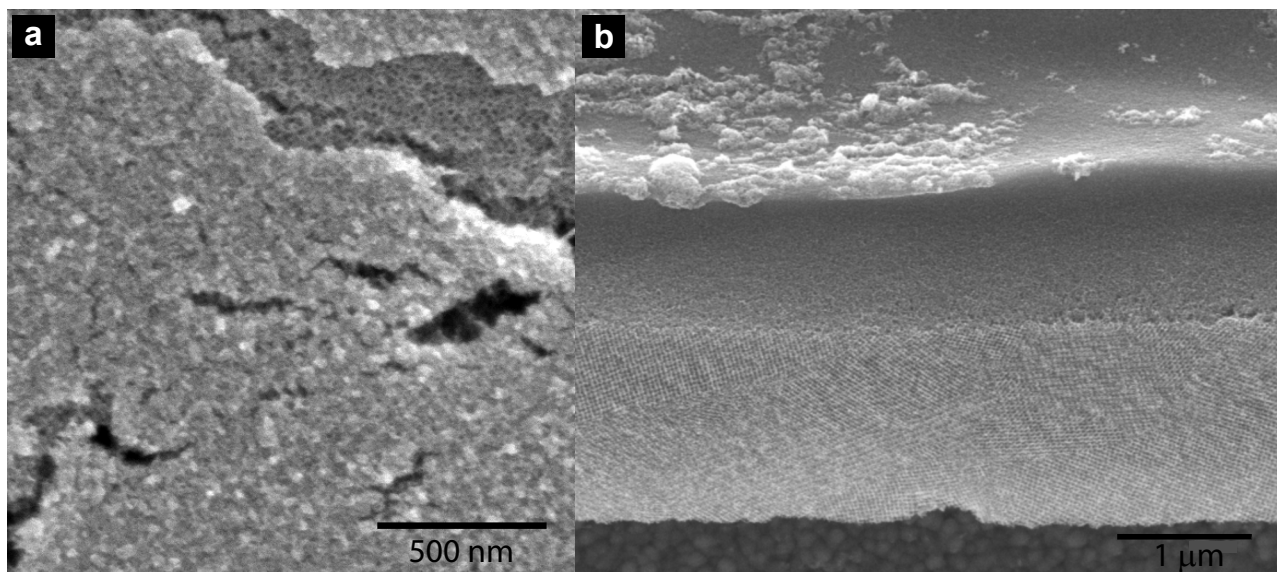


Figure 8.4: **Non-porous capping layers caused by incomplete electrochemical template filling.** (a) Top view SEM showing occasional cracks in the covering layer. (b) Side view where the array has come away from the substrate shows the covering layer peeling back from the templated layer.

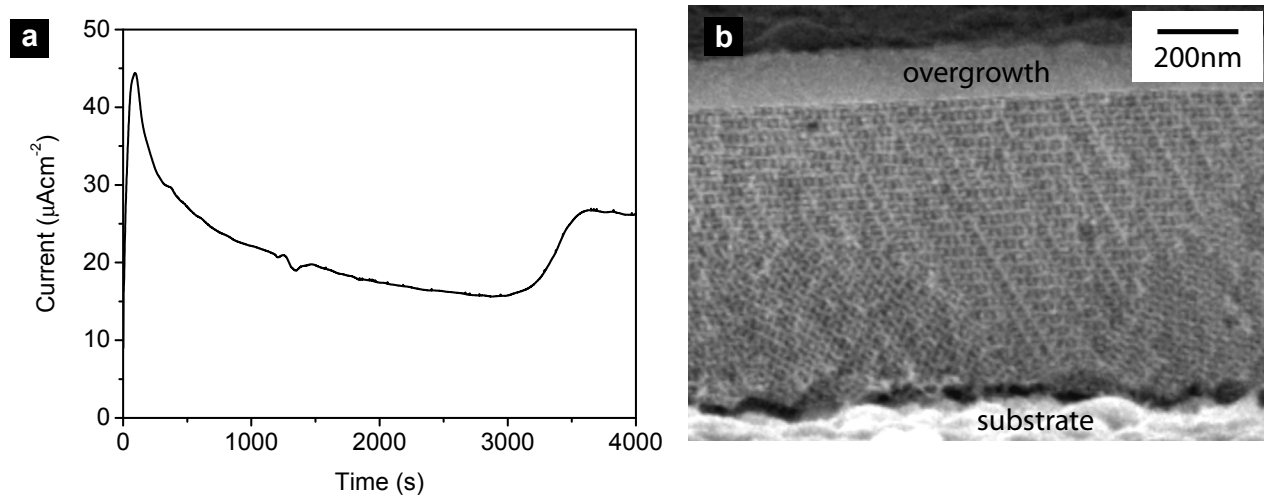


Figure 8.5: **Example of template filling by monitoring electrochemical current.** (a) Anodic current density in a 780 nm template on TiO_2 substrate. The current increases by a factor of ~ 1.8 on filling of the polymer template (accounting for the steady fall in current with a single exponential decay fit). (b) Cross section of templated array after removal of PFS matrix by UV ozone etching shows the uniform layer of overgrowth over the template surface.

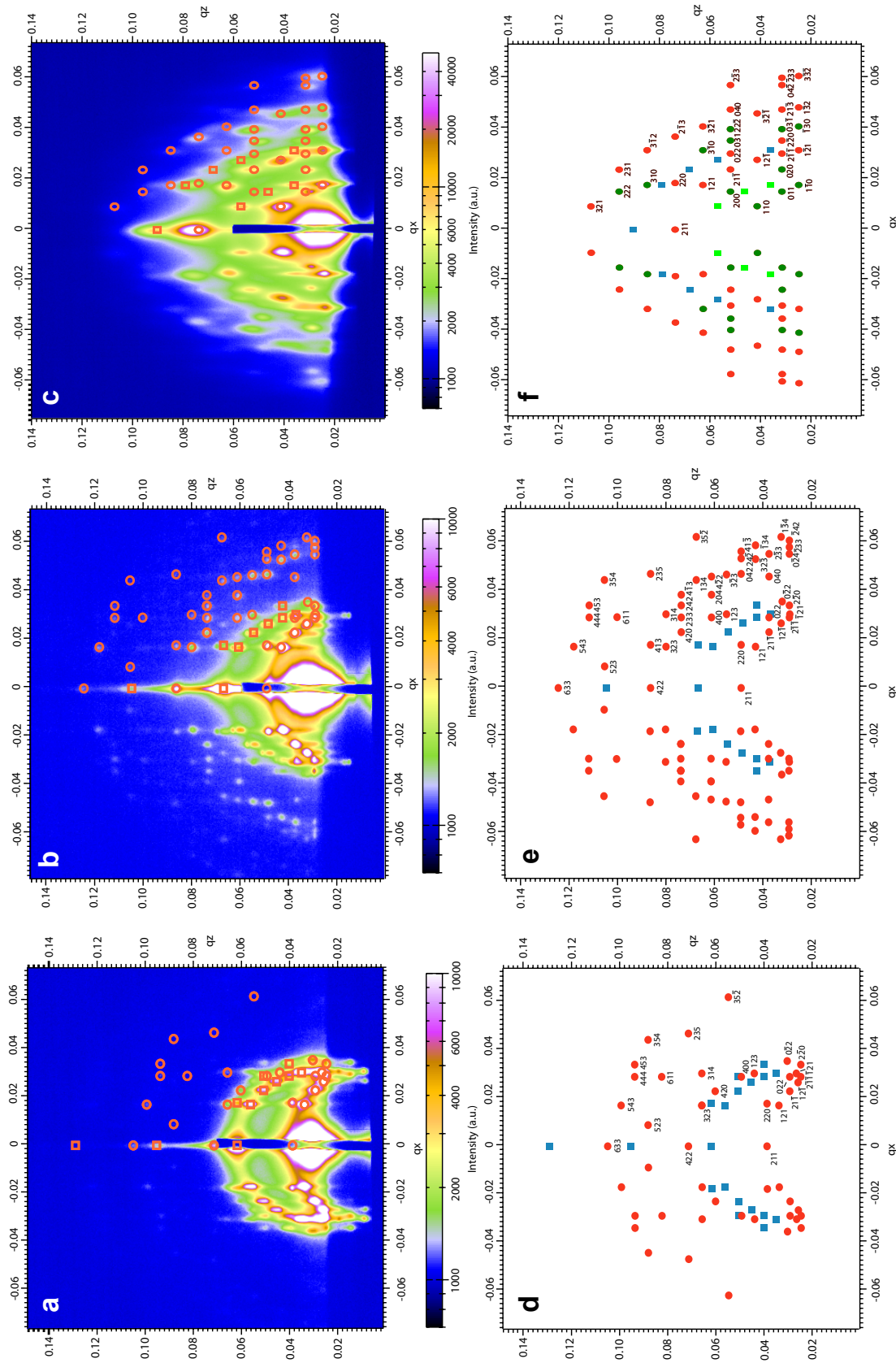


Figure 8.6: Characterization of the gyroid morphology by GISAXS. Experimental GISAXS pattern and indexation [7] of a voided PFS template after removal of minority component (a,d), nanostructured hydrated Ti(IV) oxide films with the PFS block still in place (b,e) and annealed titania network array (c,f). The patterns were analyzed using the distorted wave Born approximation to account for scattering of both the direct and reflected beam [8, 9]. ● and ■ denote the diffraction peaks due to scattering of the direct and reflected X-ray beams, respectively. ● and ■ indicate 'forbidden' reflections. Only the diffraction peaks due to the direct beam scattering are indexed and only observed peaks are marked.

The unlabeled peaks in the range $0 < q_z < 0.02 \text{ nm}^{-1}$ are probably transmission peaks through the edges of the sample, since they appear below the critical angle of the film. Compression of a cubic lattice breaks some of the symmetries of the $\text{Ia}\bar{3}\text{d}$ space-group and forbidden 110, 200, 310, and 222 reflections are observed [3, 11]. The relatively high intensity of the 110 peak compared to the 211 reflections might be caused by a shift of the two nanowire networks relative to each other [12]. Another mechanism leading to bright 110 reflections arises if only one of the two distinct networks of the double-gyroid survives the calcination process in parts of the sample.

Both the orientation and high temperature contraction can be directly observed using SEM and TEM imaging. Firstly, as described in Chapter 7, exclusively the (211) gyroid planes are seen on the free surface of the polymer film. With uniform template replication, both the porous (polymer) and relief (Ti(IV) oxide networks) projections can be imaged at the film surface in the polymer template and templated network structure, respectively (Figure 8.7). A simulation with a unit cell dimension of 47 nm was used to match these SEM images.

Figure 8.8a,d show low magnification SEM cross sections of a Ti(IV) oxide-filled template before and after annealing at 500°C with a corresponding compression of $\sim 40\%$. High magnification views of the array after UV ozone (low temperature) removal of the PFS template (Figure 8.8b), or high temperature annealing (Figure 8.8e), allow comparison of the simulated compression from the cubic lattice. Simulated projection matches to the non-annealed and heat annealed sections show a

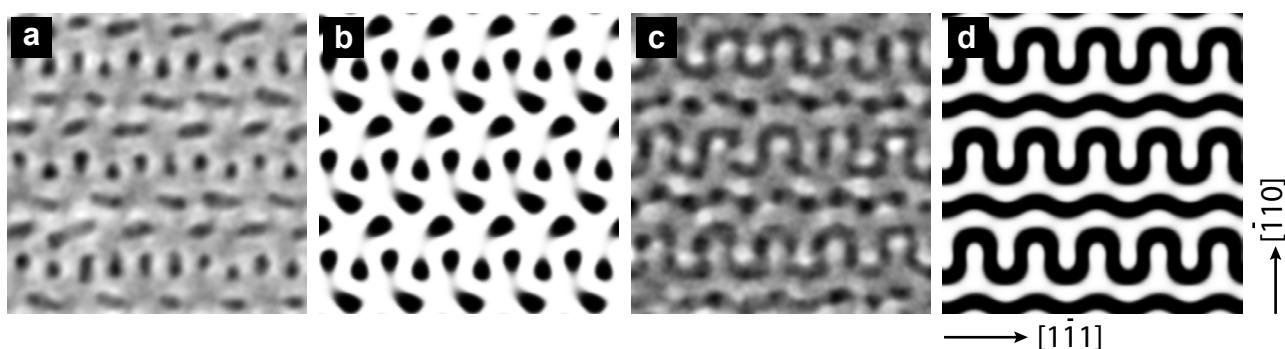


Figure 8.7: **Surface SEM images of porous and relief [211] projections.** (a) SEM image of a porous polymer template and (b) the simulated [211] porous projection with a unit cell dimension of 47 nm. (c) SEM image of replicated Ti(IV) oxide nanostructure electrochemically deposited into the template followed by dissolution of the polymer and (d) comparison to the [211] simulated relief projection.

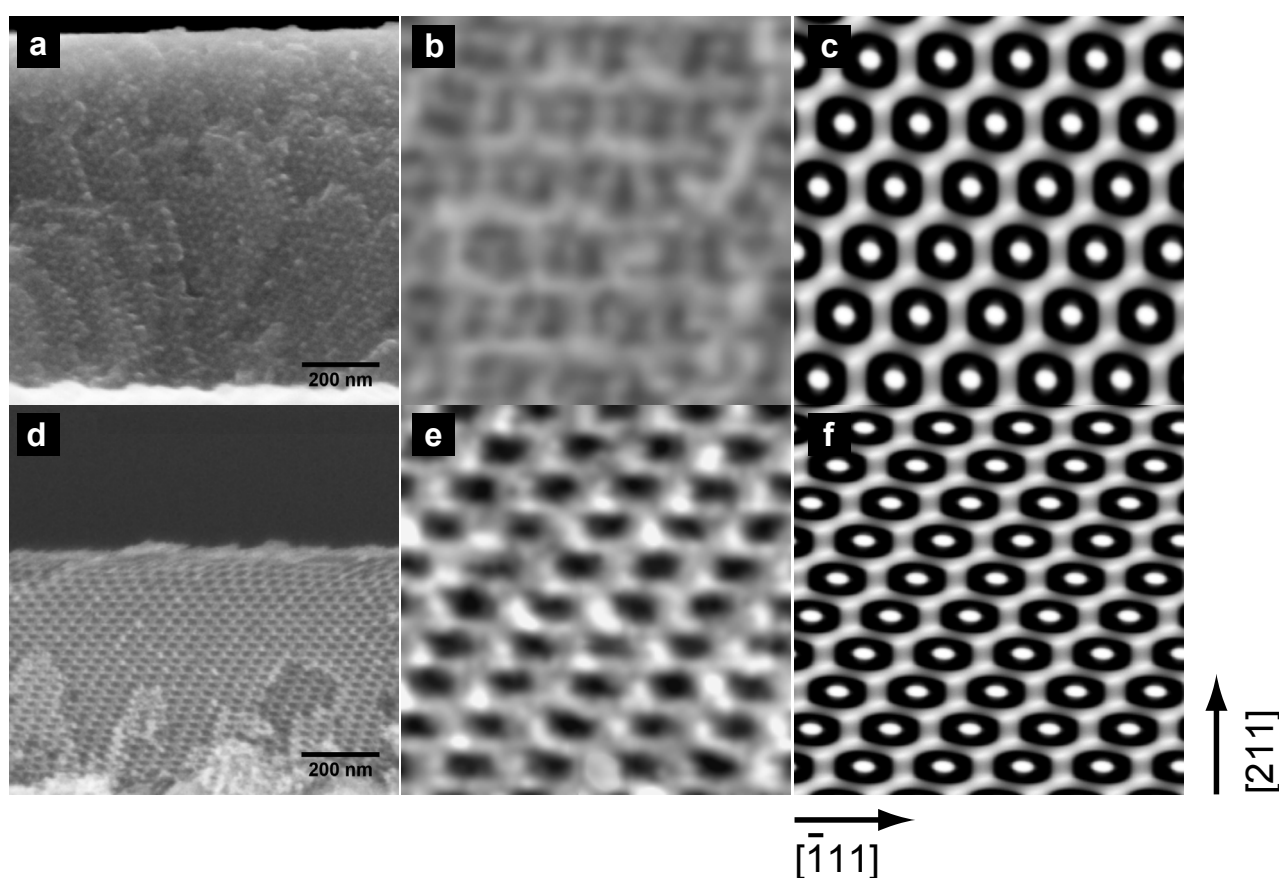


Figure 8.8: **Direct observation of vertical compression in the gyroid structure after 500 °C crystallization of Ti (IV) oxide into anatase TiO_2 .** (a,d) Cross sectional views of gyroid template electrochemically filled with Ti (IV) oxide before and after annealing at 500 °C for 2 h. The film thickness compression in (d) is $\sim 40\%$. (b) Magnified view of network after low temperature UV ozone template removal. (e) magnified view of the compressed network in (d). (c) simulated $[01\bar{1}]$ projection with 14% compression in $[211]$ direction. (f) Simulated $[01\bar{1}]$ projection with 50% compression in $[211]$ direction. Image size in (b,c,e,f) 200 nm, 50 nm simulation unit cell size.

14% and 48% vertical compression respectively, both aligned with the $[211]$ lattice direction. There is some variation in the compression observed in non-annealed fractured cross sections, between roughly 10% and 22%. On one hand, these most likely reflect sample-to-sample variation since the real contraction is likely to be sensitive to the exact electrodeposition conditions (such as the levels of dissolved oxygen). Also, assignment of compression assumes a viewing angle of 90° to the fracture plane. Failure to account for a tilt away from this perpendicular orientation could lead to incorrect quantification of compression. In practice this can be mitigated by selecting large single grain regions, with well defined fracture edges. The gyroid structural compression observed by direct imaging is

consistent with the fitted compression from GISAXS.

8.3.2 TEM Cross sectioning

A complete and general interpretation of all morphologies seen in the SEM cryo-fracture sections by comparison to simulated projections is difficult since the fracture edge is not necessarily a simple plane perpendicular to the substrate. The face actually viewed could reflect local cleavage planes corresponding to certain lattice planes, or simply follow roughly the fracture edge of the substrate. Hashimoto *et al.* found that the (211) and (110) faces of a porous gyroid structure are the most common cleavage planes since they contain adjacent sections with alternating high and low fractions of the matrix phase [13]. While the characteristic patterns seen in the cross section allow identification of the gyroid morphology, the orientation of the structure relative to the substrate cannot be conclusively determined without a well defined cross section. A sample of fracture-edge structures seen in the SEM are shown in Figure 8.9.

Microtomed cross sections on the other hand have the advantage of a well defined sectioning plane defined by the knife edge direction. Figure 8.10 shows a TEM image of such a cross section made from a Ti (IV) oxide array removed from an Au substrate coated with an undecanethiol monolayer. We see grains aligned in both a [211] vertical state (Figure 8.10d,f) but also with other alignments (Figure 8.10b,c). The compression of the structure when fitted to a simulation is parallel to the film

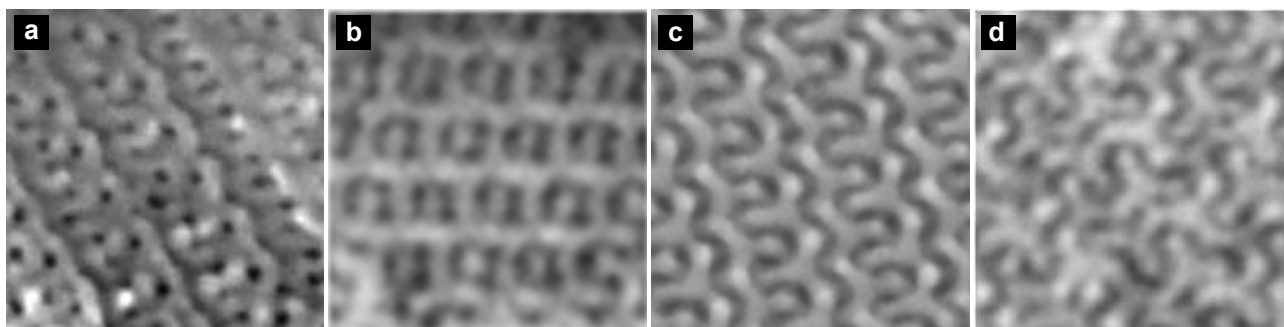


Figure 8.9: **Sample of cross section SEM morphologies in cryo-fractured gyroid templates and Ti(IV) oxide replicates.** (a) Porous PFS polymer template showing the [211] projection. (b) Ti(IV) oxide replicate showing a [110] projection. (c) Ti(IV) oxide replicate showing a [211] projection. (d) Ti(IV) oxide replicate with three-fold elements of a [111] type projection which does not perfectly match a (111) plane. Image size 200 nm.

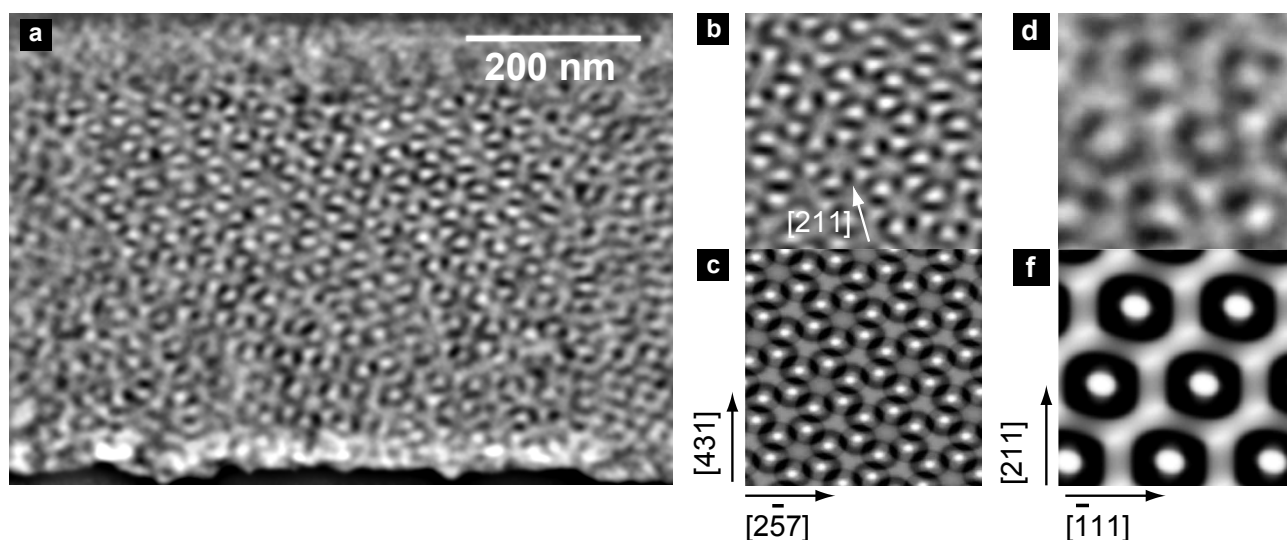


Figure 8.10: **Cross sectional TEM of a replicated Ti(IV) oxide film** (a) Complete film cross section prepared by microtoming a ($\sim 50 - 100$ nm thick section with lower surface that was originally in contact with a thiol SAM coated gold substrate. The image is shown in negative such that the bright areas correspond to high electron density TiO_2 compared to an epoxy embedding medium. (b) 200 nm enlarged region of (a), the vertical direction is the film normal. (c) Simulated $[\bar{1}11]$ type projection with unit cell of 53 nm and a 23 % uniaxial compression along the $[431]$ direction, which is aligned with the film normal. (d) 55 nm enlarged image of another grain orientation. (f) simulated $[0\bar{1}1]$ type projection with a unit cell of 55 nm and a 20 % uniaxial compression along the $[211]$ direction, which is aligned with the film normal.

normal regardless of the orientation. This is as expected since a film geometry can only accommodate a volume compression in the vertical direction. The compression magnitude was 20 to 25 % in all fitted images. Assuming that the orientation on both gold and FTO substrates is the same, these results show that while the majority of domains are aligned in a $[211]$ vertical state, there are other grain alignments present in the film. No further attempts were made to quantify the fraction of $[211]$ aligned grains using real-space TEM cross sectional imaging.

8.3.3 Material characterization

Grazing incidence wide-angle X-ray scattering (GIWAXS) patterns of the 500°C annealed arrays are consistent with nanocrystalline anatase TiO_2 with an average crystallite diameter of 9 nm, calculated by Debye-Scherrer peak width analysis (Fig. 8.11d). These assignments are supported by high resolution transmission electron microscopy (HRTEM) studies (Fig. 8.11), showing polycrystalline gyroid

network struts made up of anatase grains with sizes of the order of the strut diameter (~ 10 nm). No lattice fringes or X-ray scattering peaks were discernable for the non-annealed arrays, consistent with an amorphous Ti(IV) oxide material expected from the electrochemical deposition [14].

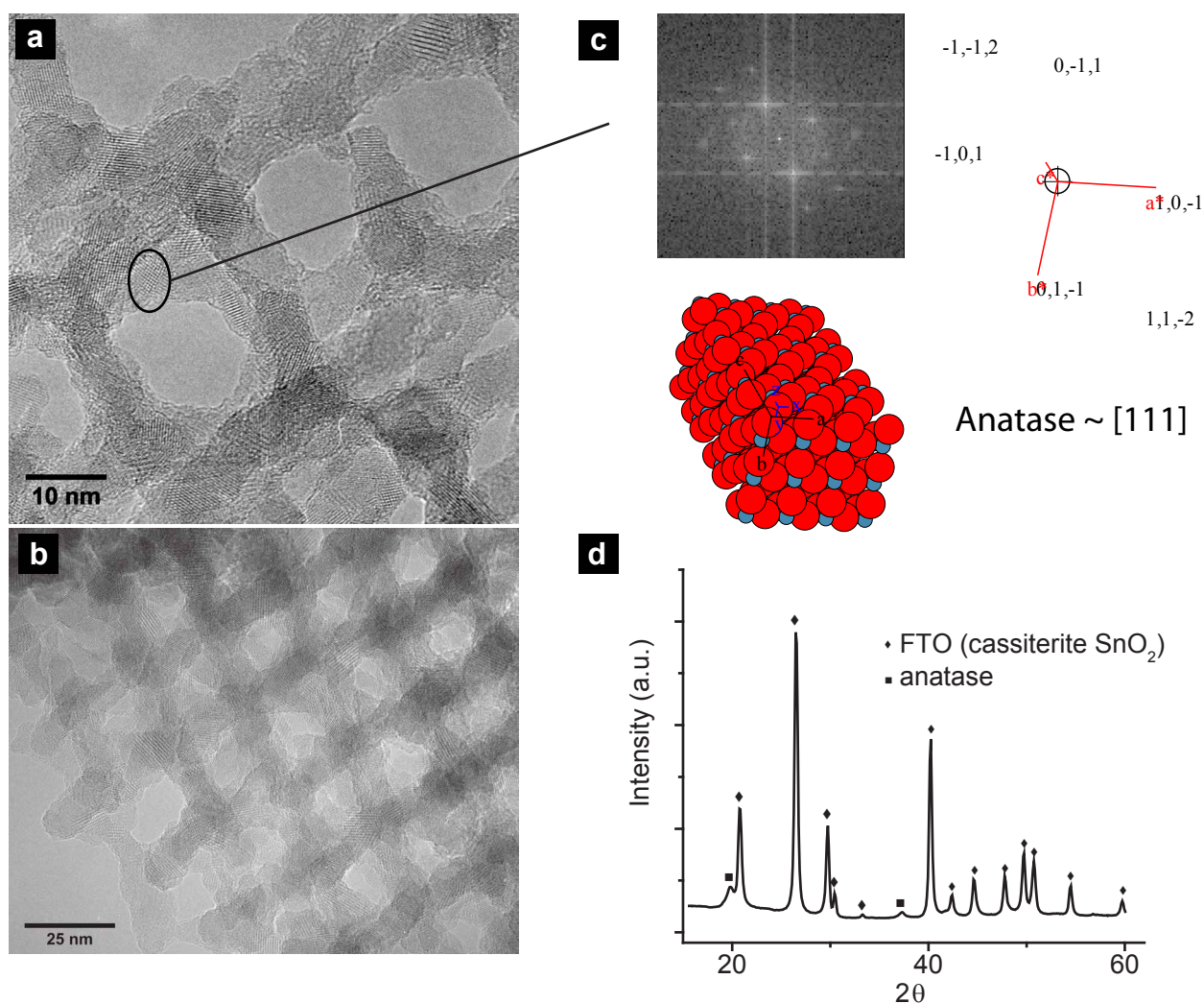


Figure 8.11: **Material characterization by HRESTEM and X-ray scattering after annealing at 500 °C.** (a,b) High and low magnification views of gyroid arrays showing ~ 10 nm anatase crystallites, which are roughly the same size as the structural confinement. (c) indexing of crystallite lattice fringes to the [111] view of anatase TiO_2 . (d) GIWAXS trace indexed to anatase TiO_2 , with an estimated 9 nm average crystallite size from peak width analysis.

8.4 Liquid electrolyte dye-sensitized solar cells

The performance of the TiO_2 gyroid arrays in a photovoltaic device was first probed in a liquid electrolyte DSSC. The titania films were subjected to a surface treatment by immersion in TiCl_4 described in Chapter 4 and sensitized with a bi-pyridyl NCS ligand ruthenium complex dye (N719). Closed cells were assembled with a Pt coated FTO counter electrode and ‘Robust’ liquid electrolyte [15] was infiltrated into the cell via vacuum back-filling [16] (for further details see Chapter 4). The photovoltaic action spectra of a $1.2\ \mu\text{m}$ thick TiO_2 gyroid DSSC showed a peak external quantum efficiency (EQE) of 27 % at 500 nm (Fig. 8.12a). The current-voltage characteristics of a 400 nm and a $1.2\ \mu\text{m}$ thick solar cell measured under simulated AM 1.5 solar illumination of $100\ \text{mW cm}^{-2}$ are shown in Fig. 8.12b. The 400-nm device has a maximum power conversion efficiency of 0.85 %, which rises to 3.0 % for the $1.2\ \mu\text{m}$ thick array.

8.5 Solid-state dye-sensitized solar cells

Solid-state DSSCs were constructed by infiltration of the solid-state hole-transporter 2,2',7,7'-tetrakis-(N,N-di-methoxyphenyl-amine)-9,9'-spirobifluorine (Spiro-MeOTAD) [17]. The titania was sensitized with either the standard bi-pyridyl ruthenium complex Z907 [18] or the high extinction coefficient indoline dye D149 [19, 20] and Spiro-MeOTAD was infiltrated into the porous layer by spin-coating from a chlorobenzene solution containing Li-TFSI and tert-butylpyridine. A thermally evaporated Ag counter electrode completed the device (for further details see Chapter 4).

The solid-state DSSCs incorporating $\sim 400\ \text{nm}$ thick TiO_2 gyroid arrays sensitized with Z907 and D149 had peak EQEs of 14 % and 33 % respectively (Fig. 8.12c). Current-voltage characteristics measured under simulated AM 1.5 solar illumination of $100\ \text{mW cm}^{-2}$ for the same devices are shown in Fig. 8.12d, exhibiting overall power conversion efficiencies of 0.67 % for Z907 sensitization and 1.73 % using D149. A cross section of the Z907 device is shown in Figure 8.13.

Regarding the infiltration of Spiro-MeOTAD into the gyroid arrays, Figure 8.14a shows a SEM image of a cryo-fractured cross-section of a solid-state device, and that of a similar film section before hole transporter infiltration (inset). A $\sim 400\ \text{nm}$ thick Spiro-MeOTAD capping layer is clearly visible

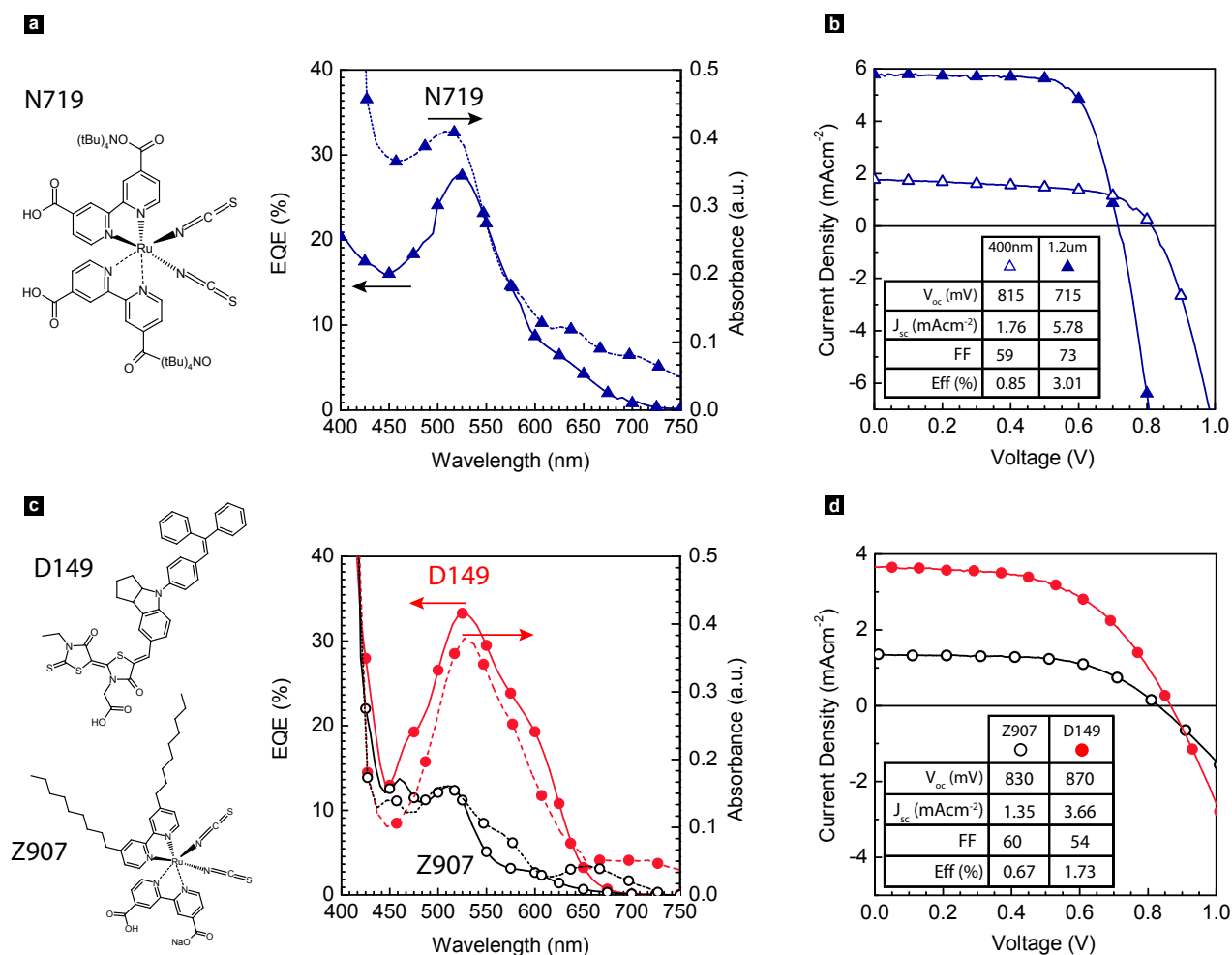


Figure 8.12: **Liquid and solid state electrolyte dye sensitized solar cell performance incorporating gyroid-patterned TiO₂ films.** (a) External quantum efficiency, EQE, (full lines) and absorption (dashed lines) for a liquid electrolyte dye sensitized solar cell made using a 1.2 μm TiO₂ anatase array sensitized with N719 ($\blacktriangle$). The peak EQE is 27 %. (b) Current-voltage curves for the 1.2 μm array in (a) along with an equivalent device 400 nm thick. (c) EQE, (full lines) and absorption (dashed lines) for a solid-state DSSC made using a 400 nm array sensitized with D149 ($\bullet$) and Z907 ($\circ$). The peak EQE values are 33 % and 13 % respectively. (d) Current-voltage curves for the devices shown in (c). Device performance characteristics are summarized in the inset tables.

on top of the titania film. It is apparent from the images that the hole-transporter has uniformly infiltrated the micrometre-thick film. When spin-cast onto a flat (unstructured) surface the same Spiro-MeOTAD solution gave a $\sim 1\mu\text{m}$ thick film. In order to estimate the degree of 'pore filling' we can make the simplifying assumption that the amount of Spiro-MeOTAD in the device (including

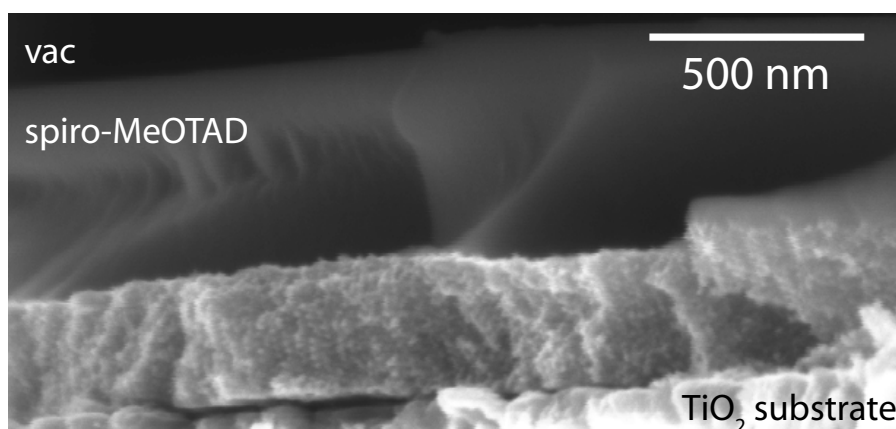


Figure 8.13: **Cross section of a 400 nm thick solid state device**

the capping layer) is equal that of the homogenous film plus the amount of Spiro-MeOTAD in the solution that has penetrated the pores. For a 400 nm capping layer and a $1.4\text{ }\mu\text{m}$ thick titania film with a porosity of 60 % this results in a pore filling of $\sim 86\%$. While clearly an approximation this illustrates that the gyroid structure is very well suited for near-complete infiltration with solid-state hole-transporters.

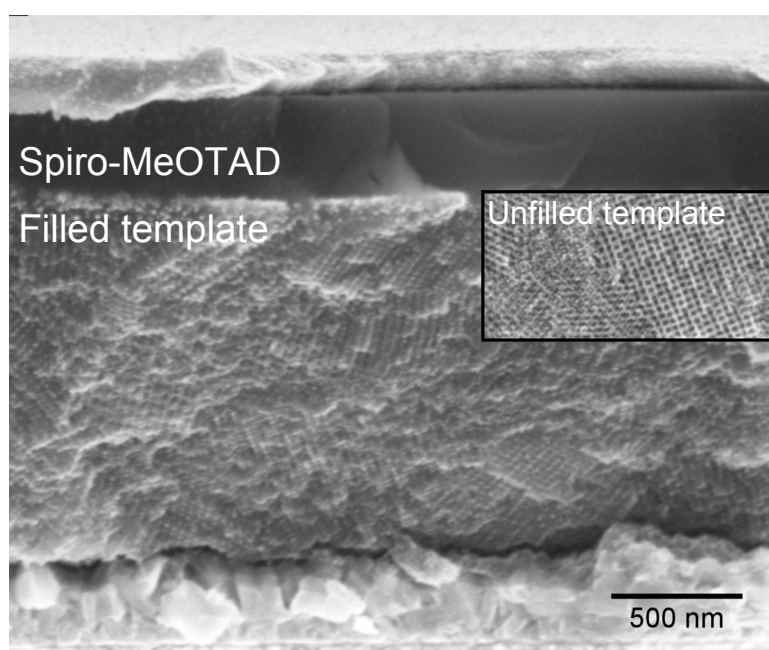


Figure 8.14: **SEM fracture cross section image of a TiO_2 solid-state DSSC.** $1.4\text{ }\mu\text{m}$ thick TiO_2 solid state DSSC cross section showing effective infiltration of Spiro-MeOTAD.

8.6 TiCl_4 surface treatment

In order to probe the effects of a post growth surface treatment in TiCl_4 solution, solid-state DSSC devices were constructed from a single array with post-annealing thickness of 300 nm. Half of the array was subjected to the standard surface treatment stage in TiCl_4 , while the other was immersed in dye without additional processing. The solar cell performances of these devices are summarized in Figure 8.15. Under low intensity (0.1 mW cm^{-2}) illumination the treated device shows a significantly improved peak EQE of 13.7 % compared to 2.4 % for the untreated device. Under full sun illumination the treated device produces a power conversion efficiency of 0.47 % compared to 0.29 % for the untreated array.

The effects of post-growth TiCl_4 treatment were even more pronounced in thicker arrays used in liquid electrolyte cells. Figure 8.16 shows the current-voltage curves for a liquid electrolyte DSSC containing a $1.2 \mu\text{m}$ thick film with and without the surface treatment. Although the light absorption was not significantly altered, the untreated device reached a power conversion efficiency of only 0.3 % - a tenfold reduction in current and power conversion efficiency at AM 1.5 compared to the surface treated array. This significant improvement is possibly indicative of mechanical faults in the TiO_2 structure which are to some extent 'healed' upon exposure to the TiCl_4 solution and further annealing. Indeed, no further improvement in device performance was observed in thicker arrays, which show signs of cracking and delamination from the substrate, caused by stress during the annealing process. The stress is expected to be concentrated at the substrate interface, where the thermal expansivity changes abruptly, and increases with increasing layer thickness. Clearly, if partial fracture and delamination of the layer occurs near the substrate, a potentially significant fraction of generated charge cannot be collected at the anode. Figure 8.17a,b illustrates a $4 \mu\text{m}$ array failure by cracking and delamination at the substrate.

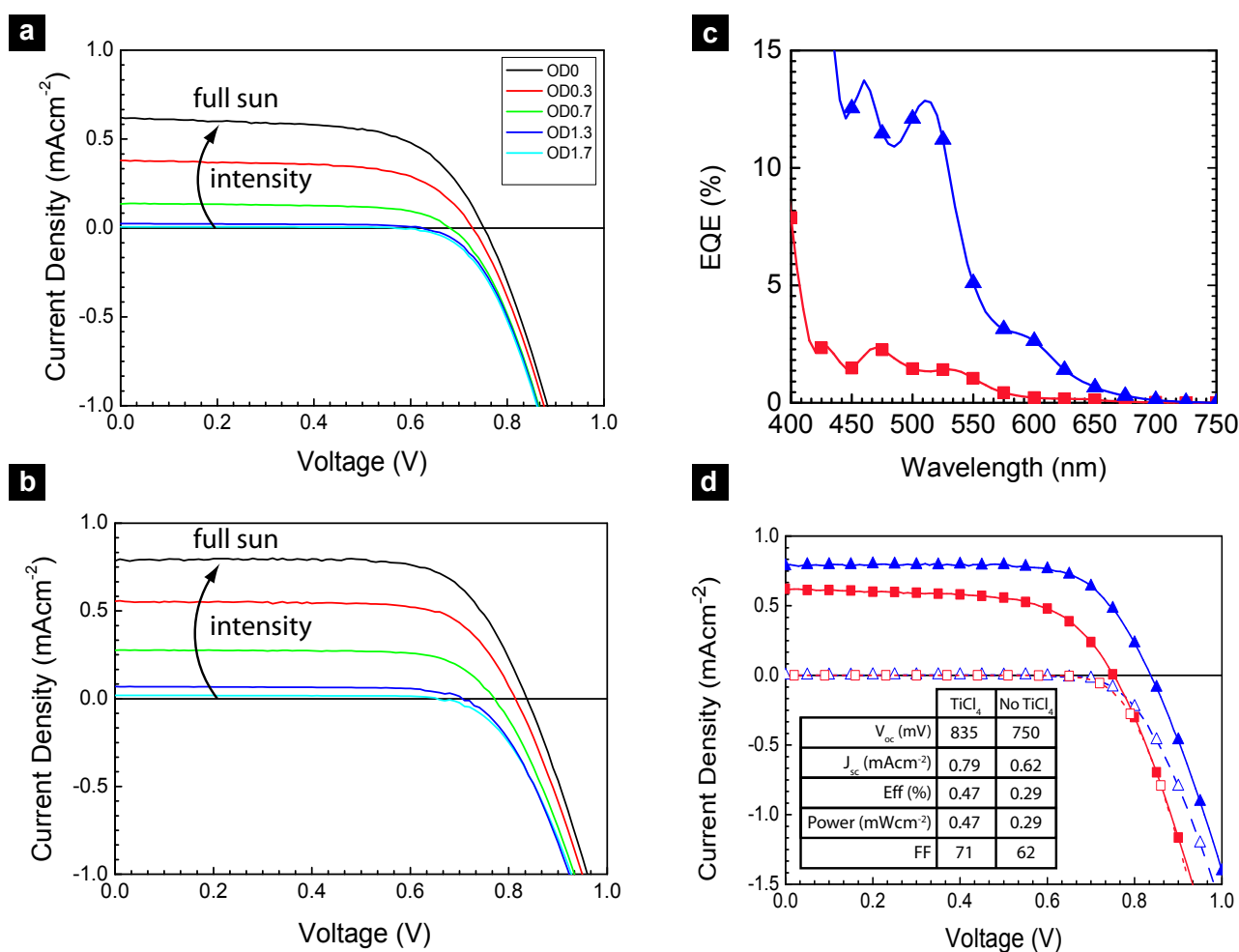


Figure 8.15: **Effect of TiCl_4 surface treatment on solid-state gyroid array DSSCs.** (a) Current-voltage curves for a device made with no surface treatment for different illumination intensities. (b) Equivalent current-voltage curves for a device with TiCl_4 surface treatment prior to Z907 dye sensitization. (c) Spectral response for (▲) treated and (■) non-treated devices under low intensity illumination. (d) Comparison of current-voltage characteristics under full-sun illumination with and without surface treatment.

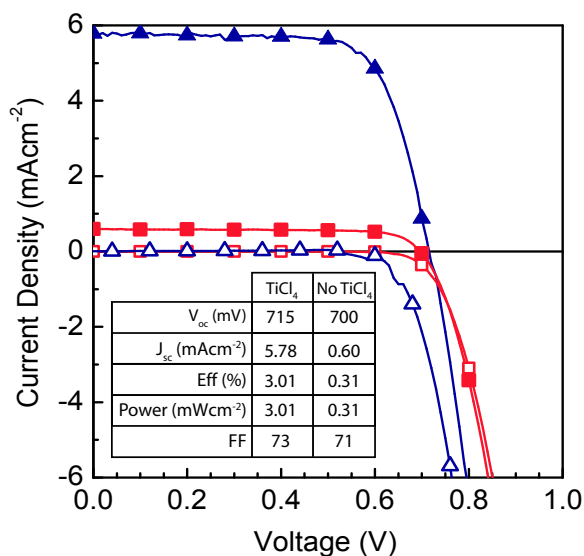


Figure 8.16: **Effect of TiCl₄ surface treatment on 1.2 μm thick liquid electrolyte gyroid-array DSSCs.** Current-voltage curves for a thick gyroid liquid electrolyte DSSC under AM 1.5 illumination with ($\blacktriangle$) and without ($\blacksquare$) TiCl₄ treatment. The power conversion efficiency is 3.01 % for the surface treated array compared to 0.31 % for the untreated layer.

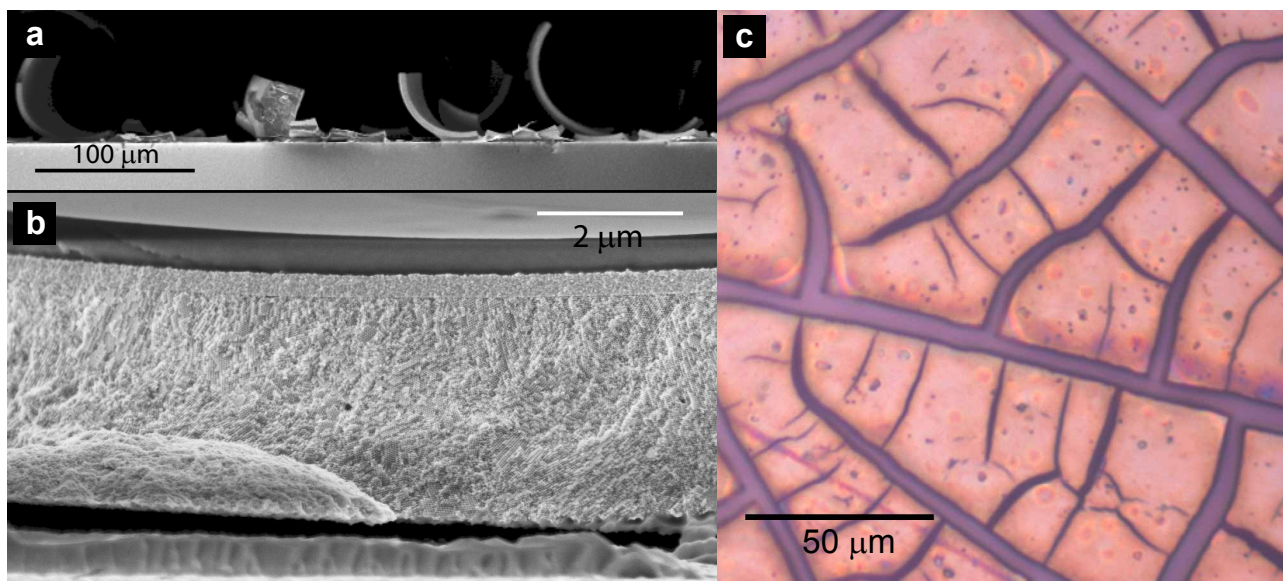


Figure 8.17: **Film failure by cracking during high temperature annealing.** (a,b) Low and high magnification SEM cross section views of 4 μm TiO₂ gyroid arrays after 500 °C annealing for 2 h. Lateral stress is relieved by cracking and buckling of $\sim 50 - 100 \mu\text{m}$ pieces of the array which delaminate from the substrate. The failure plane is at the interface with the substrate. (c) Cracking and partial delamination of a 1.5 μm thick array after annealing. Cells made from the cracked arrays were not reproducible in the solid state devices.

8.7 Titania deposition growth rate effects

The growth rate of Ti(IV) oxide was controlled by galvanostatic (constant current) operation of the electrochemical cell. Three templates were replicated with electrochemical current densities of 2, 10, and $30 \mu\text{A cm}^{-2}$ corresponding to growth rates of 0.04, 0.2 and 0.6 nm s^{-1} . The arrays were incorporated into solid-state DSSCs sensitized with Z907 which are summarized in Figure 8.18.

The spectral response under low intensity illumination ($\sim 0.1 \text{ mW cm}^{-2}$) shows a vastly improved response from the slow-growth arrays, producing a peak EQE of 4.5 % compared to 1.2 % for the fast-growth arrays. Under 100 mW cm^{-2} illumination, the fast-growth array remains the poorest performing solar cell, with a short-circuit current J_{sc} of 0.53 mA cm^{-2} and a power conversion efficiency η of 0.31 %. However, the slow-growth array does not show the greatest power conversion efficiency despite its superiority at low light levels; with $J_{sc} = 0.64 \text{ mA cm}^{-2}$, and $\eta = 0.34 \%$ compared to

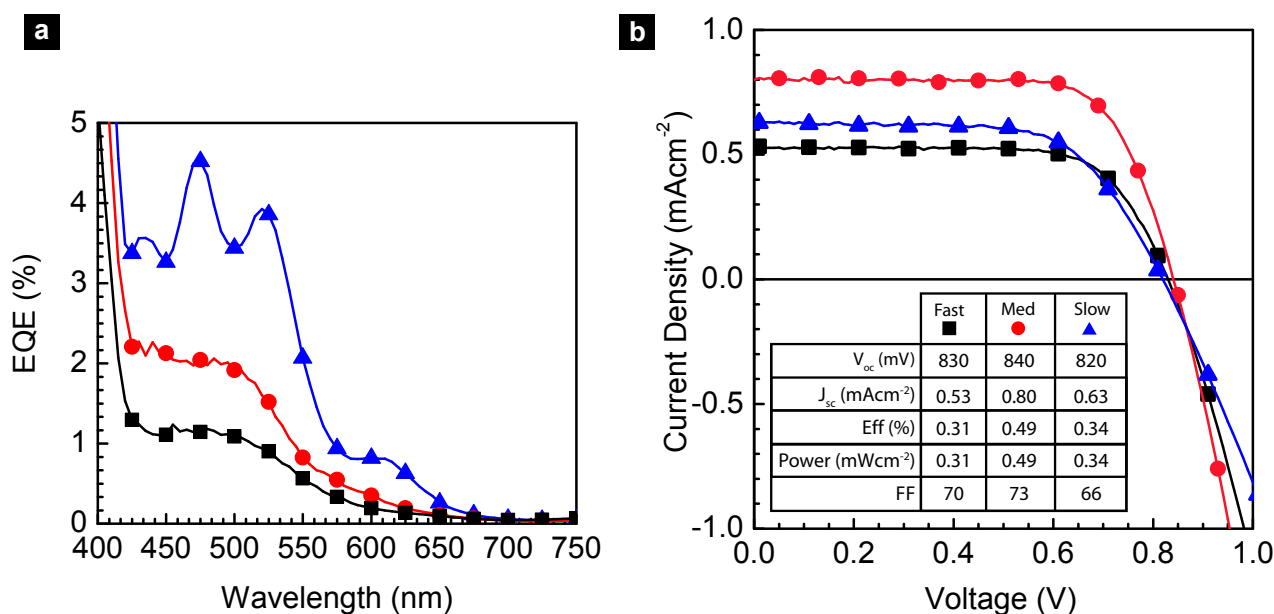


Figure 8.18: **Effect of electrochemical growth rate on solid-state DSSC performance** (a) Spectral response for 0.04 ($\blacktriangle$), 0.2 ($\bullet$), and 0.7 nm s^{-1} ($\blacksquare$) gyroid arrays. The peak EQE increases with reducing growth rate from 1.2 to 4.5 % under low intensity ($\sim 0.1 \text{ mW cm}^{-2}$) illumination. (b) Current-voltage curves for the arrays in (a), with device characteristics listed in the inset. The device thicknesses are 260 nm ($\blacksquare, \bullet$) and 200 nm ($\blacktriangle$). The power conversion efficiencies under full sun illumination are 0.31, 0.49, and 0.34 % for the fast, medium and slow-growth arrays respectively.

$J_{sc} = 0.80 \text{ mA cm}^{-2}$, and $\eta = 0.49 \%$ for the medium-growth rate device. This apparent inconsistency could be explained by a difference in the electron trap density and/or energetic distribution in the three TiO_2 arrays. Energetically deep traps are the first to be filled as the TiO_2 charge density increases at greater illumination intensity [21]. A greater density of deep trap states will therefore have a strong retarding effect on electron transport under low intensity illumination and lead to lower collection efficiencies. However at full sun illumination, the traps are filled and the transport of the different arrays become comparable. Coupled with these considerations is the fact that the slow-grown array is actually 25 % thinner than the other two arraysⁱ leading to a lower dye loading.

Measurements of the relative electron transport and recombination rates (for example using the methods described in Chapter 9) under similar illumination is required to confirm these tentative explanations. However, these measurements are difficult at low light levels owing to the low current transients delivered by such thin devices. The observed trend in device performance at low light intensities suggests that the properties of the slow-growth arrays may be in principle superior if they can be translated into arrays of significant thickness.

8.8 Discussion

It is instructive to compare the power conversion efficiencies with the established TiO_2 nanoparticle devices in more detail. Peak power conversion efficiencies for the gyroid devices are 1.73 % for the solid-state cells and 3.0 % for the liquid electrolyte cells. While state-of-the-art values for liquid electrolyte (11%) [16] and solid state cells (5%) [21] are higher, they are achieved in significantly thicker cells, i.e. with TiO_2 layers of 15 and 5 times thicker than these devices. An available area some 1000 times greater than the projected substrate is generally required to achieve significant absorption cross section using the Z907 sensitizer [22]. From rough estimates and electrochemical surface area measurements, the gyroid arrays have a roughness factor of ~ 130 , meaning an array of $\sim 7 \mu\text{m}$ would be required to compete with the nanoparticle system in this regard.

The impressive performance of the gyroid arrays is attributed to the highly defined porosity of

ⁱThe actual array thickness is not measured until a final fracture cross section is made; evidently this template was not quite filled despite the passage of the expected electrochemical charge. This deviation illustrates the range of deposition efficiencies experienced from the electrochemical system used.

the gyroid pore structure. Random nanoparticle assemblies lead to poorly controlled pore sizes and are likely to have partial domains that are not electronically connected to the continuous TiO_2 structure. For solid state DSSCs, extremely small pores and dead-ends are not easily filled by the bulky hole transporter. In contrast the gyroid morphology has nearly monodisperse pore diameters and all channels and struts are fully interconnected, resulting in an improved performance for both the liquid electrolyte and solid state DSSCs. Indeed, careful examination of the cross-sectional SEM image in Fig. 8.14 reveals near complete filling of the gyroid pore structure with Spiro-MeOTAD.

Stability of thick arrays

The gyroid templating procedure itself can be extended to very thick layers; the network voids retain uniform porosity from the film surface to the underlying substrate for arrays which are up to $10\mu\text{m}$ thick (no upper limit was found). The remarkable continuity of the gyroid network through thick template layers is demonstrated in Figure 8.19, showing the cross section of a $\sim 4\mu\text{m}$ thick replicated gyroid network. Clearly the array has grown uniformly through the entire thickness, and grains of $\sim 1\mu\text{m}$ are evident, with complete connectivity. The connectivity demonstrated by electrochemical replication indicates that the full thickness of the array is in electronic contact with the substrate throughout replication. By extension, the template matrix phase is also fully continuous, which bodes well for the uniform filling of solid-state hole transporting materials through very thick layers.

The limiting factor in applying the gyroid arrays to DSSCs is the layer stability when subjected to volume contraction during high temperature processing. Macroscopic signs of cracking appeared for template thicknesses of around 900 nm and upwards. Kavan *et al.* reported cracking of non-structured electrodeposited Ti(IV) oxide layers above 250 nm. Eventually the films crack apart and buckle from the substrate as shown in Figure 8.17, and result in irreproducible cells. Complete delamination occurs above this thickness. In practice for the solid state arrays, reproducible performance could be achieved in layers up to around 500 nm thick. The liquid electrolyte system was found to be more tolerant of the effects of mechanical stresses in the array, and up to $1.2\mu\text{m}$ thick cells could be made when coupled with a TiCl_4 post-deposition surface treatment.

A good deal of effort was invested in improving the stability of thick network arrays in order to produce thicker device layers. Conceptually this should be possible by increasing the density of the

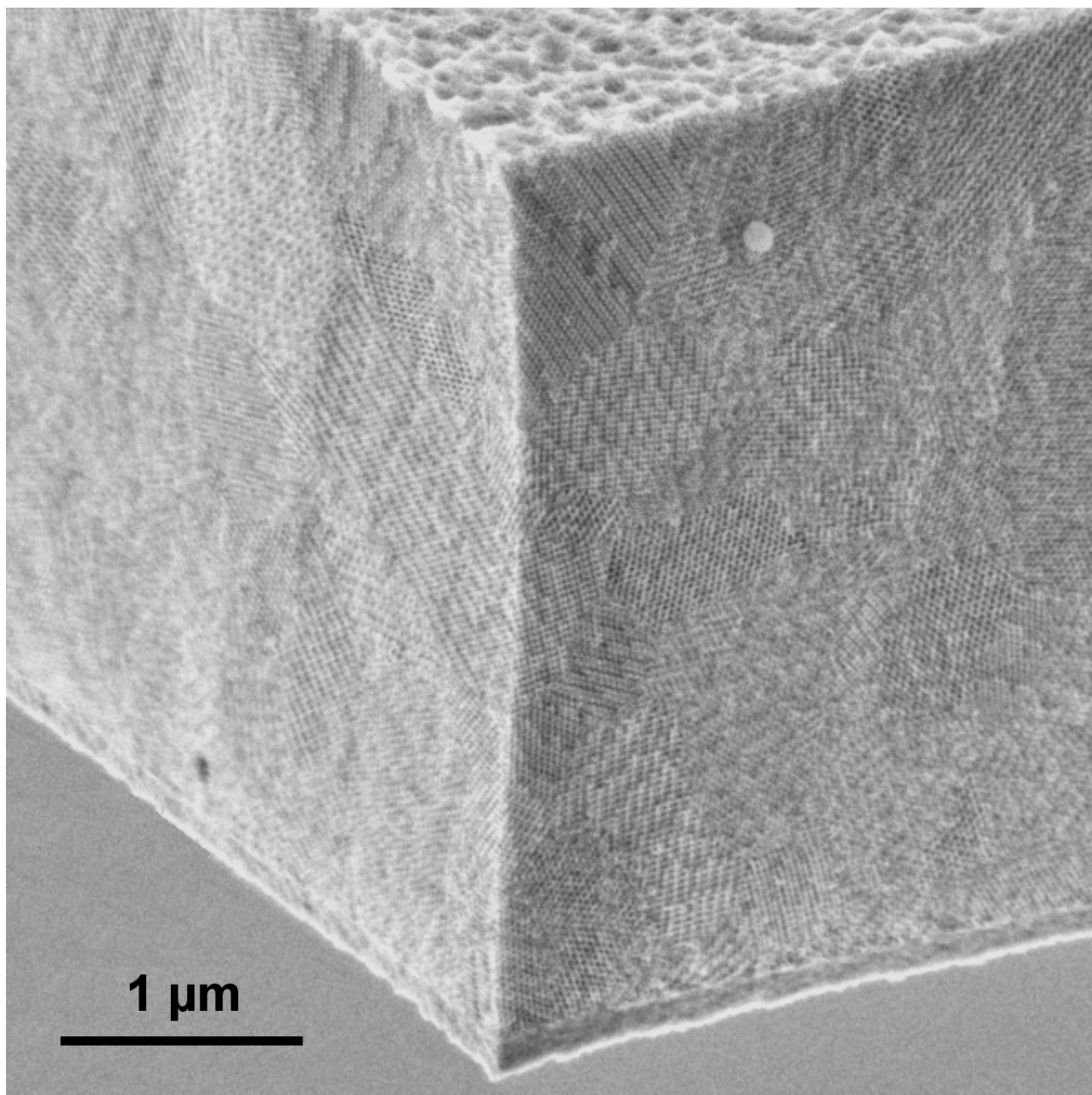


Figure 8.19: **SEM image of thick gyroid template replication in TiO_2 .** A $\sim 4\ \mu\text{m}$ thick TiO_2 array demonstrates that the gyroid template remains fully porous in much thicker films, enabling deposition of thick arrays which grow uniformly upwards from the underlying substrate.

initially deposited material, ideally to form directly a fully crystalline material, to reduce or eliminate volume contraction. The rate of electrodeposition was slowed (by electronic control) or increased (by raising the bath temperature to up to 50°C). However, no significant improvement was observed. The

growth rate could not be reduced significantly for thick template deposition owing to instability of the electrolyte over long time periods (despite constant purging with nitrogen gas). The heating rate protocol from ambient to 500 °C was adjusted between 1 to ~ 20 degree/minute which again resulted in no significant reduction in the tendency of thick arrays to crack and delaminate. Finally, anaerobic high temperature annealing has been shown to increase the stability of bulk mesoporous oxides prepared by block copolymer sol gel routes [23]. This method also failed to sufficiently improve the layer stability to avoid delamination. Various promising approaches to overcoming the thickness limitations of this system will be discussed in Chapter 11.

8.9 Summary

Uniform freestanding arrays of TiO_2 in the bicontinuous gyroid network phase with a 10 nm characteristic size were successfully templated using a PFS-*b*-PLA sacrificial block copolymer template and anodic electrochemical deposition. GISAXS analysis shows that both template and replicate are consistent with the gyroid morphology with the 211 planes aligned with the plane of the substrate. The final cubic structure has an accumulated uniaxial compression of ~ 50% after drying and crystallization at 500 °C. This compression is consistent with the reduction in volume of the electrodeposited material and is confirmed by direct observation of cross sectional structures fitted to computer simulated patterns of the gyroid morphology. GIWAXS and HRTEM indexing confirm an anatase nanocrystalline structure with a domain size comparable to the scale of templated confinement.

The freestanding arrays were used to construct liquid electrolyte and solid-state DSSCs. Peak power conversion efficiencies of 1.7 % and 0.63 % were found in solid-state cells made from 400 nm TiO_2 arrays sensitized with D149 and Z907 dyes respectively. The open pore structure of the gyroid network is extremely well suited to infiltration with a solid-state hole transporting medium. Liquid electrolyte cells made from 1.2 μm thick arrays sensitized with N719 dye reached a power conversion efficiency of 3 %. The performance of these devices is currently limited by the maximum array thickness possible without cracking and delamination caused by thermal shrinkage of the electrodeposited Ti(IV) oxide material. Further improvements of the deposition protocol and exploration of materials other than TiO_2 should allow the manufacture of thicker DSSCs, resulting in significantly improved

overall power conversion efficiencies.

These results are the first reported example of a freestanding gyroid nanostructure templated in a functional semiconductor, as well as the first functioning electronic device exploiting the bicontinuous gyroid morphology. The procedure requires no processing-intensive alignment stages on suitable substrates for preparation of solar cell devices, and as such is extremely attractive as a large scale self-assembly patterning application. Finally, it should be emphasised that this method of using a copolymer gyroid morphology as a sacrificial template is quite general and may easily be adapted to manufacture DSSCs based on different materials, bulk heterojunction solar cells and other applications such as batteries and fuel cells where a large and controlled internal surface is required.

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Block copolymer morphologies in dye-sensitized solar cells: probing the photovoltaic structure-function relation

We report the application of oriented block copolymer cylinder and bicontinuous gyroid network arrays with 10 nm characteristic features in liquid electrolyte dye-sensitized solar cells. 1D columnar and 3D gyroid self-assembled morphologies were compared to current state-of-the-art disordered nanoparticle mesoporous layers in terms of their performance in solar cells. Power conversion efficiencies of 3.0, 2.7, and 1.1 % were found for $\sim 1.2\mu\text{m}$ gyroid, nanoparticle, and nanowire arrays. Charge transport and recombination kinetics were probed using transient photocurrent and photovoltage spectroscopy. While standing nanowire arrays exhibit up to twofold enhanced transport over the equivalent 3D gyroid network, real cell performance is significantly reduced owing to partial wire collapse reducing available surface for dye loading. These results represent the first use of quasi 1D block copolymer templated nanowire arrays in functioning electronic device and illustrate the combined roll of charge transport and recombination, real surface areas and structural stability in determining optimum functionality.

9.1 Introduction

A major goal of nanotechnology is to achieve enhanced and novel functionality by gaining control of nanoscale material architectures. The detailed morphology and orientation of these nanostructures are key parameters determining their effectiveness in real devices applications. Emerging solar energy technologies based on excitonic photovoltaic systems [1] are a prime example in which low-cost and highly processable material components rely on mutual nanoscale organization in order to deliver efficient performance. Two-component organic solar cells rely on exciton separation at the $p-n$ organic interface, requiring a high degree of interdigitation of the two components combined with continuous electrical conductivity of both phases with the respective electrodes. Dye-sensitized heterojunctions on the other hand, have a molecular absorbing component located directly at the interface itself, and rely on the enormous surface area of a mesostructured semiconductor film to achieve sufficient optical depth in the active layer. Both concepts call for a large interface in a two component material couple with mutually continuous transport pathways through the device to the external circuit.

Self assembled morphologies are suitable candidates for ideal photovoltaic heterojunctions. Quasi 1D structures such as standing nanowire arrays have attracted particular interest owing to the possibility of direct charge extraction pathways throughout the device thickness. The success of any structure is, however, a combination of many factors, such as charge transport and recombination kinetics, interfacial contact area and structural stability. These parameters are determined both directly by the nature of the topology (for example direct versus tortuous conduction paths), and indirectly by intrinsic properties of the material (such as the density of defect sites) both of which are strongly affected by the structure fabrication processes. In practice, probing the influence of structural morphology in a real working device is crucial since there are many unforeseen factors which will govern the performance of a given nano-morphology.

The effect of structure on device performance is difficult to isolate because of the different procedures usually required to create the various nano-structures. One very promising way to produce

a range of controlled and highly ordered morphologies in the same material system and on the same scale is to replicate self-assembled structures from sacrificial templating systems [2, 3, 4]. Porous diblock copolymer morphologies offer an unique toolbox for exploring nanotechnology applications since with a given polymer chemical makeup, we have access to a number of microphase morphologies by simply tuning the relative volume fraction of each block [5, 6]. With standing cylinders (nanowires) and gyroid network arrays we are now able therefore to replicate two functional material nanostructures with identical characteristic length scales (~ 10 nm) but with fundamentally different structural morphologies.

Here, we probe the performance of cylinder and gyroid network block-copolymer morphologies replicated in anatase titania, incorporated in liquid electrolyte and solid-state dye-sensitized solar cells (DSSCs). In this system, a molecular dye is used to sensitize a pre-structured wide band-gap inorganic metal oxide [7]. A liquid electrolyte containing a redox couple surrounds the structure and acts as an electron shuttle from the counter electrode to regenerate the oxidized dye molecule, thereby completing the circuit. The most extensively studied, and still most successful implementation of this device scheme utilizes a disordered mesoporous inorganic layer made up of sintered TiO_2 nanoparticles with around 60% porosity. The charge collection efficiency in nanoparticulate TiO_2 liquid electrolyte DSSCs is high owing to an effective electron diffusion length greater than the required device thickness. This electrochemical system has been extensively modeled and studied experimentally and therefore provides an ideal testing ground for characterizing novel nanostructured electrodes. Our results for these systems are of particular importance for related DSSC cell designs incorporating alternative hole transporting materials, such as solid-state molecular semiconductors, where the optimal device thickness remains far lower than the optical depth at peak absorbance [8, 9].

9.2 Experimental

The two poly(4-fluorostyrene)-*b*-poly(D,L-lactide) [PFS-*b*-PLA] block-copolymers used in this chapter are MHI41 (here termed P_{gyr}) and MHI42 (termed P_{cyl}). Thin films of P_{cyl} and P_{gyr} were prepared

by doctor-blade coating from toluene solutions onto conductive fluorine-doped tin oxide (FTO) glass substrates, which were pre-coated with a ~ 50 nm thick compact layer of TiO_2 by spray pyrolysis. The P_{gyr} films were annealed at 180°C in a N_2 atmosphere for 35 h and allowed to cool to room temperature over 3 hours. P_{cyl} was annealed under the same thermal conditions with an applied electric field of $120 \text{ V}\mu\text{m}^{-1}$. After annealing the P_{gyr} films adopted the gyroid microphase morphology, while P_{cyl} formed a hexagonal PLA cylinder phase with cylinders spanning the film thickness. No electric field was applied to P_{gyr} .

The PLA minority component was selectively removed from the copolymer films by immersion in a $0.05 \text{ M NaOH}_{(\text{aq})}$ solution containing $40\%_{\text{vol}}$ MeOH at room temperature. The resulting porous PFS films were used as templates for potentiostatic electrochemical growth of titanium (IV) oxide. In order to remove the supporting PFS matrix with minimal mechanical perturbation to the templated Ti(IV) oxide nanostructures, the filled P_{cyl} films were first exposed to oxygen plasma for 200 s. The plasma exposed filled P_{cyl} films and the untreated filled P_{gyr} films were then heated to 500°C for 2 h on a hotplate under nitrogen, and for a further 1 h under oxygen. This treatment leads to crystallization of TiO_2 and, in the case of the P_{gyr} composite films, the simultaneous oxidative removal of the polymer template. Nanoparticle-based mesoporous titania films were made via blade coating of a titania paste (20 nm nanoparticles, courtesy of École Polytechnique Fédérale de Lausanne) onto compact TiO_2 coated FTO glass, followed by slow heating to 500°C for 30 minutes in oxygen, as described previously [10, 11].

9.3 Nanowire, Gyroid and Nanoparticle Structures

Scanning electron microscopy (SEM) characterization of the three morphologies are shown in Figure 9.1. In the case of P_{cyl} (Figure 9.1a), standing TiO_2 nanowires are formed with a diameter of 12 nm, centre-to-centre separation of 21 nm, and hexagonal packing density of $2.6 \times 10^{11} \text{ cm}^{-2}$. A volume contraction in the wire films of $\sim 25\%$ is accommodated by a reduction in film thickness, determined by film profilometry and cross sectional SEM imaging. Replication of the P_{gyr} template (Figure 9.1b)

produces a continuous interwoven TiO_2 gyroid network with an approximate strut diameter of 12 nm. The nanoparticle film (Figure 9.1c) consists of a disordered mesoporous network of ~ 20 nm TiO_2 particles with approximately 60% porosity [10].

The gyroid networks are successfully made freestanding by simultaneous oxidative removal of the polymer template during the 500 °C TiO_2 crystallization processing. Standing nanowire arrays, on the other hand, were not stable during this process, and were instead freed by exposure to O_2 plasma before TiO_2 crystallization (Figure 9.1d). Figure 9.2 shows SEM images of completely collapsed nanowires that were heated to 500 °C with the template still in place.

Estimates of the available surface area of each array can be calculated from a model topology assuming a smooth TiO_2 surface (i.e. neglecting sub-mesoscale roughness). The nanowire array is

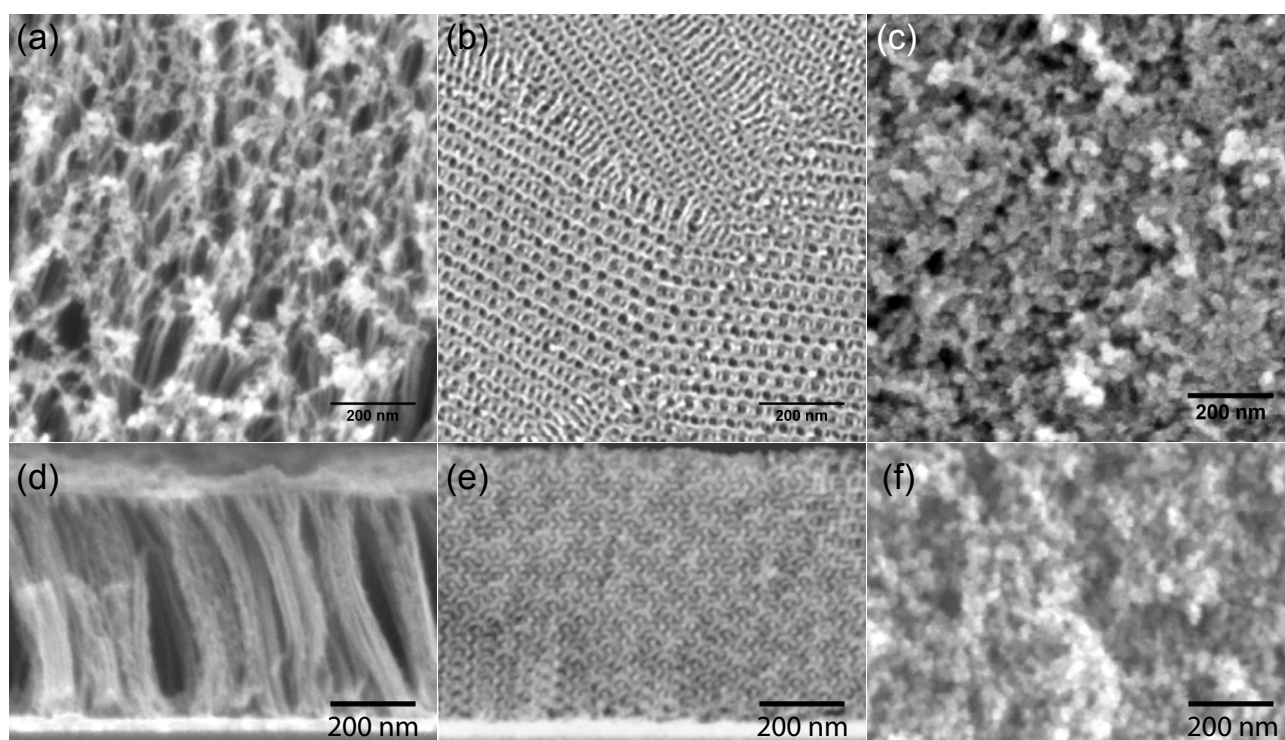


Figure 9.1: **SEM structural summary of nanostructures used for solar cell construction.** Top and cross-sectional perspectives of (a,d) standing TiO_2 cylinders. In (d), the wire stability is improved by a thin, partially continuous layer of electrochemical overgrowth at the array surface which hinders lateral collapse. (b,e) Gyroid network cross section. (c,f) Sintered nanoparticle mesoporous layer.

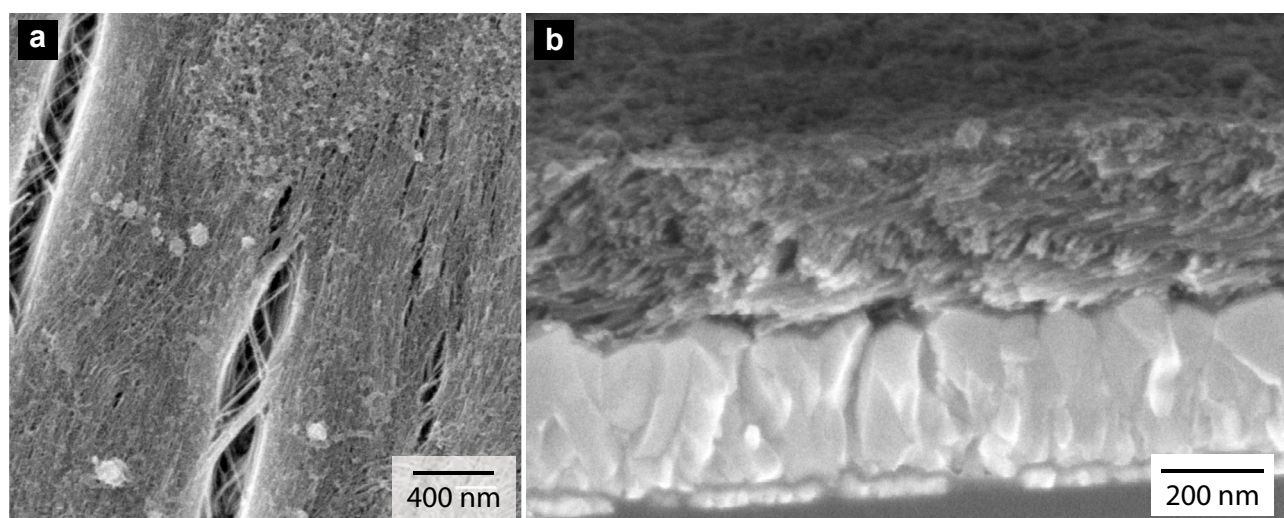


Figure 9.2: Collapse of nanowire arrays caused by 500 °C annealing with the polymer template in place. (a) Top and (b) side view SEM images of lying TiO_2 nanowires after high temperature oxidative removal of the PFS template.

modeled as a hexagonally ordered array of cylinders with a 21 nm centre-to-centre distance and 12 nm diameter giving a surface multiplicity ('roughness factor' (RF)) of $100/\mu\text{m}$. A simple cylindrical rod model can be used to approximate the gyroid morphology [12]; assuming a rod diameter of 12 nm and a 50 nm cubic unit cell gives a RF of $130/\mu\text{m}$. Finally, modelling the nanoparticle film as a 60 % porous assembly of 20 nm spheres yields a RF of $120/\mu\text{m}$.

Measurements of the wire and gyroid array surface areas were made via the electrochemically accessible area for proton adsorption using identical morphologies replicated in platinum (see Chapter 3). The measured roughness factors of the wires and gyroid arrays were 60 and 130, respectively. Template removal by rinsing in toluene did not alter the measured surface area of the released gyroid array (i.e. the Pt surface area appears unaffected by the plasma treatment). The surface area of identical nanoparticle arrays to those used here have a reported roughness factor of 116, measured by nitrogen absorption [13]. The calculated and measured roughness factors are summarized in Table 9.1. Both the nanoparticle and gyroid network structures have measured internal surface areas in good agreement with the predicted value, demonstrating that these structures form robust self supporting networks which remain stable when incorporated into the device geometry. The nanowire array how-

ever has only 60% of the predicted RF, indicating a loss in real surface where neighbouring wires touch after removal of the templating matrix.

Table 9.1: Calculated and measured roughness factors for each array morphology and photovoltaic performances in $1.2\mu\text{m}$ liquid electrolyte cells under AM1.5 illumination.

Morphology	$\text{RF}_{\text{calc}}^{\text{a}}$	RF_{meas}	Porosity (%)	J_{SC} (mA cm^{-2})	V_{OC} (mV)	FF	η (%)
Wires	100	60	65	1.79	845	71	1.07
Gyroid	125	130	60	5.83	713	71	2.97
Particles	120	116[13]	60	5.42	785	63	2.67

^a Model calculations using ‘smooth’ geometric constructions. Wires: 12 nm diameter, 21 nm centre-to-centre hexagonal standing rods; cubic gyroid: 50 nm unit cell, consisting of cylindrical rods of 12 nm diameter; nanoparticles: 20 nm diameter spheres, 60 % porosity with point-like inter-particle contact.

Partial wire collapse and a degree of structural disorder can be imaged directly by surface view SEM imaging (Figure 9.3). The morphology shown in Figure 9.3b is the state of the array immediately prior to dye sensitization and solar cell construction.

9.3.1 Nanocrystalline morphology of structured arrays

High resolution transmission electron microscopy was used to probe the TiO_2 crystal phase and characteristic grain size in each of the three morphologies (Figure 9.4). In both the wire and gyroid structure the crystallite size is of the same order as the structural confinement (~ 10 nm). In the wire structures the crystallite dimensions may exceed this confinement length along the wire axis in some places (Figure 9.4(a) inset). The disordered nanoparticle network (Figure 9.4c) is made up of ~ 20 nm randomly contacted single crystal nanoparticles. Electron diffraction patterns were indexed to anatase TiO_2 in all cases (Figure 9.5).

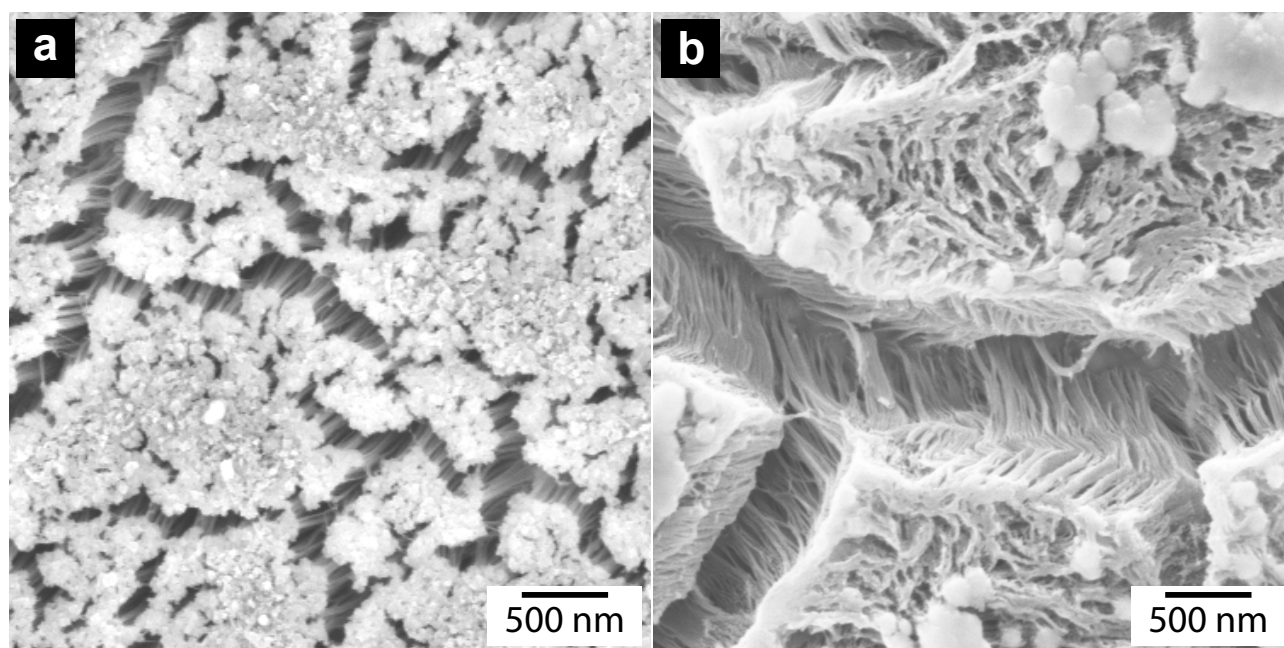


Figure 9.3: **SEM imaging of wire instability during processing.** (a) After removal of PFS polymer template by plasma etching. (b) After surface treatment in TiCl_4 neighbouring wires appear to touch in places caused by capillary forces during solvent drying.

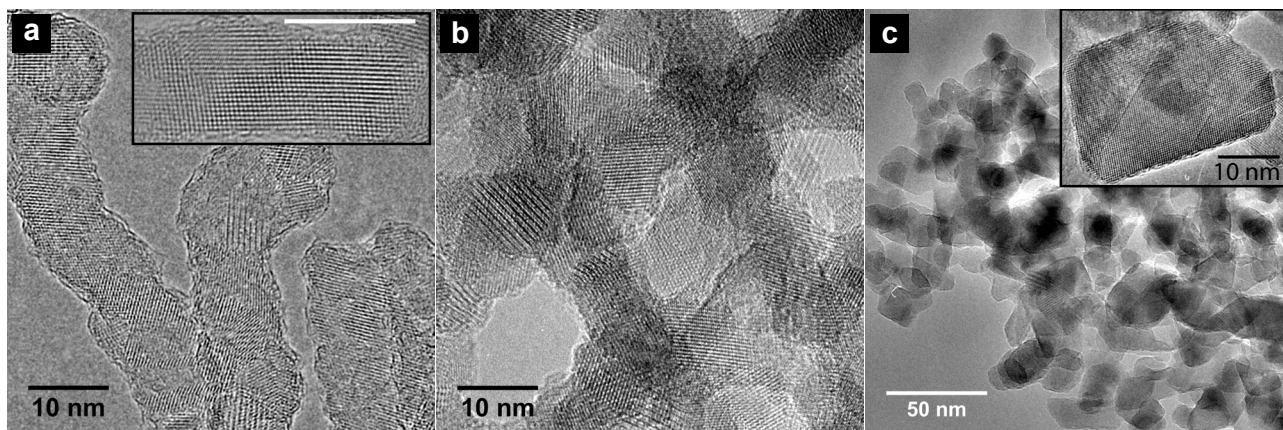


Figure 9.4: **HRTEM images of crystal structure within TiO_2 arrays.** (a) Nanowires, (b) gyroid network, (c) Nanoparticles. The lattice fringes can be indexed to anatase TiO_2 . In both wires and gyroid structure the crystallite size is of the same order as the structural confinement (~ 10 nm). In some wire structures individual crystal domains persist along the wire growth direction ((a) inset, scale bar 10 nm). The low magnification view of the nanoparticle array in (c) reveals the disordered packing of ~ 20 nm individual particles into a mesoporous layer, while a high magnification view (inset) on the same scale as (a) and (b) indicates that the nanoparticles are single domain anatase crystallites.

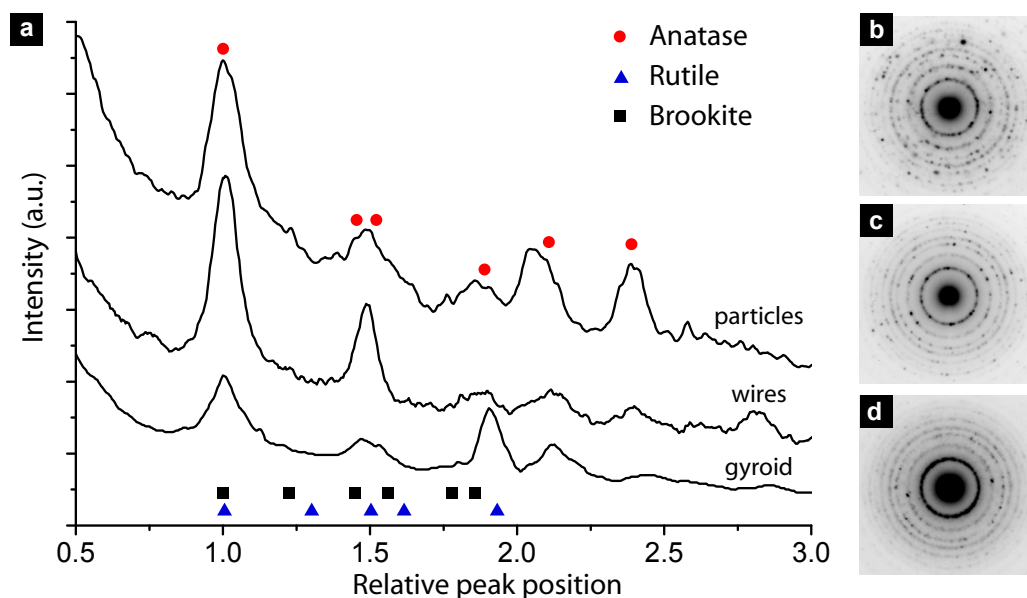


Figure 9.5: **Indexing of electron diffraction patterns.** (a) Diffraction line profile for particles, wires, and gyroid clearly identifies the anatase TiO_2 polymorph in all three structures. The diffraction rings are shown for (b) particles, (c) wires, and (d) gyroid.

9.4 Dye-Sensitized Solar Cell Performance

9.4.1 Nanowires in solid-state dye-sensitized solar cells

Standing nanowire arrays were tested in solid-state dye-sensitized solar cells (sDSSC) using infiltration of spiro-MeOTAD hole transport material from the solution phase via spin coating.

Figure 9.6a shows a cross section from a device made using a $1.4\mu\text{m}$ nanowire array that has collapsed under the spiro-meOTAD layer. The external quantum efficiency and current-voltage curves from this device, sensitized using the Z907 dye are shown in Figure 9.6b and c, respectively. The peak EQE is only 0.5 %, which compares to 13 % for a 400 nm thick gyroid network array (see Chapter 8). Under simulated sun illumination the device gives a power conversion efficiency of only 0.01 %. The most likely explanation for the poor performance of nanowire arrays in solid-state cells is collapse

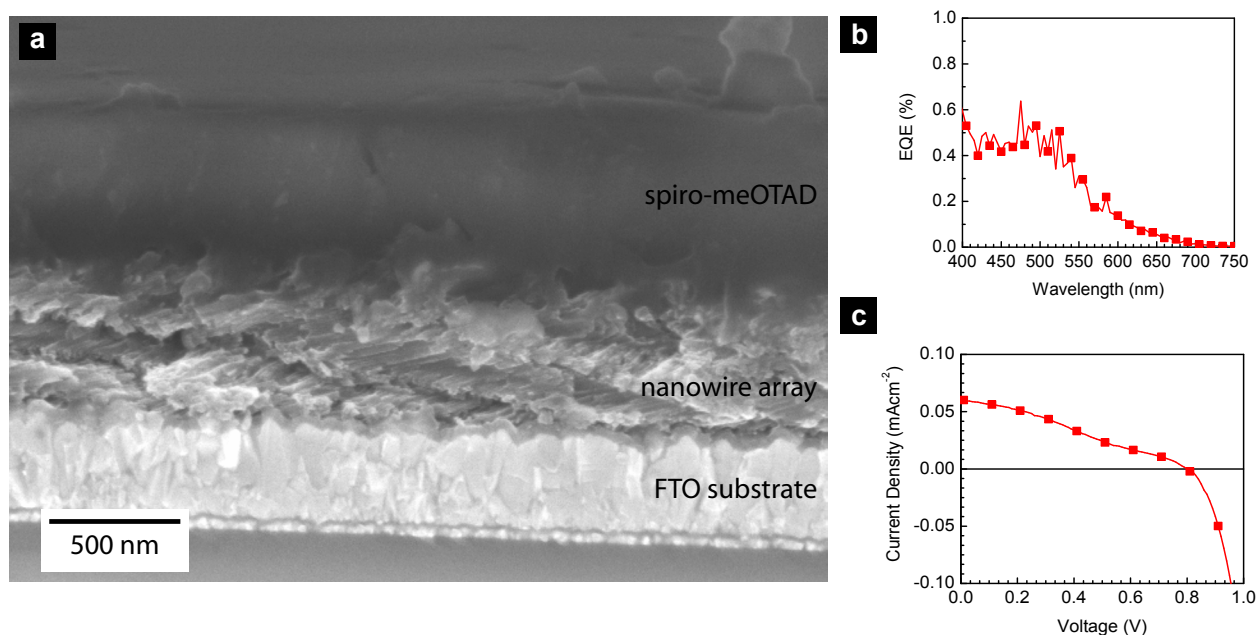


Figure 9.6: **Nanowire performance in solid-state solar cells.** (a) SEM cross-section of a solid state device made from a $1.4\mu\text{m}$ nanowire array. The wires (bright) have collapsed to $\sim 500\text{ nm}$ after deposition of Spiro-MeOTAD hole transporter layer (dark). (b) External quantum efficiency, EQE and (c) current-voltage curves for the device in (a) sensitized with Z907 dye.

caused by the spiro-meOTAD infiltration. Not only does this collapse imply physical damage to the TiO_2 charge extraction pathways, but would also hinder further infiltration of spiro-meOTAD which must make intimate contact with the surface in order to regenerate the oxidized dye. No further progress was made with solid-state devices using nanowire arrays.

9.4.2 Liquid electrolyte dye-sensitized solar cells

The performance of the three array morphologies was tested in liquid electrolyte dye-sensitized solar cells. Anatase titania arrays of $\sim 1.2\ \mu\text{m}$ in thickness were prepared and first subjected to a standard surface treatment by soaking in aqueous TiCl_4 solution (40 mM) at 80°C for 30 minutes, with subsequent annealing at 500°C for 30 minutes.[13] After cooling to 70°C the arrays were immersed overnight in an acetonitrile:*tert*-butyl alcohol (1:1 vol:vol) 0.5 mM solution of bi-pyridyl NCS ligand ruthenium complex dye, termed N719. Closed cells were assembled with a Pt coated FTO counter electrode and 'Robust' liquid electrolyte (0.8 M PMII, 0.15 M iodine, 0.1 M GuNCS, and 0.5 M NMBI in 3-methoxypropionitrile) was infiltrated into the cell via vacuum back-filling.[14]

Figure 9.7(a) shows the absorption spectra of the N719 sensitized arrays before cell construction. Both the gyroid and wire spectra show vertical offsets caused by scattering in the titania array. When considering the peak OD of each array corrected for the scattering offset at 800 nm the nanoparticle and gyroid arrays have comparable degrees of dye-loading. The nanowire structure, on the other hand, has only half the peak OD seen in the gyroid and particle arrays, indicating a considerably lower accessible area in the actual device geometry for dye uptake.

The spectral response of liquid electrolyte DSSCs based on the three array structures are shown in Figure 9.7b. At low illumination intensities ($\sim 0.1\ \text{mW cm}^{-2}$) the nanoparticle film shows the highest peak external quantum efficiency (EQE) of 34 % compared to 28 % for the gyroid array. The nanowire cell produces a peak EQE of only 9 %. Figure 9.7c shows the current-voltage curves for the cells under simulated AM 1.5 illumination at $100\ \text{mW cm}^{-2}$. The device performances are summarized in Table 9.1. The gyroid, nanoparticle and nanowire cells have power conversion efficiencies of 3.0, 2.7

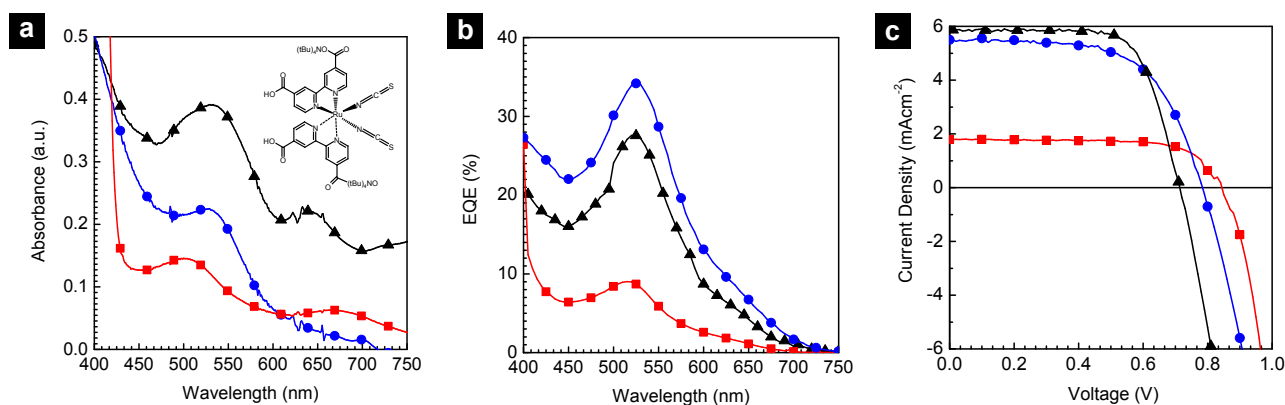


Figure 9.7: **Solar cell characteristics.** 1.2 μm thick nanowire (■), 1.2 μm thick gyroid (▲), and 1.4 μm thick nanoparticle (●) TiO₂ arrays. (a) Absorption spectra after sensitization with N719 (inset). (b) Spectral response of liquid electrolyte dye-sensitized solar cells. (c) Current-voltage curves under simulated AM 1.5 100 mW cm⁻² solar illumination.

and 1.1 % respectively. Considering the nanowire based device, the combination of relatively weak adsorption, EQE and power conversion efficiencies are consistent with a low dye loading. Indeed, the measured roughness factor for a nanowire array was only 60% of the predicted value of 100/μm (Table 9.1) for a perfect standing array. A second reason for the low power conversion efficiency may arise from the one-dimensional nature of these extremely high aspect ratio structures (~ 100); physical damage to a wire during processing could prevent collection of any charge above the level of the fracture. This loss mechanism alone however does not explain the lower than expected dye loading and therefore does not appear to be a dominant factor here.

The power conversion efficiency of the gyroid network device (3.0 %) is slightly greater than the nanoparticle array (2.7 %) in the liquid electrolyte cell. These roughly comparable performances are not surprising considering the similar light harvesting ability of the layers. The measured internal surface areas of the film are similar (RF gyroid 130, nanoparticles 116), which is reflected in the similar peak OD of N719 sensitized gyroid and nanoparticle arrays. The significant enhancement in performance of both the nanoparticle and gyroid device over the nanowire cell is most likely due to the structural stability of the network structure.

9.5 Charge Transport and Recombination

The electron transport and recombination properties of the three DSSC arrays were probed by transient photocurrent and photovoltage spectroscopy [15]. The photocurrent decay rate at short-circuit is characteristic of the time for electron transport out of the device while the voltage decay rates at open-circuit are proportional to the rate of charge recombination.[16] The short-circuit charge collection times are shown in Figure 9.8a.

Charge transport in mesoporous titania is expected to be governed by a multiple-trapping process, where the electrons thermally de-trap from sub-bandgap states to the conduction band, and are transported a short distance before being re-trapped [15]. However, the location of the traps, trap densities, and limitations to transport are still debatable and are probably variable between different titania preparation routes [8]. With all other parameters equal, and assuming that electron motion is a random walk between uniformly distributed trap sites, idealized one dimensional diffusion should be three times faster than in a fully three dimensional case [17]. The scale on which the dimensionality of the mesostructure plays a role will depend upon the exact limiting factors to charge transport

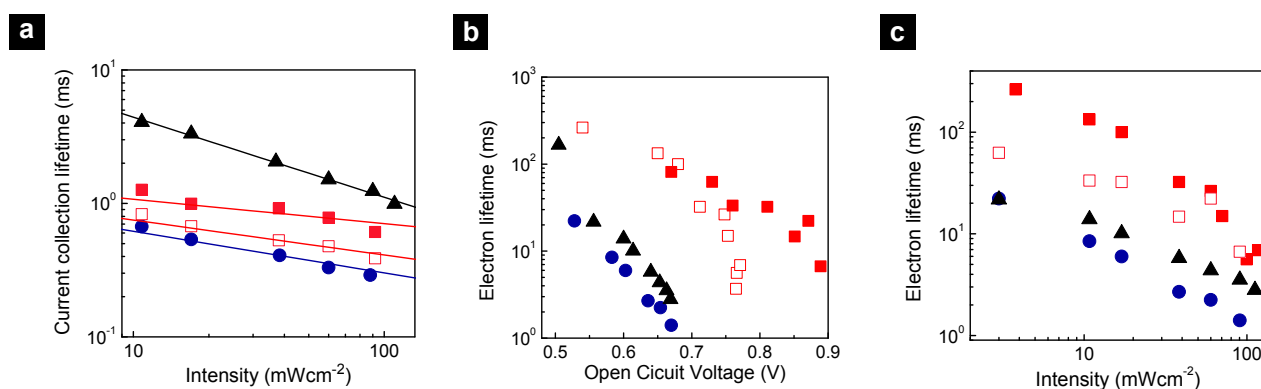


Figure 9.8: **Transport and recombination characteristics.** (a) Current collection lifetimes for the samples in Figure 9.7, $1.2\ \mu\text{m}$ thick nanowire (■), $1.2\ \mu\text{m}$ thick gyroid (▲) and $1.4\ \mu\text{m}$ thick nanoparticle (●) TiO_2 arrays. The second nanowire-array data set (□) is shown to illustrate the variation in transport response from this type of device. Recombination lifetimes for the arrays shown in (a), measured at open-circuit, are plotted as a function of (b) cell voltage and (c) illumination intensity.

and electronic structure of the material. For instance if the transport is limited by scattering at grain boundaries, then the dimensionality needs to be on the order of the crystal size. If the transport is limited by detrapping throughout the material irrespective of grain boundaries, then the dimensionality would be required to be on the inter-trap lengthscale. Here, the charge collection times measured in the wire arrays are approximately twice as fast as those in the gyroid networks under 100 mW cm^{-2} illumination. With identical structural sizes and fabrication protocols, it seems reasonable to expect comparable trap densities in both the wire and gyroid structures. In this case the transport performance of the wires is slightly below the three-fold improvement predicted for ideal 1D transport. This could be due to a number of reasons; electronically, the trap density may be greater than one per nano crystal. Physically, contacts exist between some of the wires and because the wires are not self supporting there is a degree of disorder in their alignment in the standing array. The two data sets included in Figure 9.8 are indicative of the spread in measured collection times for the wire arrays. Despite this variation, the transport along the wires always appears faster than in the gyroid network arrays.

The transport times in the disordered nanoparticle films are approximately four times faster than in the 3D gyroid networks, and roughly 40 % faster than the nanowire arrays. Considering dimensionality and uniformity of the gyroid mesostructure, this is not expected. However, Kopidakis *et al.* have demonstrated a strong dependence of electron diffusion with crystal size [18] and the standard nanoparticle dimensions here are approximately twice as large as the nanocrystallites in the electrochemically deposited films. The fabrication procedure for the particulate titania films is very different, and one would expect the trap density and location to vary considerably. In particular, the ways in which each array topology can accommodate material stresses differ between the electrochemically deposited arrays and the nanoparticle film. The gyroid network is not able to relieve stress built up by material shrinkage in the same manner as structurally isolated wires because it is pinned to the lateral dimensions of the substrate. Local cracking in the layer, particularly at the array-substrate interface will introduce a highly non-uniform distribution of charge traps to the array and could ac-

count for slow charge extraction times. Therefore, quantitative comparison between the particle and electrochemically deposited materials is not justified.

The recombination lifetime at open-circuit is shown in Figure 9.8b, plotted against the open-circuit voltage since this is likely to be most representative of comparable charge densities within the devices. Figure 9.8c also shows the electron lifetime plotted against incident light intensity in which the trends are unaltered. Interestingly, both the gyroid and the nanowire devices exhibit longer electron lifetimes than the standard nanoparticle device. And, most significantly, the nanowire film has up to an order of magnitude longer electron lifetime than both the gyroid and the particle devices at any given voltage. Again, the exact spatial distribution of trap sites is likely to be critical; for the nanoparticle films, a large surface trap density is likely. Electrons residing on the particle surface have a greater likelihood of recombining with a hole in the electrolyte than electrons trapped within the bulk of the structures. The HRTEM images of the electrochemically deposited materials show that there is a large ‘internal’ contact area between nanocrystalline domains. Recombination between charges trapped in defect sites at these contacts and holes in the electrolyte will be very slow. Furthermore, surface area, dye uptake, and SEM studies of nanowire films show a degree of structural collapse. If these ‘self-contacting’ regions are not contacted by electrolyte, then charges trapped on the internal surfaces of the wire bundles will be inhibited from recombination. Slower recombination kinetics in oriented wires are consistent with behaviour observed in TiO₂ nanotube arrays by Zhu *et al.* [19] An interesting concept which follows from this observation is to design nanowire arrays with a large ‘internal’ trap density, in order to inhibit recombination.

9.6 Summary

In summary, we have fabricated free-standing arrays of 1D titania nanowires and 3D gyroid structured titania films by employing diblock copolymer templates. Integration of these films into dye-sensitized solar cells yields important information concerning the charge transport in mesostructured material composites. Although the 1D system exhibited enhanced charge transport and significantly inhibited

charge recombination compared to an equivalent 3D network, the lack of structural integrity resulted in a much reduced internal surface area compared to the conceptually ideal structure, and the resulting photocurrent and efficiency generated from the solar cells were significantly less than the 3D gyroid devices. Nanowire arrays were not suited to solid-state dye-sensitized cells, most likely owing to collapse of the array during infiltration of the hole transport material.

In future work we will seek to improve the mechanical stability of wire-type systems to exploit their excellent electronic properties. One option is to exploit critical point CO₂ drying procedures throughout all solution processing stages, a method that circumvents liquid capillary forces during drying and has been shown to produce perfect 50 nm diameter standing wire arrays grown by anodization of titanium foils [19] or from anodized alumina templates [20]. The electronic properties of three dimensionally structured semiconductor arrays are inextricably linked to processing parameters such as material shrinkage. New replication methods must be developed to capitalise fully on their superior structural integrity over 1D arrays. These results are the first exploratory study comparing two key block copolymer morphologies in functioning devices, demonstrating the complex interplay of factors determining ideal morphologies for bulk heterojunctions. Further studies of this type, investigation of different material systems, and further structural refinement should greatly enhance our understanding of the role of nanoscale structure upon this new generation of optoelectronic devices.

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Chapter 10

Porous Semiconducting Block Copolymer Films: Preliminary Results

The following chapter presents preliminary investigation of the microphase-separation of a diblock copolymer containing hole conducting functionality coupled to a selectively removable minority component. A poly(styryltriarylamine)-*b*-poly(D,L-lactide) (PSTA-*b*-PLA) block copolymer is shown to phase separate to form ordered 13 nm cylindrical PLA microdomains embedded in a semiconducting PSTA matrix with a hole mobility of the order $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Application of DC and AC electric fields applied at elevated temperature failed to align the PLA microdomains in a direction normal to the substrate. However, a partially ordered and film-spanning cylindrical domain structure is identified in films immediately after spin-coating from toluene solutions on conducting Au substrates. A mesoporous, hole conducting polymer matrix is formed successfully after selective, mild etching of the PLA minority domains. The pore structure is replicated electrochemically in Pt metal, demonstrating the viability of this approach to producing intimately connected heterojunction structures in thin films.

10.1 Introduction

Applications requiring intimate interdigitation of functional materials such as donor-acceptor semiconductor bulk heterojunctions benefit directly from ordered copolymer microphase-separation on the 10 nm length scale. Partially sacrificial copolymer templating combines electronic charge transport characteristics of one component, with a second block that is removable after phase separation under mild chemical conditions to leave a functional matrix with well-defined mesoporosity [1]. The second material with complementary electronic properties can be backfilled into the pore structure of the first. Choice of the second component is not limited to polymeric materials synthetically compatible with the primary polymer as is the case with fully-functional donor-acceptor copolymers; electrodeposited inorganic semiconductors, nanoparticles or small molecules can potentially be infiltrated into the ready-structured junction.

In this chapter, a poly(styryltriarylamine)-*b*-poly(D,L-lactide) (PSTA-*b*-PLA) diblock copolymer, synthesized via RAFT polymerization, is used as a partially sacrificial template for bulk heterojunction patterning. Charge mobility characteristics for hole transport are introduced to the PSTA com-

poly(styryltriarylamine)_m - *b* - poly(D,L-lactide)_n

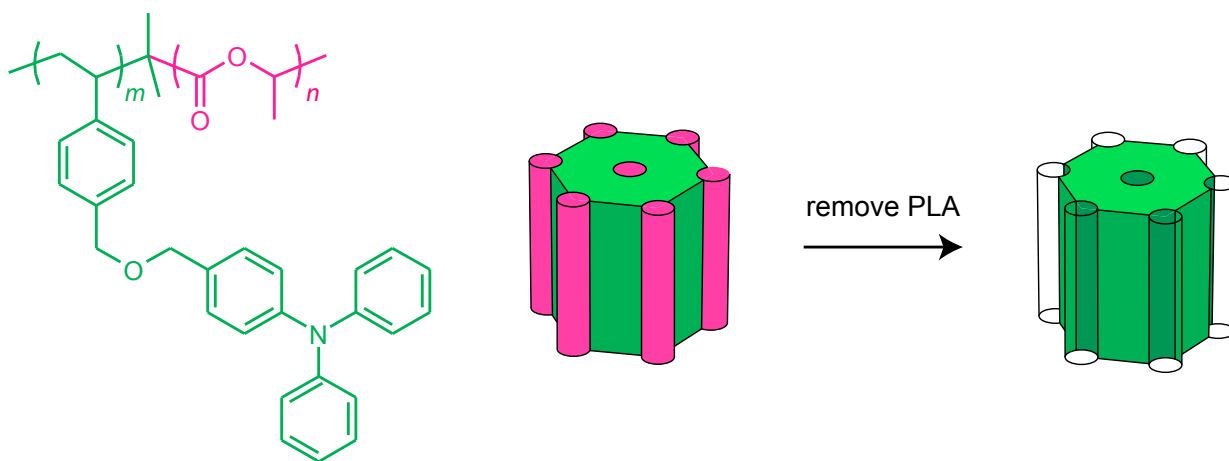


Figure 10.1: Cylinder-forming poly(styryltriarylamine)-*b*-poly(D,L-lactide) copolymer with selectively degradable PLA channels

ponent by inclusion of triarylamine sidegroups attached to the main polystyrene polymer backbone via a flexible linkages [2]. Snaith *et al.* demonstrated the utility of similar side group polymers in mesostructured heterojunction solar cells based on polyacrylate brushes with triarylamine side groups infiltrated with CdSe nanoparticles [3, 4]. Thelakkat *et al.* recently coupled a polyacrylate chain with triarylamine sidegroups to another with perylene diimide side groups to produce a D-A copolymer [5, 6]. The resulting heterojunction solar cells displayed an order of magnitude improvement in power conversion efficiency over an equivalent polymer blend of the two components. In PSTA-*b*-PLA, the minority PLA component is susceptible to mild hydrolytic degradation in aqueous base and therefore introduces a functionality designed to produce well defined, ~10 nm scale pores within the semiconducting polymer matrix (Figure 10.1).

The results presented here demonstrate the first stages of bulk heterojunction device manufacture by successfully producing a mesoporous hole conducting polymer film with well-defined 10 nm pores. Crucially, the pore structure penetrates the full thickness of the layer, so that charge extraction pathways will exist through both donor and acceptor phases to the external electrodes in a final heterojunction structure. Future work will aim to complete the device by infiltration of a suitable electron acceptor material into the void structure.

10.2 Experimental

Synthesis of the poly(styryltriarylamine)-*b*-poly(D,L-lactide) block copolymer described in this chapter, termed MHI37, is described in Chapter 4. The overall molecular weight was 30.8 kg/mol with 62 %_{wt} PSTA, and a polydispersity of 1.36. Differential scanning calorimetry (DSC) traces showed two glass transition temperatures (T_g) at 52 °C and 88 °C, attributable to the PLA and PSTA components, respectively. The homopolymer of PSTA (*h*-PLA) used for mobility measurements had a molecular weight of 7.5 Kg/mol and a polydispersity of 1.28 determined by SEC.

Copolymer films were formed by spin coating from 10 %_{vol} solutions in toluene onto Au coated silicon substrates. An identical protocol to the electric field alignment of PFS-*b*-PLA films (Chapter

5) was applied to films heated to 120, 140, and 180 °C under a nitrogen atmosphere for 35 h using the parallel plate capacitor geometry in Figure 10.2a. AC electric fields of $40 \text{ V}_{\text{RMS}} \mu\text{m}^{-1}$ at frequencies up to 100 kHz were applied to the films using a modified parallel plate capacitor geometry shown in Figure 10.2b. In this case thin dielectric spacer layers are necessary to compensate for power limitations of the high voltage supply at high frequency.

Field-effect transistors (FETs) were fabricated in a bottom-gate bottom-contact configuration on highly doped Si wafers with a 300 nm thermally grown SiO_2 layer acting as gate dielectric. The freshly O_2 plasma-cleaned substrates were first treated with a hexamethyldisiloxane (HMDS) layer by sealing overnight in a glass vessel containing a saturated HMDS vapour. Au source and drain electrodes were defined by standard photolithography (channel length $L = 5 \mu\text{m}$, width $W = 10 \text{ mm}$). The FETs were characterized using a HP4155B semiconductor parameter analyzer. *h*-PSTA films were deposited by spin-coating from toluene and annealed overnight at 100 °C in a nitrogen atmosphere. Field-effect mobilities (μ_{FET}) were extracted from the saturated transfer characteristics employing Equation 10.1, where I_{SD} is the source-drain current in the saturation regime, V_G and V_{SD} are the gate and source-drain voltages, C is the insulator capacitance and V_0 is the threshold voltage [7].

$$I_{\text{SD}} = \frac{W}{2L} C \mu_{\text{FET}} (V_G - V_0)^2 \quad (10.1)$$

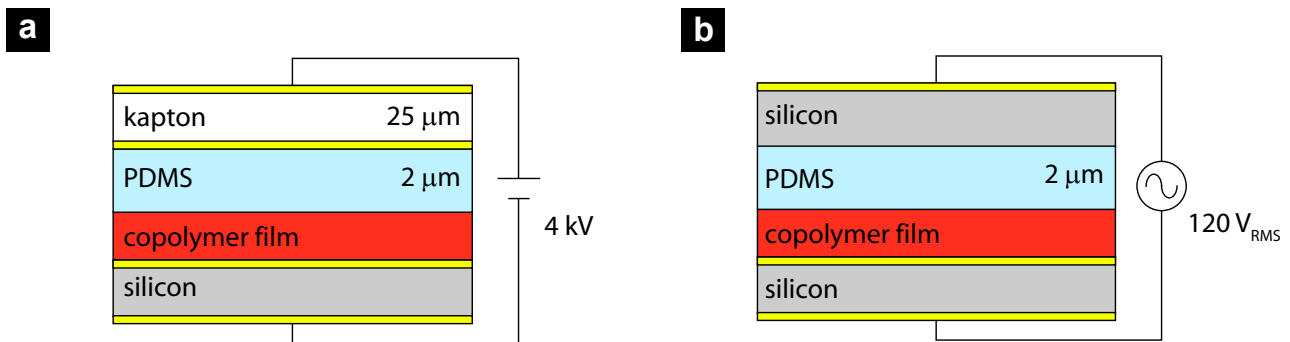


Figure 10.2: **Parallel plate capacitor geometries for application of DC and AC fields.** (a) Standard geometry outlined in Chapter 4 with a $25 \mu\text{m}$ Kapton sheet spacing layer coated with $\sim 2 \mu\text{m}$ cross linked PDMS contact layer. (b) A conducting silicon counter electrode and single $\sim 2 \mu\text{m}$ cross linked PDMS spacer used for application of $40 \text{ V}_{\text{RMS}} \mu\text{m}^{-1}$ AC field in the copolymer layer.

All FET devices measurements were made by Dr Chris Newman, Optoelectronics Group, Physics department, Cavendish Laboratories.

10.3 PSTA Hole Mobility

The charge transport characteristics of *h*-PSTA were first probed by field effect mobility measurements. Figure 10.3a shows the transfer characteristics of the polymer film at source-drain voltages of -5 V and -60 V. The hole mobility extracted from these data is $\mu_{\text{PSTA}} = 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is a respectable value in comparison to typical reported hole mobilities in non aligned polymer films [8]: poly(2-methoxy-5-(2-ethylhexoxy)-1,4-phenylene vinylene) (MEH-PPV) $\mu_{\text{MEH-PPV}} = 5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, poly(9,9-dioctylfluorene) (F8) $\mu_{\text{F8}} = 3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and regioregular poly(3-hexylthiophene) (P3HT) $\mu_{\text{P3HT}} = 2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. PSTA therefore shows good potential for application in bulk heterojunction devices from the perspective of charge transport.

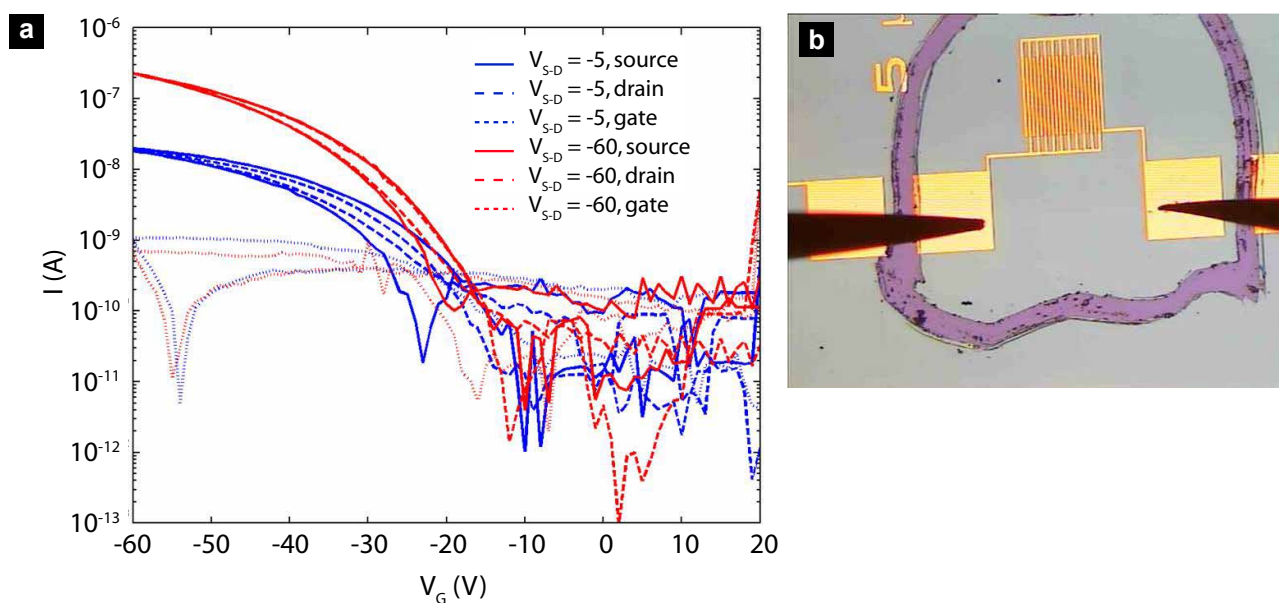


Figure 10.3: **Transfer characteristics of *h*-PSTA field effect transistor.** (a) Transfer characteristics at -5 V and -60 V gate voltage. (b) Optical image of interdigitated Au electrode transistor device and probe contacts.

10.4 Porous PSTA films

An insight into the microdomain morphology of PSTA-*b*-PLA thin films is obtained by imaging the PSTA morphology before the various thermal annealing stages; that is, immediately after spin-coating. MHI37 films after spin-coating from toluene solutions were found to microphase-separate during solvent evaporation into a partially ordered cylindrical morphology. Figure 10.4a shows an SEM top view of such a spin-coated film after 30 mins in 0.05 M NaOH etching solution for the PLA component, with a well ordered, hexagonally packed array of pores at the free surface. The pores have a centre-to-centre distance of 21 ± 2 nm and an average diameter of 13 ± 2 nm (Figure 10.4c). This structure, assuming a cylindrical morphology is consistent with a standing $C_{\perp}$ alignment of minority PLA domains at the free surface.

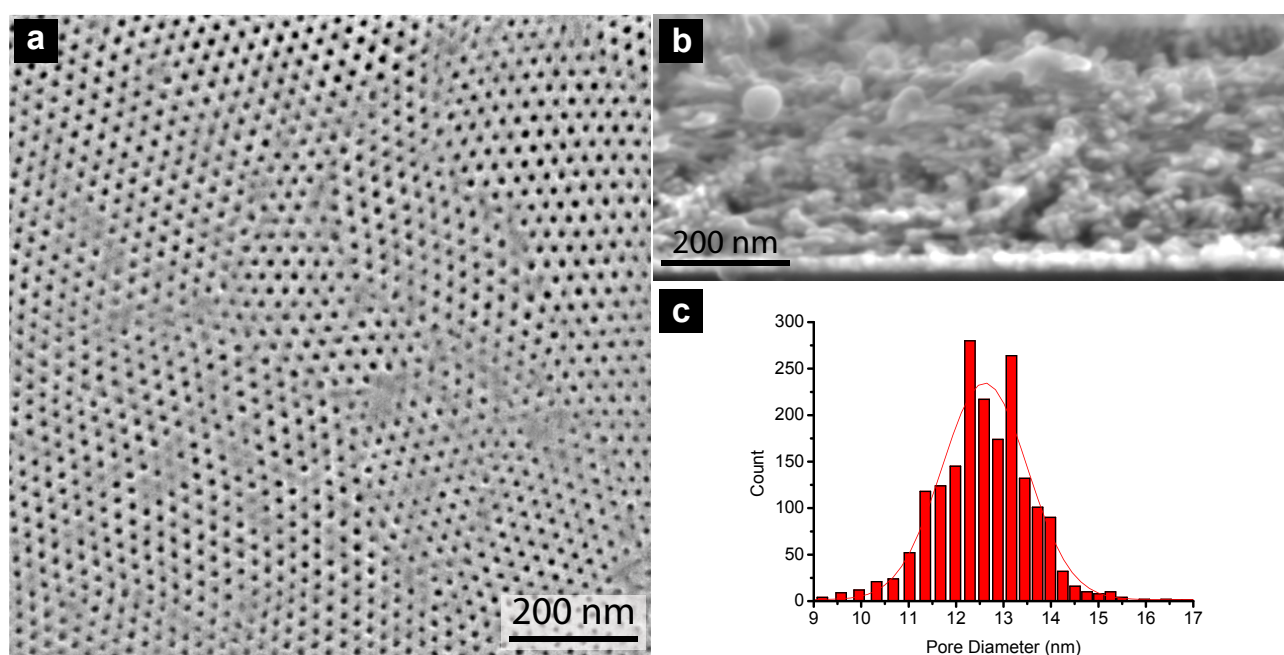


Figure 10.4: **Porous PSTA templates as formed immediately after spin-coating from toluene solution.** (a) Surface SEM image showing hexagonal ordering of pores in a PSTA matrix after PLA removal (film thickness 340 nm). The centre-to-centre spacing is 21 ± 2 nm. (b) cross sectional SEM view of electrochemical replication of the pore structure in (a) with platinum followed by rinsing away of PSTA matrix in toluene. The replication indicates that the porous structure penetrates the full film section to the conducting Au substrate. (c) Pore diameter distribution of the surface morphology in (a) with average diameter 13 ± 2 nm.

The pore-density at the free surface is $1950\mu\text{m}^{-2}$, as determined by counting threshold-defined circular features in an SEM image over several square microns using ImageJ analysis software. Sampling a ‘single crystal’ area of hexagonal pores gives a hole density of $2000\mu\text{m}^{-2}$, indicating the high degree of $C_{\perp}$ alignment at the surface. Electrochemical deposition of Pt was used as a probe of the pore structure in the same manner as used for the doubly-sacrificial PFS-*b*-PLA films. The success of this procedure identified a continuous pore structure through the layer to the conducting substrate. Figure 10.4b shows the freestanding Pt network structure left after rinsing away the PSTA matrix in toluene. Close inspection of the structure reveals a densely packed network of tangled cylinders (i.e. with no preferential orientation) that penetrate the full film thickness to the Au substrate. Uniform electrochemical replication, as opposed to sporadic patches of deposition, is indicative of a ‘uniform’ porous connection to the substrate over the entire film area.

A film-spanning microphase-separated PLA minority domain structure immediately after spin-coating is remarkable. The well-ordered $C_{\perp}$ morphology at the free surface is indicative of surface energy neutrality of the solvent swollen copolymer components during solvent evaporation from the drying film. Kim and coworkers studied solvent annealing and solvent extraction as a means of producing vertically aligned cylindrical domains in poly(styrene)-*b*-poly(ethylene oxide) (PS-*b*-PEO) films [9, 10]. As with the present case, thermal annealing of PS-*b*-PEO produced lying cylinders owing to the asymmetric surface energy ($\gamma_{PS} = 33\text{ mN m}^{-1} < \gamma_{PEO} = 43\text{ mN m}^{-1}$) causing preferential wetting of PS to the free surface, while $C_{\perp}$ standing PEO cylinders were observed at the free surface immediately after spin-coating.

In a dilute solution, the presence of solvent molecules mediates non-favourable interactions between the immiscible blocks, resulting in a single disordered phase. After the flow-induced thinning of the film during spin-coating, solvent evaporation from the layer causes a disorder to order transition. Interfacial interactions are strongly mediated by the presence of solvent molecules in both phases, which reduces any preferential affinity of the blocks to the free surface or substrate. The polymer chains therefore tend to align parallel to the interface, and consequently the microdomain morphol-

ogy aligns normal to the interface [11, 12]. In fact, in the case of highly immiscible blocks such as PS-*b*-PEO, the $C_{\perp}$ alignment was found to propagate through the complete film thickness, whereas in PSTA-*b*-PLA the ordered pores are confined to the close vicinity (roughly one domain spacing) of the free surface. Propagation of surface alignment into the bulk is caused by a strong gradient in polymer concentration that develops normal to the layer as the solvent near the free surface evaporates first. An ordering front therefore sweeps down through the layer, directing the alignment of the ordered phase with the now glassy microdomain structure at the surface in the manner of a classical zone-refinement [10]. No such vertical alignment was seen in cylinder-forming PS-*b*-PMMA copolymer films, which is attributable to the lesser degree of incompatibility ($\chi_{\text{PS-PEO}} = -7.05 \times 10^{-3} + 21.3/T$, $\chi_{\text{PS-PMMA}} = -28 \times 10^{-3} + 3.9/T$) [13, 14] between this pair of polymers, reducing the driving force to align with the initially separated regions. These comparisons suggest that the same is true of the PSTA-*b*-PLA pair.

10.5 Electric Field Alignment of PSTA-*b*-PLA

10.5.1 Application of DC fields

Electric field alignment was tested as a means of producing ordered, standing arrays of PLA cylinders spanning the full film thickness. These structures provide theoretically ideal direct charge transport out of the active layer in a solar cell device architecture. PSTA-*b*-PLA copolymer films were first annealed at 120 °C (above the glass transition of both components) for 35 h under a series of steadily increasing DC fields up to $130 \text{ V } \mu\text{m}^{-1}$ applied using the standard capacitor geometry in Figure 10.2a. The surface morphologies were imaged by SEM after removal of the top electrode and etching of the PLA component (Figure 10.5). A mix of pores and lying cylinders are seen at the surface for all applied fields. The density of pores is also equal in all cases, within error, to $1250 \pm 200 \text{ } \mu\text{m}^{-2}$; that is, a lesser degree of standing alignment is present at the upper surface than at the free surface of the as-spun film. PSTA-*b*-PLA films annealed with a free (unconfined) surface at 120 °C showed

a smooth, featureless surface morphology (after PLA etching), suggesting a uniform surface wetting layer of the PSTA component.

Cryo-fracture cross sections were made of the films annealed at 120 °C both with and without a

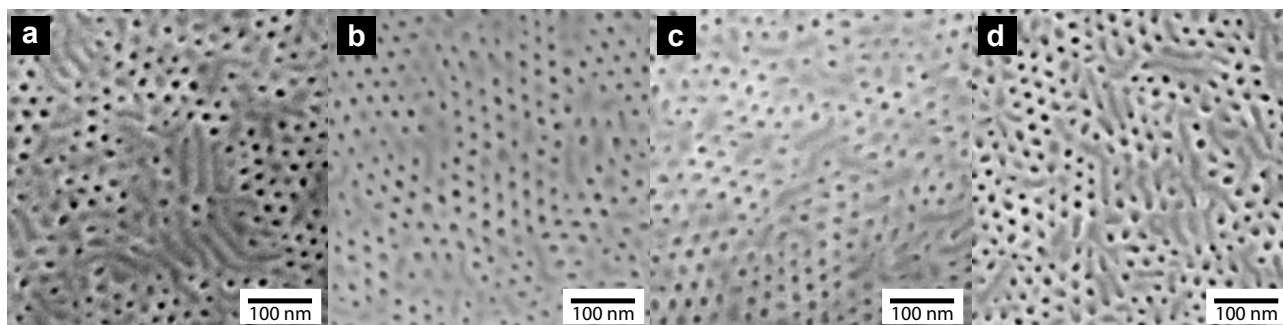


Figure 10.5: **Application of a DC electric field to a PSTA-*b*-PLA copolymer.** Top view SEM images of 240 nm thick porous PSTA film after removal of PLA. The film in (a) was assembled into the parallel-plate capacitor with no applied voltage and annealed under N₂ for 35 h at 120 °C. Images (b) to (d) show the surface morphology after the same annealing period with applied electric fields of 43, 86 and 130 V μm⁻¹. The density of cylindrical pores at the surface is equal in all films within error margins (1250 ± 200 holes μm²).

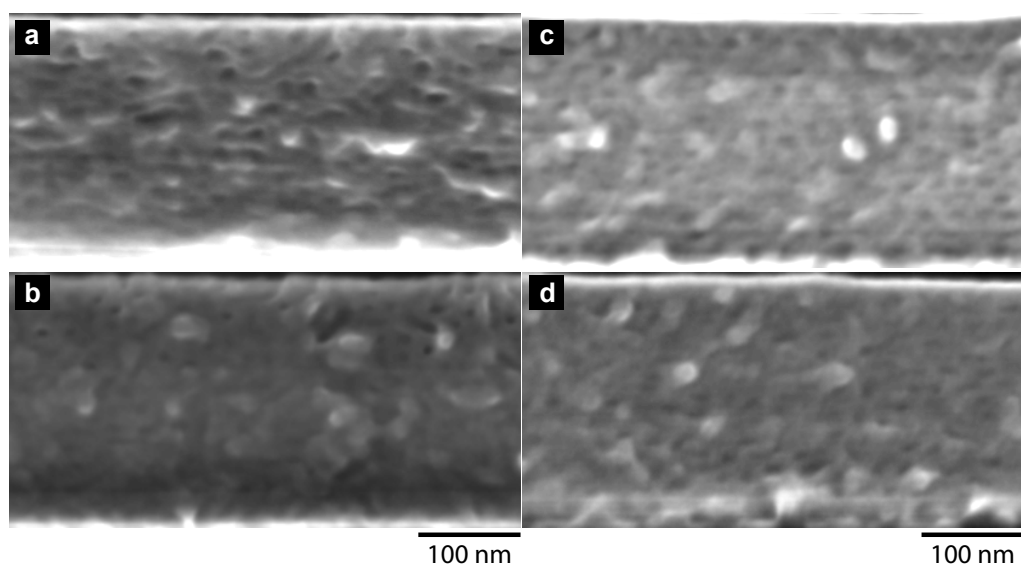


Figure 10.6: **Cryo-fractured cross sections of porous PSTA films.** Cross sectional SEM images after removal of the PLA component for a film annealed for 35 h at 120 °C under (a,b) an applied field of 130 V μm⁻¹ and (c,d) no applied field. Neither of the two films contain continuous porosity from surface to substrate, indicated by the absence of electrochemical contact with the Au working electrode. Two sections are shown for each sample to illustrate the variation in visible morphologies. The upper surfaces of films (a) and (b) are shown in Figure 10.5d and a, respectively.

$130 \text{ V } \mu\text{m}^{-1}$ DC electric field. Two images of each film are shown since the ‘quality’ of the fracture edge is not everywhere the same which leads to some ambiguity in the apparent morphologies. Whilst not conclusive, both film cross sections show the presence of cylinders that are neither standing nor parallel to the substrate. In fact, some areas of the electric field treated sample appear to show relatively few $C_{\parallel}$ structures (Figure 10.6b). However, one should be careful drawing absolute conclusions from these images since the fracture edge may not be perfectly perpendicular to the substrate in all places. What appear to be $C_{\perp}$ structures at the substrate contact layer of Figure 10.6b may in fact be $C_{\parallel}$ running into the page, with a non-planar fracture edge. One firm conclusion can however be drawn; that is, the electric field does not result in an ordered $C_{\perp}$ array of PLA cylinders running through the full layer thickness. The pore structure does not fully penetrate the layer in either films, as determined by absence of electrochemical current in a Pt plating electrolyte.

Further electric field alignment tests were conducted at higher temperatures between 140 and 180 °C for 35 h both with and without a $120 \text{ V } \mu\text{m}^{-1}$ DC electric field. After removal of the PDMS counter electrode the films were immersed in the standard 0.05 M $\text{NaOH}_{(\text{aq})}$ etching solution for the PLA component for 30 minutes. A TappingModeTMSFM height map of the surface of an electric field treated sample at 140 °C (Figure 10.7a) now shows a microphase separated morphology consistent with completely lying cylinders ($C_{\parallel}$). An identical sample annealed under the same conditions without applied voltage (referred to as ‘blank’) shows the same $C_{\parallel}$ morphology at the top surface. The principle feature spacing determined by Fourier transform of the image is $27 \pm 4 \text{ nm}$. DC alignment experiments repeated with a steadily increasing temperature up to 180 °C resulted in the same $C_{\parallel}$ morphology.

PSTA-*b*-PLA films annealed with a free (unconfined) surface at 140 °C showed the same featureless topology as those annealed at 120 °C. TappingModeTMSFM height images of this surface (Figure 10.8) show faint traces of a $C_{\parallel}$ morphology. The corresponding phase image reveals the internal $C_{\parallel}$ structure lying underneath the wetting layer.

Cross sectional TEM was used to probe the microphase morphology in the bulk of the layers.

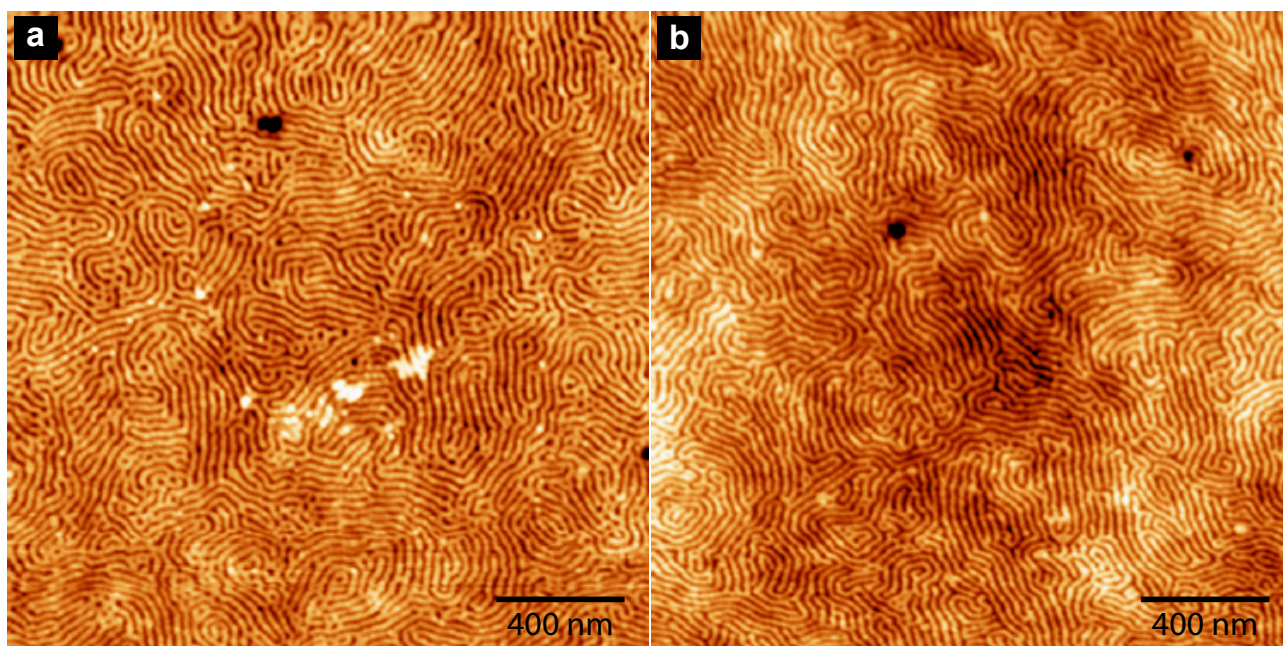


Figure 10.7: **DC electric field annealing of PSTA-*b*-PLA films.** TappingMode™ SFM height maps of PSTA films (after PLA etching) annealed at 140 °C for 35 h with (a) no applied field and (b) 120 V μm^{-1} . Identical lying morphologies were found on films annealed at up to 180 °C. The films are 240 nm thick on Au substrates.

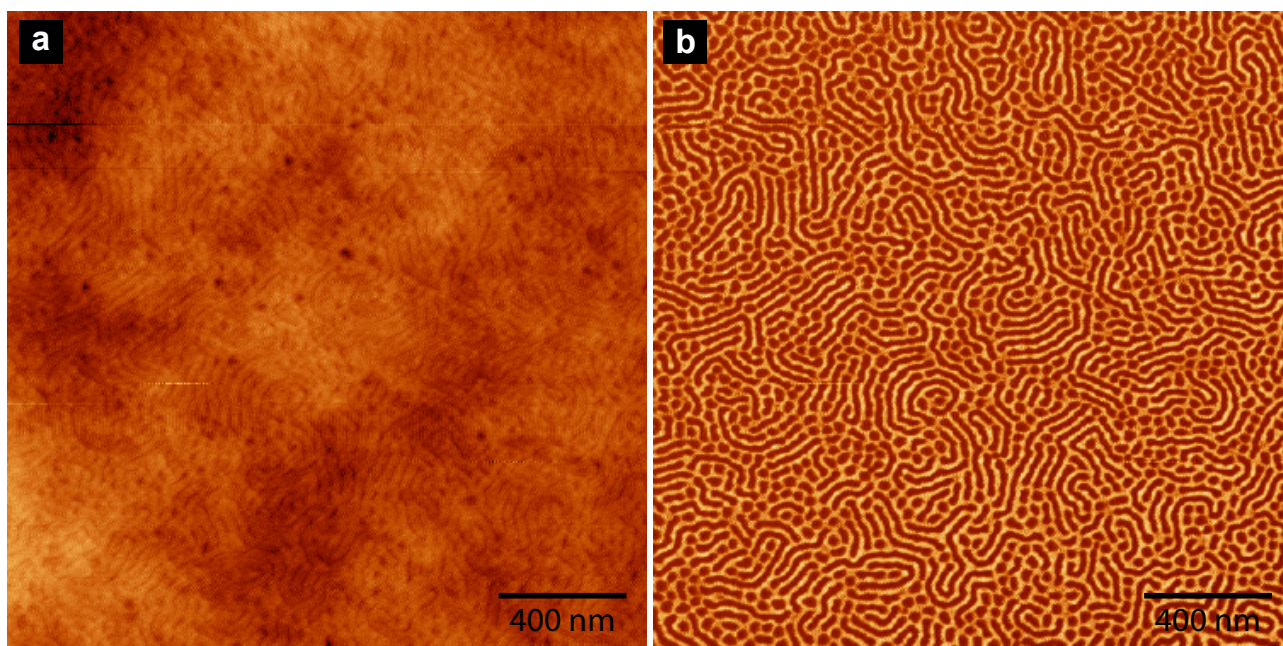


Figure 10.8: **Free surface of PSTA-*b*-PLA film after thermal annealing at 140 °C for 35 h.** (a) TappingMode™ SFM height image after PLA etching shows a faint outline of lying cylinder features. (b) phase image reveals a clear microphase morphology lying underneath a surface wetting layer of the PSTA component.

Thin sections prepared using an ultramicrotome (see Chapter 3) were exposed to ruthenium tetroxide vapours, expected to act as a selective stain for the aromatic double bonds in PSTA. Figure 10.9 shows the resulting bright field TEM cross section of a PSTA-*b*-PLA film annealed at 150 °C for 30 h with no applied electric field. The majority phase appears dark, consistent with the expected staining of the PSTA phase. These images provide further evidence of a $C_{||}$ morphology, driven by preferential affinity of the substrate for the PSTA component.

Taken together, the results of DC field application at 120 °C and 140 °C suggest that the electric field driving force for standing alignment is dominated by surface fields. Presumably the morphologies observed at 120 °C are simply kinetically retarded and will tend towards fully lying cylinders similar to those seen at 140 °C and above with sufficient time. All thermally annealed morphologies show a lesser degree of vertical alignment at the free surface than immediately after spin coating. Considering the thermodynamic driving force, the free energy penalty of misaligned dielectric interfaces scales with the square of the dielectric contrast [15]. The measured dielectric constants for the PSTA-*b*-PLA component polymer phases are $\epsilon_{\text{PSTA}} = 3.6$ and $\epsilon_{\text{PLA}} = 3.4$. The thermodynamic driving force for alignment is therefore reduced by roughly a factor of four compared to the PFS-*b*-PLA copolymer ($\epsilon_{\text{PFS}} = 3.0$). One must consider the possibility that electric fields within experimental reach (i.e. that do not lead to dielectric breakdown) are not sufficient to overcome surface alignment fields for the PSTA-*b*-PLA copolymer.

A further possibility however is that a static electric field build-up may be prevented in a polymer layer with finite (if small) charge mobility. In this case, free charges on the electrode are able to move through the PSTA phase and compensate the applied field in the polymer (the majority phase is continuous through the film thickness regardless of lying or standing cylinder alignment). If this is indeed a limiting factor then one way to negate this effect is to electrically isolate the copolymer layer from the external power source such that no free charge is able to reach the film.

A PSTA-*b*-PLA film was spin-coated onto a 25 μm thick Kapton foil precoated on both sides with a 40 nm thick conducting Au layer. The counter electrode was a second 25 μm Kapton foil with a

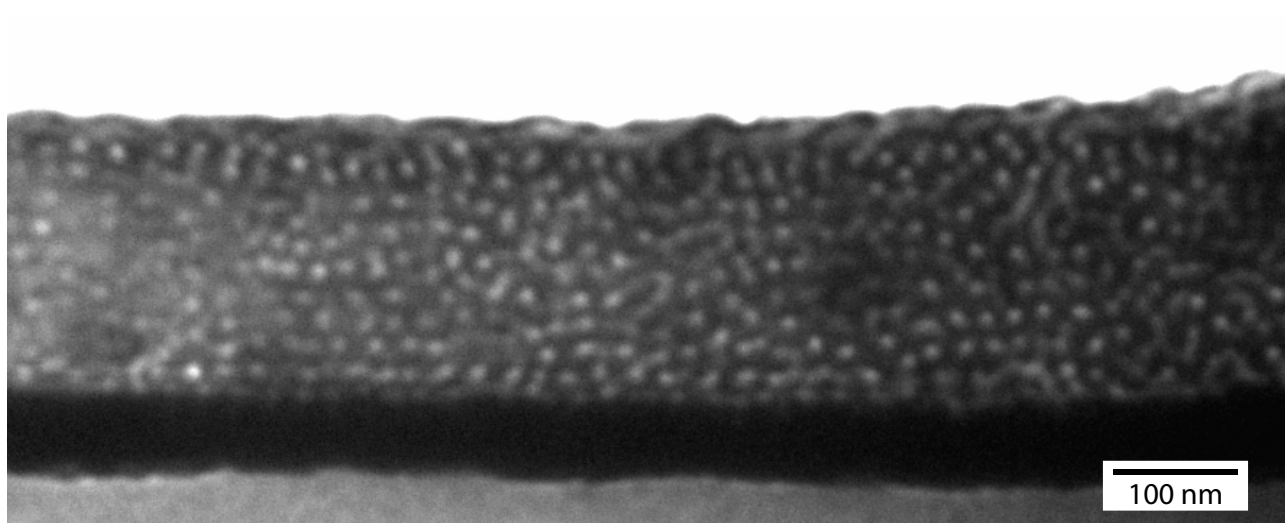


Figure 10.9: **TEM cross section of PSTA-*b*-PLA.** Film annealed at 150 °C for 30 h on a Au substrate with no applied field. The PSTA matrix phase was stained with ruthenium tetroxide vapours, the PLA domains appear bright.

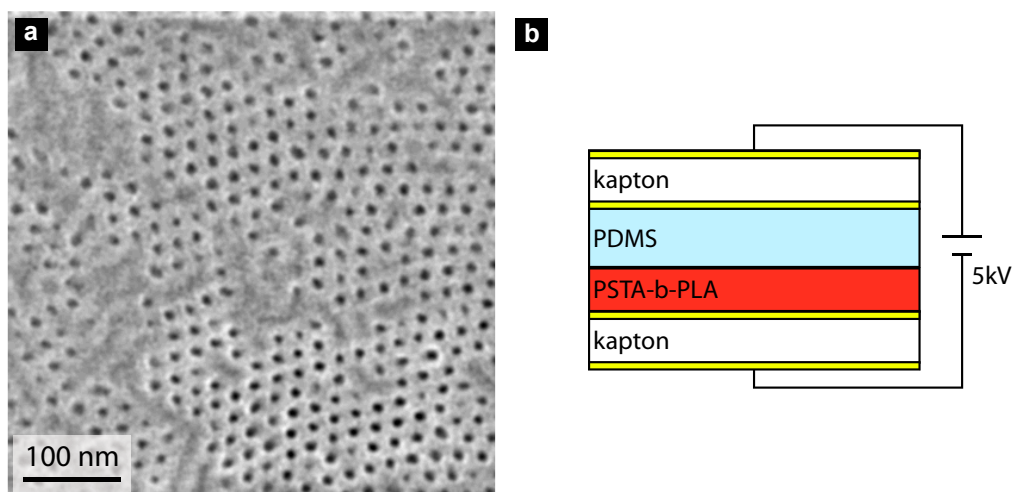


Figure 10.10: **Electronically isolated PSTA-*b*-PLA film annealed under electric field.** (a) Surface SEM after PLA removal of film annealed at 150 °C for 30 h with an applied field of $\sim 100 \text{ V } \mu\text{m}^{-1}$. (b) Schematic of an electronically isolated parallel plate capacitor set-up used to apply an electric field. Identical surface morphologies were observed on both 210 and 350 nm thick films.

PDMS contact layer on the copolymer-facing side, and a 40 nm conducting Au coating on the reverse side for electrical contact (Figure 10.10b). The copolymer film is now flanked by thick insulating dielectrics on both sides. The surface morphology after annealing at 150 °C for 30 h with an applied field of $\sim 100 \text{ V } \mu\text{m}^{-1}$ is shown in Figure 10.10a after removal of the PLA component. Interestingly a

mixed morphology of hexagonally-ordered pores and lying cylinder structures is observed at the upper surface, similar to that seen at 120 °C for the standard DC field alignment. Electrochemical probes again found that the pores at the surface do not penetrate the layer to the Au substrate. Unfortunately the structure of these pores further in the layer could not easily be determined owing to difficulties in removing the film from the substrate for sectioning. One plausible conclusion is that the competing alignment forces in the film are now more delicately balanced (although a surface field parallel alignment still overpowers any vertical alignment), causing a mixed morphology in the layer. Given the similarity of this morphology to the 120 °C morphologies we should also consider the possibility that the real temperature in the layer is less than expected, owing to the thermally insulating properties of the Kapton foil (compared to the silicon substrate).

10.5.2 Application of AC fields

Mobile free charge compensation of the applied field may also be circumvented by application of an alternating (AC) field. The drift velocity v_D of a hole in an electric field E is given by $v_D = \mu E$, so that the distance traveled in time t is $d = v_D t = \mu E t$. An order of magnitude estimate of the required field frequency (f) to prevent charge compensation can therefore be extracted from the limit of a hole making one complete transit of the (~ 500 nm) thick copolymer layer in a time given by half the period ($T = 1/f$) of the applied field. The measured PSTA hole mobility is $\mu_{\text{PSTA}} = 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, translating to a frequency $f \sim 40 \text{ kHz}$ for a field strength of $40 \text{ V } \mu\text{m}^{-1}$.

Practical limitations mean that a maximum AC voltage of $120 \text{ V}_{\text{RMS}}$ could be applied across the capacitor set-up at frequencies up to 100 kHz. The thick Kapton dielectric spacer layer in Figure 10.2a would in this case produce only a very small field strength in the copolymer layer. Therefore a modified parallel plate capacitor design was used with a conducting silicon counter electrode coated with $2 \mu\text{m}$ PDMS as shown in Figure 10.2b. The applied field strength in a 300 nm copolymer layer is $40 \text{ V } \mu\text{m}^{-1}$.

Figure 10.11 shows that the application of a $40 \text{ V } \mu\text{m}^{-1}$ AC field of up to 100 kHz had no noticeable

effect on the $C_{||}$ morphology after annealing at 150 °C for 35 h. Identical worm-like structures were observed on the upper surface of all samples after removal of the PLA component.

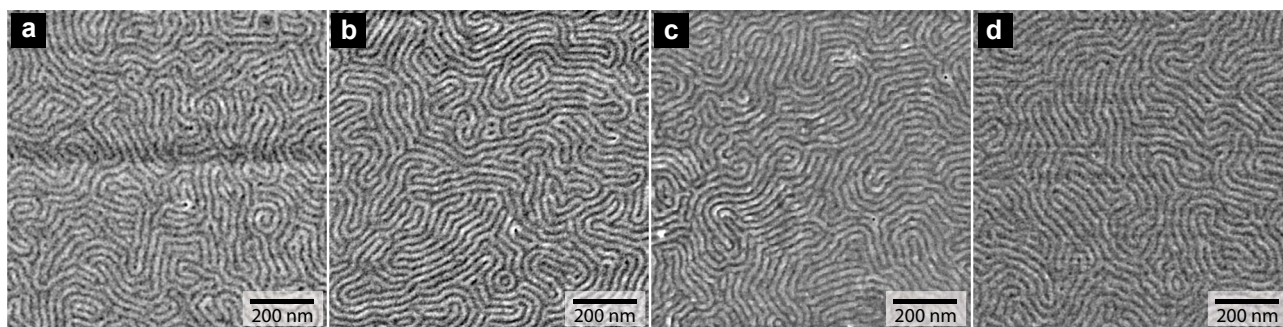


Figure 10.11: **PSTA surface morphologies after annealing at 150 °C under AC applied fields.** (a) Surface SEM image after removal of PLA component showing lying cylinder structures after 35 h with no applied field. Images (b) to (d) show the surface morphologies after annealing for the same period with an applied AC electric field of $\sim 40 \text{ V } \mu\text{m}^{-1}$ at 500 Hz, 10 kHz and 100 kHz. The film thickness is 340 nm in all cases.

10.6 Summary

These results demonstrate successful ordered microphase separation into a cylindrical morphology of a diblock copolymer with a semiconducting majority phase, and minority cylindrical domains of a selectively sacrificial component. The hole mobility of the PSTA homopolymer phase is $\mu_{\text{PSTA}} = 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The minority PLA was successfully removed from films immediately after spin-coating to produce a mesoporous polymer hole conductor with 13 nm cylindrical channels fully penetrating the layer to a conducting substrate. The channels could be electrochemically replicated in Pt metal.

Thus far we have no control over the alignment of the cylindrical microdomains using external electric fields. Static (DC) fields of up to $120 \text{ V } \mu\text{m}^{-1}$ and AC fields of $40 \text{ V } \mu\text{m}^{-1}$ at up to 100 kHz failed to produce standing arrays of ordered cylinders spanning the layer thickness as was demonstrated for PFS-*b*-PLA doubly sacrificial films. The range of applied fields and processing conditions suggest that this is most likely owing to a lack of dielectric contrast between the PSTA and PLA components ($\Delta = 0.2$).

From the perspective of bulk heterojunction photovoltaics, the failure to align these templates prevents the formation of an idealized, comb-like interdigitation of donor-acceptor components with vertical transport routes out of the layer. However, the successful microphase separation into a partially ordered and film-spanning cylindrical morphology means that an intimately mixed junction is still possible in which both components are fully continuous to external electrodes. These structures in fact represent a very interesting development from the point of view of real applications as there is no longer a need for the difficult and time consuming alignment stage. The active layer is both deposited and structured by self-assembly in a single simple step that could be applied to reel-to-reel processing.

With a suitable mesoporous matrix morphology in place, future work will attempt to backfill the second active component into the pore structure to produce a working photovoltaic device. Likely

inorganic candidate donor materials are II-VI semiconductors such as CdSe which has good absorbance in the solar spectrum and can be deposited electrochemically [16, 17] or solution processed in nanoparticulate form [18]. A further possibility is infiltration of small organic molecules such as perylene. It should be noted that the PSTA polymer employed infiltrated with a perylene would be a remarkably similar device structure to that obtained from direct microphase separation of a D-A copolymer synthesized by Lindner *et al.* Their device demonstrated encouraging performance in bulk heterojunction solar cells [5]. However a major limitation in their devices was a high series resistance and a corresponding low fill factor associated with a parallel alignment of wire-like microphase separated domains, meaning that few direct charge collection pathways exist out of the device layer. The microphase separation and alignment observed in PSTA-*b*-PLA therefore show real promise for future device applications.

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Summary and Suggestions for Further Work

11.1 Summary

The goal of this thesis was to explore the use of block copolymer self assembly as a means of patterning functional materials on the 10 nm length scale. The structures thus made were incorporated into thin film bulk heterojunction solar cells containing both organic and inorganic components. PLA containing block copolymers, synthesized by RAFT polymerization, were chosen to introduce selectively degradable minority domains into microphase separated films. With suitable orientation of the microphase morphology, the PLA domains could be removed by hydrolysis in mild chemical conditions to leave a polymer matrix with a well defined internal porosity. These mesoporous coatings formed a template for the electrochemical deposition of selected semiconducting materials from the underlying conducting substrate.

PFS-*b*-PLA copolymers played the role of a doubly sacrificial template, in that the majority PFS phase is also removed after deposition of the semiconductor, such that none of the original copolymer remains in the final device. Cylinder-forming PFS-*b*-PLA films were found to microphase separate into a disorganized network of PLA cylinders immediately after spin coating from toluene solutions. A simple 3-electrode electrochemical probe in conjunction with ellipsometry was used to monitor successful removal of the PLA phase, which formed a film-spanning microdomain morphol-

ogy. Freestanding platinum nanostructures, consisting of a tangled array of ~ 12 nm wires were made by electrochemical replication of the pores, followed by solvent dissolution or UV-ozone etching of the PFS template.

In order to produce a conceptually ideal vertical interdigitation of semiconductor phases for the bulk heterojunction, the PFS-*b*-PLA films were thermally annealed above the glass transition temperature of both components in the presence of an electric field applied in a parallel plate capacitor geometry. The contrasting dielectric constants of the phase separated components resulted in a free energy driving force for vertical alignment of the PLA cylinders with the electric field vector. The electric field was in competition with asymmetric interaction energies of each component with the film interfaces that favour alignment of the domains in the plane of the film. The greatest degrees of alignment were obtained for strong fields (up to $150 \text{ V } \mu\text{m}^{-1}$) and weakly asymmetric surface interactions. Applied electric fields of $120 \text{ V } \mu\text{m}^{-1}$ were sufficient to produce standing arrays of hexagonally ordered PLA cylinders that spanned the full thickness of the film.

By changing the relative volume fractions of the PFS and PLA components, a PFS-*b*-PLA copolymer was synthesized that adopted either the bicontinuous gyroid phase or cylindrical phase in the bulk at 180°C and 150°C , respectively. Application of a $120 \text{ V } \mu\text{m}^{-1}$ electric field to thin films at 150°C resulted in standing arrays of L, HPL, and C phases which were electrochemically replicated to produce mixed arrays of nanosheets and nanowires. These observations demonstrate the utility of an electric field in directing the alignment of block copolymer microphases. At 180°C the films adopted the gyroid phase which could be electrochemically replicated to produce freestanding gyroid network arrays. The surface reconstruction layer, influenced by both surface energy and roughness, was crucial in determining continuity of the minority PLA domains to the conducting substrate.

The dye-sensitized solar cell is a particularly promising example of a bulk heterojunction solar cell containing both organic and inorganic materials. Vertically aligned freestanding nanowires and gyroid network arrays were replicated in anatase TiO_2 on transparent conducting substrates and incorporated into liquid electrolyte and solid-state dye-sensitized solar cells (DSSCs). The available

surface for dye-adsorption, measured in equivalent Pt arrays, was 130 and 60 times greater than the flat substrate for each micron in array thickness for the gyroid and wires, respectively. While the measured gyroid area compares well to the calculated surface area, the measured wire surface area was only 60 % of the expected value. This reduction is attributed to the partial collapse of these quasi 1D nanostructures following removal of the polymer template. The stability of the freestanding arrays has wider implications for their application in solar cells. Only very poorly functioning solid-state DSSCs could be made from the standing wire arrays owing to collapse of the structures during the infiltration of an organic molecular hole transporting material (Spiro-MeOTAD). The gyroid networks, on the other hand, were very well suited to infiltration from the solution phase and arrays only 500 nm thick demonstrated power conversion efficiencies of up to 1.73 % using a high extinction coefficient organic indoline dye (D149) and 0.63 % with the Z907 ruthenium complex dye. These are remarkably high efficiencies for such thin active layers and correspondingly low adsorption profiles. The performance of these devices was limited by the thickness of the gyroid array which showed signs of cracking and delamination owing to significant reduction in volume upon high temperature annealing. The gyroid templating protocol itself however was robust in templates many microns thick. Therefore development of a semiconductor replication procedure that does not result in significant contraction should lead to significant improvement of these devices. The possibility of a completely low temperature processing procedure would also be extremely interesting from a the point of view of scale-up and production economics.

The electronic properties of nanowire and gyroid arrays were probed in liquid electrolyte DSSCs using transient photocurrent and photovoltage spectroscopy. Further comparison was made to state-of-the art mesoporous TiO_2 films made from sintered arrays of anatase nanoparticles. High resolution TEM imaging of the structures revealed that the TiO_2 arrays had a nanocrystalline structure with domain sizes roughly comparable to the structural confinement: ~ 10 nm for the electrodeposited structures, and ~ 20 nm for the nanoparticles. The disordered nanoparticle film actually showed the fastest charge extraction rates at short-circuit through a $1.4\ \mu\text{m}$ thick layer, an observation that could

be explained by the larger nanoparticle crystal size and a reduced charge trap density in comparison to the electrodeposited material. In the copolymer templated arrays, which in principle differ only in mesoscale morphology, charge collection times from the wire arrays were approximately twice as fast as those in the gyroid networks under 100 mW cm^{-2} illumination. The improvement is attributable to more direct charge extraction routes out of the device for the standing wires. Charge recombination was considerably slower in the nanowire film, with up to an order of magnitude longer electron lifetime than in the gyroid and nanoparticle networks at any given voltage.

Despite the impressive electronic properties of the nanowires, DSSCs fabricated from the wire arrays showed the lowest power conversion efficiencies of the three structures; 1.1 % compared to 2.7 % and 3.0 % for the nanoparticle and gyroid arrays respectively. Again this trend is most likely attributable to the comparatively poor structural stability of the nanowire arrays, leading to a loss of available surface for dye loading and therefore weak light adsorption.

A partially sacrificial approach to bulk heterojunction fabrication was investigated using a PSTA-*b*-PLA block copolymer in which the majority PSTA phase itself demonstrated a hole mobility of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Thin films of the copolymer were found to microphase separate into 13 nm PLA cylinders embedded in the PSTA majority phase immediately after spin coating. Again the PLA phase could be removed by hydrolysis in basic conditions. The voided channels left by the PLA removal were found to penetrate the full film thickness is a disorganized pathway and could be electrochemically replicated in Pt as proof of principle for heterojunction fabrication. This approach avoids the formation of a freestanding array structure and could therefore more easily benefit from the electronic properties of interdigitated nanowire bulk heterojunction. However, the cylindrical morphology could not be aligned in a vertical direction using DC or AC electric fields. Thermal annealing of PSTA-*b*-PLA films resulted in PLA cylinders that lie in the plane of the film owing to the dominant influence of asymmetric surface interaction energies. The fully porous structure immediately after spin coating is however an encouraging result. Further work is require to explore filling of the pores with a light adsorbing semiconductor phase to complete the heterojunction.

11.2 Further Work

Perhaps the most intriguing outcome of this thesis is the successful generation of mesoporous bi-continuous gyroid polymer films that can be used as templates for an enormous range of functional materials. A specific application was demonstrated with TiO_2 in dye-sensitized solar cells that, despite showing encouraging performance, are currently limited by the accessible stable thickness of the deposited material. Further development could go in one of two interesting directions. Firstly, a deposition route for TiO_2 or alternative wide band-gap metal oxide semiconductor with minimum material contraction on crystallization could be developed. Electrochemical deposition remains a viable technique in this regard; both copper oxide and zinc oxide have reported low temperature electrochemical routes to highly crystalline materials [1, 2] and are extremely promising candidates for dye sensitized solar cells.

Atomic layer deposition (ALD) offers a potential template filling technique to replace electrodeposition. ALD is a chemical vapor deposition technique suitable for depositing conformal inorganic layers with thickness down to a fraction of a monolayer, based on sequential exposure to self-terminating gas-solid reactions (see reference [3] for a comprehensive review of this technique). ALD of TiO_2 into porous gyroid films was explored in collaboration with Dr Robin Ras and Mathias Kolle in the Helsinki University of Technology. Preliminary results using a previously reported low temperature protocol (substrate temperature 70°C) with alternating cycles of TiCl_4 and H_2O reactant vapours, showed successful replication of the pore structure (Figure 11.1). Further investigation will be required to probe the crystalline structure of this material, the shrinkage during annealing, and the suitability of ALD to gyroid templates many microns thick where the pore aspect ratio can reach ~ 1000 . Since ALD proceeds by a layer-by-layer growth mechanism on the pore walls, the early success of these tests raises the intriguing possibility of core-shell networks with improved electronic properties, or indeed hollow tubular structures with doubled area for dye adsorption.

A second direction would be to incorporate thin arrays ($\sim 500\text{ nm}$ and below) into other bulk

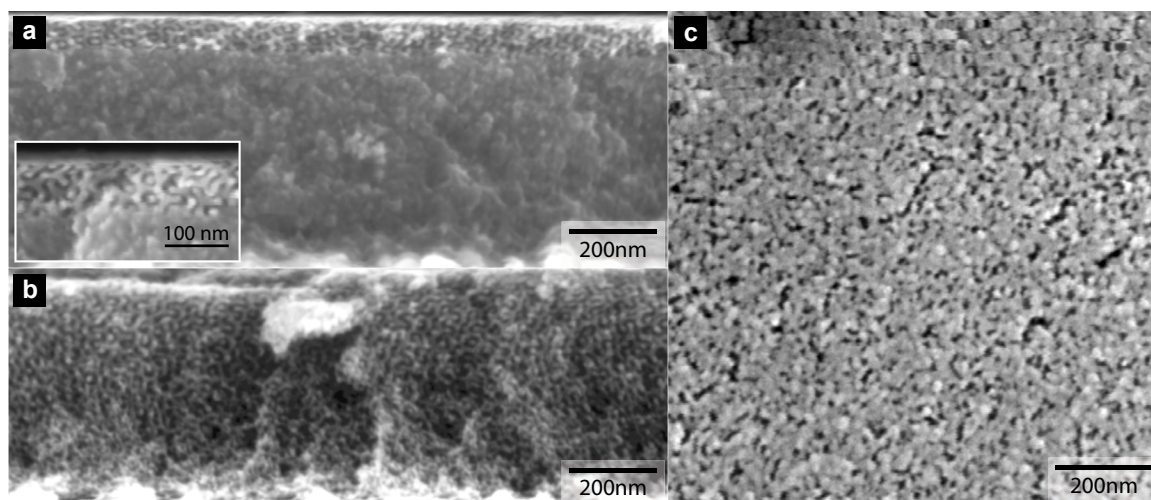


Figure 11.1: **Atomic layer deposition of TiO_2 into porous gyroid templates.** (a) Cross sectional SEM image of a filled template after exposure to O_2 plasma for 5 minutes to etch the PFS template. An etching front of the PFS can be seen near the film surface as it progresses down through the layer (inset). (b) The freestanding network array after complete etching of the PFS. (c) Surface view SEM of the film in (b) showing conformal coating of the template including a fraction of the upper template surface. The ALD deposition protocol was 100 repeat cycles of: (I) 3 s TiCl_4 vapour, (II) 6 s N_2 purge, (III) 3 s H_2O vapour and (IV) 6 s N_2 purge.

heterojunction combinations such as those formed by infiltration of an absorbing semiconducting polymers (explored for example by McGehee *et al.* and others [4, 5]), that would benefit from the extremely open and well ordered porosity of the gyroid network. In these systems only a few hundred nanometres device thickness is required to achieve significant adsorption [6]. The gyroid network could also be fabricated in an alternative low band-gap semiconductor already sensitive to solar radiation such as CdSe or PbS, all of which are accessible by electrochemical or chemical bath deposition routes [7, 8]. In fact, a room temperature chemical bath deposition of PbS following the protocol of Meldrum *et al.* [9] was investigated as a viable template filling technique during this work in collaboration with Mathias Kolle. The method proceeds by the decomposition of thiourea in alkaline solution to produce sulfide. Precipitation of PbS occurs once the sulfide concentration increases to an extent that it exceeds the solubility product of PbS. The method successfully replicated the internal pore structure of a porous gyroid film on a TiO_2 coated FTO substrate (Figure 11.2).

This work has shown that it is possible to engineer extremely well defined bulk heterojunction

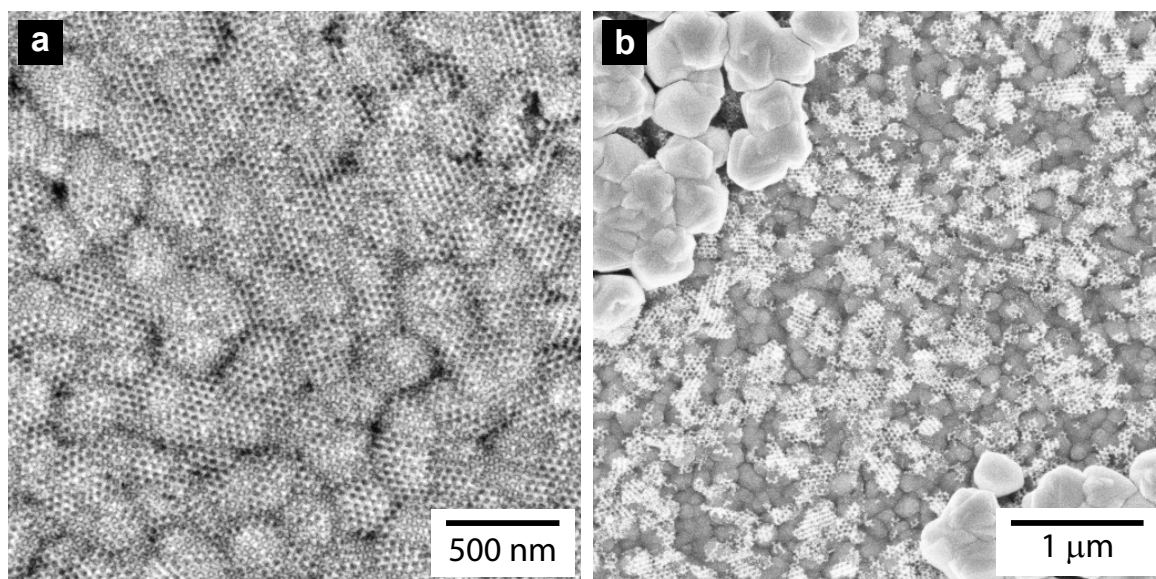


Figure 11.2: **Chemical bath deposition of PbS into porous gyroid templates.** (a) Top view SEM images of porous gyroid network replication using a chemical bath protocol for PbS deposition using copolymer films on TiO_2 coated FTO glass substrates, after solvent dissolution of the PFS template. (b) Incomplete replication of the pore structure and surface overgrowth of material above the template. The deposition solution contained 25 mM $\text{Pb}(\text{ClO}_4)_2$, 0.25 M NaOH and 0.1 M thiourea in water containing 20 %_{vol} methanol.

structures on the 10 nm length scale and that these architectures open up routes to improved performance in real photovoltaic devices. Certainly a great many interesting applications of these templating techniques remain to be explored. I hope that this work has gone some way towards demonstrating the huge potential of block copolymers and their exquisite self assembly for real applications in nanotechnology.

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Publications

"Freestanding nanowire arrays from soft-etch block copolymer templates". E. J. W. Crossland, S. Ludwigs, M. A. Hillmyer, U. Steiner, *Soft Matter*, 2007, 3, 94-98

"The biocontinuous double gyroid dye-sensitized solar cell" E. J. W. Crossland, M. Kamperman, M. Nedelcu, C. Ducati, U. Wiesner, D. M. Smilgies, G. E. S. Toombes, M. A. Hillmayer, S. Ludwigs, U. Steiner and H. J. Snaith, (submitted)

"Block copolymer morphologies in dye-sensitized solar cells: probing the photovoltaic structure-function relation" E. J. W. Crossland, S. Ludwigs, M. A. Hillmyer, U. Steiner, H. J. Snaith, (submitted)

"In situ monitoring of mesoporous block copolymer films for membrane based electrochemical synthesis" E. J. W. Crossland, P. Cunha, S. Ludwigs, M. A. Hillmyer, U. Steiner, (In preparation)

"High efficiency liquid dye-sensitized solar cells from mesoporous TiO₂ particulates" M. Nedelcu, E. J. W. Crossland, J. Lee, M. C. Orillal, S. C. Warren, U. Wiesner, U. Steiner, H. J. Snaith (submitted)

"Block-copolymer directed synthesis of mesoporous TiO₂ and its applications in solid state dye-sensitized solar cells" M. Nedelcu, J. Lee, E. J. W. Crossland, S. C. Warren, M. C. Orillal, U. Wiesner, U. Steiner and H. J. Snaith (submitted)

"Solvent vapour assisted imprint lithography" N. E. Voicu, S. Ludwigs, E. J. W. Crossland, P. Andrew, U. Steiner, *Adv. Mater.* 2007 19, 757-761

"High-speed photography and spectroscopy in determining the nature, number and evolution of hot spots in energetic materials" W. G. Proud, E. J. W. Crossland, J. E. Field, *Proc. SPIE* 4948 510-518