Titanium oxide nanotube arrays : template preparation, facile liquid-atomic layer deposition process (L-ALD) and potential in hybrid solar cells

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

TITANIUM OXIDE NANOTUBE ARRAYS:

**TEMPLATE PREPARATION, FACILE LIQUID-ATOMIC
LAYER DEPOSITION PROCESS (L-ALD) AND POTENTIAL
IN HYBRID SOLAR CELLS**

THELESE FOONG RU BAO

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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IN HYBRID SOLAR CELLS**

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2010

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ABSTRACT

The ordered bulk heterojunction (BHJ) is a device structure that is widely expected to alleviate problems associated with exciton dissociation and charge transport that currently limit the efficiency of excitonic organic solar cells to ca. 7.4 %. This research focuses on the development and incorporation of electron accepting and transporting arrays of TiO₂ nano-tubes in hybrid organic-inorganic solar cells, with regio-regular poly (3-hexylthiophene) (P3HT) constituting the photoactive donor material. Nano-porous anodic alumina (AAO) templates produced by anodizing Al thin films on substrates were a natural choice material to direct nano-array deposition as they offer good control over array dimensions. Although AAO templates have been exceptionally popular for nano-array fabrication, their use in opto-electronic applications has been restricted largely by the inability to stabilize Al anodization on transparent-conducting electrodes (commonly indium-tin-oxide (ITO) and fluorine-doped tin oxide (FTO)). Part of this report examines the root cause(s) for such instability and proposes the use of ultra-thin (0.2 – 0.5 nm) Ti inter-layers to passivate the Al-ITO interface, thereby stabilizing the AAO formation process. When thicker (2 – 10 nm) Ti layers were employed, thick barrier layers that prevent pore connectivity to the ITO coated glass substrate, were observed. The complex relationship between substrate properties and barrier layer formation was studied and is reported here.

Next, a liquid-phase atomic layer deposition (“liquid-ALD” or LALD) procedure established to achieve TiO₂ nano-tube arrays on ITO coated glass is detailed. Like its vapor-

phase predecessor, LALD produces non-line-of-sight TiO₂ coatings that conform to the shape of the AAO pore channels resulting in nano-tube arrays when the alumina template is removed. The wall thickness of the nano-tubes can be tuned by varying the number of cycles of TiO₂ deposition. The key objective of evolving the LALD procedure was to circumvent vacuum conditions necessary to conventional ALD that are highly energy-consuming, facilitating a greener deposition route. The feasibility of doping the TiO₂ films and nano-tubes by incorporating vanadia oxide precursors into LALD assembly thus tuning their band gaps and optical absorption properties is also discussed. Finally, device prototypes comprising P3HT and the LALD-derived arrays, with a champion efficiency of 0.3 % are reported. The nano-array dimensions were found to be ideal for exciton dissociation with strong photoluminescence quenching observed when P3HT was infiltrated into the arrays. Charge mobility studies suggest that the performance of devices with P3HT fully infiltrated was ultimately limited by the slow mobility of holes ($1.5 \times 10^{-5} \text{ cm}^2/\text{Vs}$) in P3HT as a result of the polymer chains coiling under nano-confinement inside the nano-channels and inter-tube spaces of the arrays. Several research directions for further advancements are proposed.

LIST OF AUTHOR'S PUBLICATIONS

Journal papers related to this work:

- 1) Foong, T.R.B., Sellinger, A. and Hu, X., "Origin of the Bottlenecks in Preparing Anodized Aluminum Oxide (AAO) Templates on ITO coated glass", *ACS Nano*, 2, 2250 (2008).
- 2) Foong, T.R.B., Shen, Y., Hu, X. and Sellinger, A., "Template-directed "Liquid-ALD" Growth of TiO₂ Nano-tube Arrays: Properties, and Potential in Photovoltaic Devices", submitted to *Adv. Func. Mater.*, 20, 1390 (2010). (Journal frontispiece image)
- 3) Foong, T.R.B., Sellinger, A. and Hu, X., "Charge Transfer and Transport Characteristics of Bulk Heterojunction Solar Cells Composed of Poly (3-hexylthiophene) and Order Arrays of TiO₂ Nano-tubes" (in preparation)

Conferences

- 1) Foong, T.R.B., Sellinger, A. and Hu, X., "Vertically Aligned TiO₂ Nano-tube Arrays via Anodized Aluminum Oxide Template on ITO coated glass: Synthesis and Device Application", *215th ECS Meeting*, San Francisco, May 24 – 29 (2009).
- 2) Foong, T.R.B., Shen, Y., Sellinger, A. and Hu, X., "Synthesis of Ordered Arrays of TiO₂ Nano-tubes Using AAO Templates", *Thin Films*, Singapore, July 13 – 15 (2008).
- 3) Foong, T.R.B., Sellinger, A. and Hu, X., "Hybrid Solar Cells Composed of Well-ordered and Well-spaced TiO₂ Nano-tube Arrays and a Hole-Conducting Matrix", *Europolymer Conference (EUPOC) on Advanced Polymeric Materials for the Energy Resources Exploitation: Synthesis, Properties and Applications*, Italy, June 1 – 5 (2008).
- 4) Seah, S., Foong, T.R.B., Ong, B.S. and Hu, X., "Photovoltaic Device Based on Solvent Vapour Treated PQT/PCBM Blends", *EUPOC*, Italy, June 1- 5 (2008).
- 5) Foong, T.R.B., Hu, X. and Sellinger, A., "Hybrid Photovoltaic Devices Composed of TiO₂ arrays and a Hole-Conducting Polymer", *3rd MRS-S Conference on Advanced Materials*, February 25 – 27 (2008).

- 6) Foong, T.R.B., Hu, X. and Sellinger, A., “Hybrid Photovoltaic Devices Composed of Conducting Polymer and Titania Nano-tube Array”, *4th International Conference on Materials for Advanced Technologies (ICMAT)*, Materials Research Society, Singapore, July 1 – 6 (2007).
- 7) Foong, T.R.B., Hu, X. and Sellinger, A., “Preparation of Ordered Arrays of Titania Nano-tubes for Hybrid Photovoltaic Devices”, *ICMAT*, Singapore, July 3 – 8 (2005).

CHAPTER 1 INTRODUCTION

1.1 Background information

Organic solar cells are currently the subject of intense research interests driven by the promise of a renewable energy source manufactured *via* lower-cost and lower-energy-consuming techniques (*e.g.* high throughput roll-to-roll processing, spin/dip coating, printing and vacuum sublimation) than present silicon technology. Although the highest performing class of devices (*i.e.* the bulk heterojunction (BHJ) composed of blends of thiophene-based polymers and soluble derivatives of C₆₀ fullerene) has been prominent enough to attain commercialization (by Konarka Technologies, Inc., Solarmer Energy, Inc., Plextronics, LumoFlex, *etc.*), there is still plenty of room to appreciate and harness the maximum efficiencies and benefits that organic materials can provide. The route towards higher performing solar cells is multifaceted involving the synthesis of new materials, band gap engineering, morphology control, evolution of new device structures and development of encapsulation technologies, to list a few. The pursuit of a device architecture ideal to addressing a number of issues pertinent to device operation constitutes the main focus of this research.

Of the many device geometries explored, the ordered-BHJ has been identified as a structure likely to result in breakthrough device efficiencies. It features inter-digitated donor and acceptor domains, a configuration that can 1) improve exciton harvests by providing donor-acceptor (D-A) interfaces within the exciton diffusion length-scale (3 – 10 nm) for charge transfer, and 2) effectively prevent geminate recombination by providing direct non-tortuous charge percolation pathways to the electrodes.

1.2 Motivation

Although conceptually simple, an all-organic ordered-BHJ is challenging to achieve. For example, donor and acceptor organic materials often do not self-assemble into phase-segregated columnar structures without external stimulation. Even if they do, the phase segregation may not traverse the entire volume of the active layer. Other important requirements include D-A interfaces that remain stable and well-defined over all device fabrication and characterization procedures and also, intermolecular π - π interactions in the direction favorable to charge transport. An interesting development has been to incorporate arrays of *n*-type semiconductor nano-tubes/wires in place of the organic acceptor for their structural stability, high electron mobility and ease of processing. Such arrays provide a scaffold in which the orientation and charge transport characteristics of the organic donor can be investigated.

In particular, this research looks into arrays of TiO₂ nano-tubes for device application. TiO₂ nano-tube arrays are achievable *via* hydrothermal and Ti anodization routes, which

however, provide limited control over array dimensions and morphology. Therefore, nanoporous anodic alumina (AAO) templates produced by anodizing Al-coated indium-tin-oxide (ITO)-glass electrodes were adopted to direct the deposition of well-aligned and well-spaced arrays. From literature searches, personal communications with other researchers and our own preliminary experiments, we have come to appreciate that it is practically impossible to fabricate robust and large-area templates on ITO coated glass without adverse template delamination problems. The cause for this phenomenon should be understood and if possible overcome so that a variety of other materials for various opto-electronic applications can be realized. Next, a technique to deposit TiO_2 coatings that conform to the shape of the AAO pore channels resulting in nano-tube arrays when the alumina template is removed must be established. Atomic layer deposition (ALD) is an ideal candidate for the above purpose which however, is generally costly to purchase and maintain due to vacuum conditions necessary for the process. Convenient and less energy-intensive solution-based approaches that produce films of ALD quality could be useful to the research community. Finally, the device preparation and characteristics of resulting prototypes await exploration. Although the electron mobility in metal oxide nano-structures is good, the efficiency of ordered-BHJ devices developed thus far has been limited to $\sim 0.5\%$. It is possible that the molecular orientation in the organic donor material, a subject that has not been thoroughly examined, is a factor affecting device performance.

1.3 Objectives

The primary objectives of this research are to:

- 1) understand the interplay of substrate and process factors that prevent the formation of stable AAO templates on ITO coated glass, and in so doing
- 2) establish a methodology by which the Al anodization process can be stabilized and robust templates produced for subsequent nano-array fabrication,
- 3) develop a versatile, non-line-of-sight and “wet” technique to deposit TiO_2 in the AAO pore channels thereby achieving uniform arrays of TiO_2 nano-tubes that extend vertically from the ITO coated glass electrode,
- 4) investigate the kinetics of deposition and the morphology and crystal structure of the resulting arrays,
- 5) incorporate the arrays into photovoltaic device prototypes and study the charge transfer and transport properties in the resulting architecture and finally,
- 6) provide platforms and research directions for further advancements.

1.4 Organization of the report

This report comprises 6 chapters. Chapter 1 delineates the purpose of this research, defining the motivation, objectives and scope. Chapter 2 presents a literature review on recent advances in the field of organic photovoltaics. Topics such as the fundamentals of device operation, loss mechanisms and progress in device architectural design are covered. The original work accomplished in this project is detailed in Chapters 3 to 5. Chapter 3 explains how a persistent instability issue in forming AAO templates on ITO coated glass

was understood and overcome. Chapter 4 reports the development of a new “liquid-ALD” technique as a less-energy-demanding alternative to conventional vapour-phase ALD. The morphology, crystal structure and possible in-situ doping of thin films and nano-tube arrays of TiO_2 deposited by the technique are discussed. Chapter 5 evaluates the potential of the nano-tube arrays in actual device application. Finally, Chapter 6 summarises the key achievements and conclusions thus far and proposes recommendations for follow-up investigations with preliminary groundwork detailed.

The reader is reminded that the solar cells described in this report refer to “excitonic” solar cells which operate *via* photo-induced exciton generation, dissociation and transport of free charges to the respective electrodes (Chapter 2). Although TiO_2 is also widely employed in DSSC, the mechanism and development of this class of devices is beyond the scope of this report.

CHAPTER 2 RECENT ADVANCES IN ORGANIC SOLAR CELLS – A REVIEW

2.1 Green, renewable solar energy

Harvesting electrical energy directly from sunlight using photovoltaic (PV) technology is a way to address and supplement the world's growing energy demands with a sustainable resource while minimizing detrimental effects on the environment fuelled by heavy consumption of fossil fuels. Global energy demand as of 2009 is estimated to be in excess of 10 Gtoe (gigatonne oil equivalent, 1 Gtoe is the amount of energy released when 1 gigatonne of crude oil is burnt) per year, and is expected to double to 21 Gtoe by the year 2030 in tandem with population increase. If environmental policies to reduce global fossil fuel consumption, integrate existing non-fossil fuel technologies (*e.g.* solar, wind and tidal energy) and hasten the development of new technologies are not urgently adopted, greenhouse CO₂ emissions are expected to increase by 3.1 % per annum over 2004 – 2030. By 2100, atmospheric CO₂ concentration levels of >900 ppm (currently >300 ppm) and global warming of 2.2 – 4.7°C could be anticipated.¹

PV technology presents the option of renewable power generation with zero emission. Studies show that the total yearly energy demand in the U.S. would be satisfied by a single land area of 100 km by 100 km in the Nevada or Arizona deserts (or places with high solar

insolation) covered with solar panels with power conversion efficiency (PCE) $\geq 15\%$.² Solar cells could in theory power the planet³, but at present, they account for less than 0.01 % of global energy demand.⁴ One major challenge towards widespread utilization of large-area PV modules is cost reduction. To compete with other means of power generation, production costs has to be lowered to 1 \$/peak Watt.⁵ Conventional Si based PV modules currently cost four times this amount. In addition, the energy payback time, *i.e.* the time taken for a device to generate as much energy as was put into fabricating it, should be reasonable.

2.2 Milestones in PV research

There are three main stages to the development of PV technology. The incumbent first-generation large-area single junction Si based modules still dominate $\sim 84\%$ of the total market share of solar cell types sold.⁵ These modules are capable of producing PCEs up to 23 %, approaching the theoretical Shockley-Queisser limit^{6, 7} of 31 %. However, high production costs are necessitated by high temperature ($>1000\text{ }^{\circ}\text{C}$) and high vacuum processes associated with the Czochralski growth (single crystal Si) and melt-casting (multi-crystal Si) techniques. Also, Si has an inherently low optical absorption coefficient as a result of its indirect energy band gap. The Si wafers need to be thicker than 200 μm in order to absorb sunlight effectively. Consequent PV panels are heavy, rigid and cumbersome.

The above factors propelled the development of second-generation devices² that involve materials such as amorphous Si, chalcogenides (CdS/CdTe) and chalcopyrites (CuInSe₂ (CIS), Cu(In, Ga)Se₂ (CIGS) that are deposited on both rigid (*e.g.* glass) and

flexible (*e.g.* plastics and thin metallic sheets) substrates *via* techniques that are less energy intensive (*e.g.* chemical vapor deposition (CVD), sublimation and electro deposition). For practical use however, the efficiencies of such devices (PCEs for amorphous and CIGS solar modules are 10.4 % and 13.4 % respectively) need to be improved further.

Third-generation PV technology^{2, 8-10} is relatively new and encompasses two concepts. IIIa which aims to achieve very high efficiencies surpassing the Shockley-Queisser limit of 31 % by exploring novel approaches such as multijunction tandem cell design and infrared energy harnessing is still in its infancy. The goal of IIIb is to improve the marketability of solar cells by targeting moderate efficiencies of 15-20 % while maintaining very low production costs. It is widely believed that organic solar cells (OPVs) could be capable of making a significant contribution in this category if their efficiencies and service lifetimes could be enhanced as the following section explains.

2.3 Widespread interests in organic solar cells

Since the demonstration of the first bi-layer single junction device (Fig. 2-3a) in 1986 (PCE of 1 %) ¹¹, there has been a slow but steady increase in the PCE of OPVs to the present 5 % ^{12, 13} (further increased to 7.4 % ¹⁴ and 7.9% (Solarmer Inc.) very recently) accompanied by intensifying interests in the area of research. The active organic semiconductor components that are responsible for light absorption and charge generation in a device are commonly categorized according to their molecular weight. Macromolecules with molecular weights >10,000 atomic mass unit (amu) are termed polymers while those less

than a few thousand amu are considered oligomers and/or small molecules. This distinction also dictates the methods by which each material can be processed – often, polymers (*e.g.* P3HT and MEH-PPV, Fig. 2-1) being soluble in many organic solvents are solution processed while small molecules (*e.g.* CuPc and C60) being insoluble, are sublimed. The key benefits of incorporating organic materials in PV devices are that they 1) are relatively inexpensive, 2) have a high optical absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$) (a 100 – 500 nm thick organic layer is sufficient to absorb incident light effectively)¹⁵, 3) are compatible with flexible plastic substrates making high throughput roll-to-roll processing possible, and 4) are soluble in a wide range of organic solvents or are sublimable at low temperatures (<400 °C) permitting lower-energy-consuming deposition techniques such as dip/spin-coating, doctor blading and screen/ink-jet printing, and vacuum sublimation respectively. Achieving PCEs practical for large-scale production and commercialization (15 – 20 %) and narrowing the disparity between the state-of-the-art efficiency (7.4 %) and the theoretical limit (31 %) requires concerted interdisciplinary research efforts focused on materials development, morphological control of the active constituents, device design and encapsulation to name a few. The potential of OPV technology has nevertheless been enough to warrant investments and start-up initiatives from industrial giants such as BASF, Bosch, Merck, Sharp, Shell, Mitsubishi, LG, Chevron and Exxon Mobil.

2.4 Working principles of OPVs

The ensuing sections explain the fundamental OPV photoconversion mechanisms. First it would be useful to understand how the electronic band structure (*i.e.* valence and

conduction bands and the band gap) originates from the structure of conjugated materials. Next the actual device structure, working principles *via* the energy band diagram and key device efficiency factors are detailed.

2.4.1 Materials perspective – conjugated materials as semiconductors

Conjugated materials (examples are provided in Fig. 2-1) are defined as molecules or polymers with a backbone composed of alternating single and double carbon-carbon bonds. Three in-plane σ -orbitals of the sp^2 hybridized atoms (mostly carbon and nitrogen) constitute their structural backbone: two are bonded to the neighboring atoms, the third to a side chain or atom. The fourth electron resides in the non-hybridized p_z -orbital perpendicular to the plane of the σ -orbitals. Overlap of p_z -orbitals on adjacent carbon atoms creates π bonds, which are delocalized over the length of the molecule. π -orbitals consist of lower-energy bonding π and higher-energy anti-bonding π^* states (Fig. 2-2). At ground state, the π (valence) state is filled while the π^* (conduction) state is empty. Addition of every new repeat unit to the conjugated system causes hybridization of the energy states yielding a collection of discrete states until a point where pseudo-continuous 3-D valence and conduction bands (analogous to those of inorganic semiconductors) rather than discrete energy levels are formed. The valence band-edge is known as the highest occupied molecular orbital (HOMO) while the conduction band-edge is the lowest unoccupied molecular orbital (LUMO). The energy gap (band gap) between the HOMO and LUMO decreases as the length of conjugation increases.

Figure 2-1

Examples of conjugated polymers and small molecules commonly employed in OPVs

Figure 2-2

A schematic energy level diagram showing the bonding (π) and anti-bonding orbitals (π^*) in a conjugated material at ground state. As the conjugation length increases, the number of discrete energy levels multiplies to a point where pseudo-continuous valence and conduction bands result.¹⁶

2.4.1.2*Photo-excitation in organic semiconductors*

Operation of a PV device relates to its ability to convert light energy to electrical energy. In an organic semiconductor, this translates to the absorption of a photon which promotes an electron from the HOMO to the LUMO leaving a hole in the HOMO. Contrary to inorganic semiconductors (where free electrons and holes are formed upon photo-excitation), the electrons and holes produced in their organic counterparts are electrostatically bound upon excitation. These electron-hole pairs bound by a Columbic energy of 0.1 – 1.4 eV are known as excitons.¹⁷⁻¹⁹ Excitons occur in organic semiconductors for two reasons. 1) The dielectric constant (*i.e.* the ability of a material to store charges) of organic semiconductors of $\epsilon = 4$ is low (compared to inorganic semiconductors where $\epsilon = 15$). Therefore, the Coulombic forces of attraction around electrons and holes extend over a greater volume. 2) The intermolecular Van der Waals interactions between organic molecules are weak compared to the strong interatomic covalent bonds in inorganic semiconductors. Consequently in organic semiconductors, the electron wavefunction is somewhat constrained causing it to be localized in the Coulomb well of its conjugate hole.^{20,}
²¹ Excitons are mobile, electrically neutral and at first approximation, unaffected by electric fields.

2.4.2 Device operation

The simplest device that promotes exciton formation, splitting and subsequent free charge generation, transport and collection is the bi-layer single-junction OPV (Fig. 2-3a). It is composed of a donor (material with low electron affinity, or electron rich) and an acceptor

(material with high electron affinity, or electron poor), sandwiched between a transparent-conductive (typically ITO or FTO- coated glass) and a low-work-function metal electrode (e.g. Al). Upon photon absorption, excitons that are generated diffuse towards the active interface (*i.e.* the interface between the donor and acceptor, or the heterojunction) where they are separated, driven by a drop in chemical potential energy (ϕ) across the interface (Fig. 2-3b). The energy offset ϕ between the LUMO levels of the donor and acceptor must be greater than the exciton binding energy (0.1 -1.4 eV) for exciton dissociation to occur. After dissociation, the electron-hole pairs, often still coulombically bound across the interface, are called “*geminate pairs*”. Complete charge separation and transport to the electrodes are driven in part by the built-in electric field resulting from the difference in Fermi energy levels of the respective electrodes and in part by diffusion (concentration of electrons and holes decreases with distance away from the active interface) – constituting drift and diffusion currents respectively. Finally the charges collected are channeled to power an external appliance (Fig. 2-3a).

Figure 2-3

a) An OPV device in typical bi-layer configuration. Absorption of a photon creates an exciton which diffuses towards the heterojunction between the donor and acceptor where it is separated by the energy offset ϕ in b). Transport of electrons to the cathode and electrons to the ITO anode is accomplished by both drift and diffusion. b) The corresponding MIM energy band diagram. The tilt in HOMO and LUMO energy levels of both donor and acceptor is responsible for drift current and is a result of the Fermi energy levels of the ITO and metal electrodes aligning in accordance to the MIM theory under short circuit (working) condition.

Organic solar cells are commonly characterized by measuring their current vs. voltage (I-V) characteristics under illumination from a solar simulator (a light source that replicates the solar spectrum), from which the key efficiency factors (Fig. 2-4) are extracted to compute their PCEs. Since organic semiconductors exhibit a very low intrinsic carrier concentration and are sufficiently thin (100 – 500 nm) in a device for charges to tunnel through from one electrode, the Metal-Insulator-Metal (MIM) model²² is typically adopted to explain the shape of the I-V curve (Fig. 2-5). For simplicity, a single organic layer sandwiched between ITO

(Fermi level ~ 4.7 eV) and a low-work-function Al cathode (Fermi level ~ 4.2 eV) is illustrated.

Figure 2-4

Schematic illuminated and dark current-voltage (I-V) curves typical of an organic solar cell. The intersections between the illuminated curve and the x- and y- axes give the open circuit voltage (V_{oc}) and short circuit current (I_{sc}) respectively. P_{max} , the maximum power output of the device is a product of the voltage (V_{mpp}) and current (I_{mpp}) at the maximum power point (*i.e.* the maximum area under the curve in the fourth quadrant of the graph). Dividing P_{max} by the product of V_{oc} and I_{sc} gives the fill factor (FF). The labels 1 to 4 correspond to those in Figure 2-5.

Figure 2-5

Schematic MIM energy diagrams corresponding to regions 1 to 4 in Figure 2-4 depicting the HOMO and LUMO levels of an organic semiconductor sandwiched between an ITO and an Al electrode. The direction of band tilting is similar under both illuminated and dark conditions (1 to 4 corresponding to 1' to 4'). Under illumination, the bands contain electron and holes resulting from excitation by absorbed photons. In the dark, photoexcited charges are absent, hence the bands are empty until forward bias condition where the charges are capable of overcoming the small injection energy barrier and contribute to a current.

The correlation between the characteristic I-V curve (Fig. 2-4) and the energy band diagrams (Fig. 2-5) explains how an OPV works under various operating conditions and is elaborated below (with the assumption that excitons are dissociated into free charges upon excitation such that they can move freely along the bands). In the energy diagram, the organic semiconductor is represented by its HOMO and LUMO levels while the ITO and metal electrodes are represented by their Fermi energy levels.

Under illumination

1) ***Short circuit or working condition (y-intercept):*** The current output at zero bias is known as the short circuit current (I_{sc}). Under short circuit condition in the dark, the potential difference between the Fermi levels of ITO and Al causes charges to tunnel through the organic layer from one electrode to the other until the Fermi levels are aligned and the potential difference is nullified. This results in band tilting (Fig. 2-5, 1 and 1') in accordance with the MIM band theory which creates a built-in electric field in the device. Under illumination, photo-excited electrons and holes are transported to the Al cathode and the ITO anode respectively, driven by the built-in field and the device functions as a solar cell. By convention, I_{sc} is a negative value because the photo-current flows in a direction opposite (*i.e.* away from the heterojunction) to that of the injected current.

2) ***Open-circuit or flat-band condition (x-intercept):*** A voltage corresponding to the open circuit voltage (V_{oc}) of the device is applied to the ITO electrode. This drives the Fermi levels of the electrodes back to flat-band condition. In the absence of a built-in field, there is no incentive for photo-excited charges to flow. Therefore, there is no current output from the device. Electron-hole pairs recombine either radiatively or non-radiatively.

3) **Reverse bias ($V < 0$):** A negative voltage that is applied to the ITO electrode pushes its Fermi level up towards vacuum, increasing band tilting. Photo-excited charges drift under the electric field to their respective electrodes. The field is higher than in (1) and the current generated is consequently higher. Under reverse bias, the device operates as a photodetector.

4) **Forward bias ($V > V_{oc}$):** When a positive bias is applied to the ITO electrode, its Fermi level is brought further away from vacuum. The bands tilt in a direction opposite to (1) and (3). If the bias is larger than V_{oc} , the bands tilt further to the extent that electrons are injected directly from the low-work-function Al to the LUMO and holes from the high-work-function ITO to the HOMO. If these injected charges recombine radiatively, the device functions as an organic light-emitting diode (OLED).

In the dark

The behavior of the energy bands of an OPV in the dark is largely similar to that under illumination, with a few exceptions. Under all conditions (1' to 4'), photo-excitation does not occur and hence photo-excited electrons and holes do not exist. Only injected charges are of importance. When biased in the reversed direction (3'), only a very small injected dark current can flow due to the large injection barrier between the ITO and the LUMO and Al and the HOMO. When the forward bias is large enough, spontaneous injection of electrons from Al to the LUMO and holes from the ITO to the LUMO occurs (similar to 4), giving rise to a large surge in current (4')

The power conversion efficiency (PCE) of a solar cell is the ratio of the electrical power generated by the device to the incident power input from a light source. It is calculated from the 4th quadrant of the I-V curve (Fig. 2-4) as follows:

$$PCE = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} ; \quad FF = \frac{I_{mpp} \times V_{mpp}}{I_{sc} \times V_{oc}}$$

V_{oc} , I_{sc} and FF are the open circuit voltage, the short circuit current and the fill factor respectively. Enhancing these 3 factors would enhance the PCE. I_{mpp} and V_{mpp} are the current and voltage at the maximum power point. P_{in} is the power density of incident light. To satisfy international test standards, P_{in} is commonly standardized at 100 mW/cm² with a spectral output matching that of the actual solar insolation when the sun is incident on the earth's surface at a zenith angle of 48.2°. At this angle, incident sunlight passes through 1.5 times the thickness of the earth's atmosphere. Taking into account both direct and diffused (global reflections off terrestrial objects) contributions, this incident light is termed air mass 1.5 Global (AM 1.5G) illumination. A solar simulator that provides AM 1.5G illumination in a laboratory has filters installed to convert white light from the arc lamp to the desired AM 1.5G output. Since no man-made solar simulator is perfect, a number of mathematical and experimental procedures to address any mismatch between simulated and actual terrestrial AM 1.5G illuminations have become available.^{23, 24} These allow for a more accurate determination of the V_{oc} , I_{sc} , FF and ultimately the PCE of a device.

2.4.3 The key efficiency factors

2.4.3.1 Open circuit voltage

While it is widely accepted that the maximum achievable V_{oc} of a heterojunction device can be estimated from the effective electronic band gap of the D-A system (*i.e.* the energy difference between the LUMO of the acceptor and the HOMO of the donor, Fig. 2-

6a),²⁵⁻²⁷ the origin of the Voc is still under debate and has been found experimentally to vary with factors such as choice of active materials, choice of contact electrodes and also material-electrode interactions. For instance, the dependence of the Voc of polymer: C60-PCBM blend-based devices (prominent in the field for their state-of-the-art PCE (7.4 %), Section 2.5.3) on device structure has been studied extensively. Assuming *ohmic* contacts between the donor and ITO and, the acceptor and the cathode respectively (Fig. 2-6a),^{25, 28-30} the Voc is the effective band gap between the polymer and PCBM. In the case of *non-ohmic* contacts, the Voc is governed by the difference in Fermi levels of the electrodes (similar to the MIM model) provided the levels are within the band gap but are sufficiently far away from the HOMO and LUMO levels of the active layer (Fig. 2-6b). In theory, common cathodes such as Al (4.2 eV) and Ca (2.9 eV) do not form ohmic contacts with PCBM (3.7 eV). However, due to the proximity of the energy levels, the Fermi level of the cathode becomes pinned to the LUMO of PCBM, resulting in an ohmic contact. Assuming ohmic contact at the anode, the Voc is estimated by the effective band gap model instead of the MIM model. Other than proximity of energy levels, Fermi energy pinning is also known to occur due to dipole interactions at the metal-material interface. Au (5.1 eV) for example has a strong interfacial dipole and is prone to pinning despite its Fermi level being far away from the LUMO of PCBM.³⁰ Pd which shares the same work function (5.1 eV) has a much weaker dipole and is thus unaffected. The above findings suggest that the Voc varies with material-electrode combination and interaction. The Voc should therefore be ascertained experimentally for individual materials systems rather than deduced intuitively from theoretical energy band diagrams.

2.4.3.2 Short circuit current

The short circuit current output of a device is a function of the absorption efficiency of the active material(s), the efficiency of exciton dissociation at the active interface and the efficiency of charge collection at the electrodes. Although the optical absorption coefficient of organic semiconductors is very high ($\sim 10^5 \text{ cm}^{-1}$), their absorption band gap (typically $\geq 1.9 \text{ eV}$ for common absorbers such as P3HT and the poly-phenylene-vinylenes) often does not match the wavelength of maximum terrestrial photon flux at around $1.6 - 1.8 \text{ eV}$ ($\sim 800 \text{ nm}$).³¹ Furthermore a device is composed of photoactive materials of various refractive indices sandwiched between ITO and a reflective metal electrode (Fig. 2-3a). Such configuration results in constructive and destructive optical interference patterns within the device. Careful optimization of layer thicknesses to concentrate incident optical field maximas within the active region and thus maximize the absorption of incident photons is required.³²⁻³⁶

Figure 2-6

Schematic energy band diagrams showing a) ohmic and b) non-ohmic contacts between the active materials and their respective electrodes. For devices with ohmic contacts, the V_{oc} is estimated from the effective band gap which is the energy difference between the HOMO of the donor and LUMO of the acceptor. Pinning (indicated by the broken lines and small arrows) is likely to occur when the Fermi level of the cathode is in close proximity to the LUMO of the acceptor. For devices with non-ohmic contacts, the V_{oc} is the difference in Fermi levels of the cathode and anode.

Efficient dissociation of excitons into free electrons and holes can also enhance the I_{sc} of a device. This requires the interplay of factors including an optimized D-A interface and morphological control to prevent *geminate* recombination. Upon dissociation, free electrons and holes must be successfully channeled to their respective electrodes in order to contribute to the I_{sc} . Transport relies on the availability and dependability of charge percolation pathways to the electrodes as well as on the charge mobility of the photoactive materials. The charge mobility observed in organic semiconductors (champion hole mobilities (μ_h) are about $15 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for single crystals of small molecules³⁷ and $0.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for liquid crystalline polymers³⁸ while the highest electron mobility (μ_e) is about $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ^{39, 40}) is much lower than that of their Si counterpart ($\mu_h = 450 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_e = 1400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Since charge transport in organic semiconductors occurs *via* intermolecular hopping, the inherently low mobility could be alleviated by the design of molecules that improve on intermolecular (or inter-chain) π - π interactions (or π - π stacking). Several self-stacking polymers^{41, 42} and discotic materials⁴³⁻⁴⁵ have been synthesized for this purpose. The factors discussed above are expanded further in Section 2.6.1.

2.4.3.3 Fill factor

The fill factor of a device is a measure of its diode quality. It is influenced mainly by the series (R_s) and shunt (R_{sh}) resistances. R_s and R_{sh} are estimated from the inverse of the slope of the I-V curve near $V > V_{oc}$ and $V = 0$ respectively (Fig. 2-7). It is evident that the area under the 4th quadrant of the graph can be maximized by reducing R_s and increasing R_{sh} thereby maximizing the FF. R_s can be reduced by using an ITO electrode of lower sheet resistance and by reducing the thickness of the photoactive layer to a level that is not

excessively more than required for optimal photon absorption. R_{sh} can be increased by preventing “shorts” and shunt paths in the device (*i.e.* preventing holes and electrons from reaching the wrong electrodes, Fig. 2-10). Recent research shows a strong correlation between the metal-electrode-to-photoactive-layer adhesion and the FF. Gupta *et al.*⁴⁶ reported that metal electrodes that were deposited with a fast evaporation rate showed poor contact with the photoactive layer and manifested an “S”-shape curve in the 4th quadrant (Fig. 2-7), which limited the FF severely. When the evaporation rate was slowed, the metal-material contact and consequently the FF were enhanced.

Figure 2-7

I-V curves of various shapes and their effect on the FF of a device. The inverse of the gradients at $V > V_{oc}$ and $V = 0$ give R_s and R_{sh} respectively. Low R_s and high R_{sh} maximize the FF (solid line). Increased R_s and reduced R_{sh} reduce the FF (broken line). Recent research shows that poor contact between metal electrode and photoactive layer as a consequence of a fast metal deposition rate for example, manifests an “S”-shape curve (dotted line) that also reduces the FF.

2.4.3.4 Incident photon to converted electron efficiency (IPCE)

Another performance indicator commonly used to evaluate a device is its incident photon to converted electron efficiency (IPCE). IPCE measures the number of electrons extracted from the device under short circuit condition as a fraction of the number of photons incident on the device and can be calculated using the following formula:⁴⁷

$$IPCE = \frac{1240 I_{sc}}{\lambda P_{in}}$$

where λ [nm] is the wavelength of the incident photon, I_{sc} [$\mu\text{A}/\text{cm}^2$] is the photocurrent produced at that wavelength and P_{in} [W/m^2] is the incident power. IPCE is the *external* quantum efficiency of the device. Subtracting photon losses due to reflection from the ITO electrode or transmission through the device gives the *internal* quantum efficiency which is seldom used to discuss devices. IPCE provides information on the spectral response of a device, that is, the wavelength(s) or wavelength range(s) at which the photoactive material(s) absorbs and contributes to current output. This better elucidates the role of each material put into the device, for instance, if the material is both an absorber and charge transport medium (*e.g.* polythiophenes and PPVs) or just a charge transporter (*e.g.* C60 and PCBM, which absorb closer to the UV region) in the visible wavelength spectrum. Like I_{sc} , IPCE is dependent on photon absorption, exciton dissociation and transport of dissociated charges to the electrodes (Section 2.4.3.2).

2.5 The limits to device performance

From materials standpoint, there is a need for chemists to design and synthesize new conjugated systems with reduced band gaps (1.6 – 1.8 eV) in order to capture the majority of terrestrial photon flux (Section 2.4.3.2).⁴⁸⁻⁵⁰ A crucial requirement that has till recently been frequently neglected, is for the HOMO level to be simultaneously shifted further away from vacuum (≥ 5 eV) so as to reduce the material's ionization potential (or tendency to oxidize).⁵¹ Increasing the stability of a material in air increases the overall lifetime of a device and also reduces the need for additional encapsulation procedures. Furthermore, each synthesized donor or acceptor material should have a corresponding donor/acceptor with well-positioned HOMO-LUMO levels which when put together, would maximize the effective band gap or Voc (Fig. 2-6a) of the device.⁵² In view of the objectives set forth in this dissertation, the bulk of discussions in the ensuing sections will focus mainly on device architectural designs and their effects on device performance.

2.5.1 Loss mechanisms in OPVs

To reiterate, the operation of an OPV device relies on 4 primary processes: 1) absorption of photons, 2) exciton generation and migration to the active interface, 3) dissociation of excitons into free charges at the active interface and 4) transport of charges to their respective electrodes (Fig. 2-3a). Among these, the short lifetime of excitons has been identified as a major factor limiting device efficiency.^{53, 54} In most organic semiconductors, the distance over which excitons can travel before undergoing recombination (*i.e.* exciton diffusion length) is typically 3–10 nm. This implies that while excitons generated in close proximity (3–10 nm) to the active interface can be effectively dissociated, those located

further away have a lower probability of being harvested. The active volume of the device is thus limited to a very thin region close to the interface, which however is not enough to absorb incident solar irradiation efficiently. To overcome this limitation, researchers have turned to nano-structuring the active region of devices such that more D-A interfaces are available within the exciton diffusion length-scale for exciton dissociation (Fig. 2-8), giving rise to the “bulk heterojunction (BHJ)” class of devices (*i.e.* with heterojunctions distributed over the bulk of the active layer).

2.5.2 Milestones in device architectural design

Among the first BHJs to be engineered were the interpenetrating polymer-polymer blends. Yu *et al.*⁵⁵ and Halls *et al.*⁵⁶ independently inter-mixed a donor and an acceptor PPV derivative (MEH-PPV and a cyano-PPV respectively) and observed that the photoluminescence (PL) from each polymer was quenched. This indicated that photo-generated excitons were being dissociated into free charges rapidly and efficiently as a result of the increased area of contact between the 2 polymers. Further improvements involving better choice of polymer pairs and optimization of blend morphology *via* a lamination technique eventually resulted in solar cells with an EQE of 29 % at 500 nm and a PCE of 1.9 % under AM 1.5 illumination.⁵⁷

Figure 2-8

In a bi-layer configuration (a), a device suffers from low exciton dissociation efficiency as excitons created more than a diffusion length (3 – 10 nm) away from the donor-acceptor interface recombine before they can reach the interface. Several bulk heterojunction architectures have evolved to provide more interfaces within the exciton diffusion length-scale for better exciton harvest. These include b) inter-penetrating donor-acceptor networks, c) *n*-type inorganic nano-rods dispersed in polymer and d) polymer or polymer-blend nano-spheres assembled from micro-emulsions of polymer nano-particles.

The success of the interpenetrating polymer network spawned a series of other blends including mixtures of polymer and small molecule as well as those composed entirely of small molecules. Of these, blends of polymer (as donor) and C60 fullerene or its derivatives (small molecule, as acceptor) have been investigated extensively^{24, 47, 58-62}, spurred by the discovery of strong photoluminescence quenching and ultrafast photo-induced charge transfer⁶³⁻⁶⁶ from polymer to fullerene in the year 1992.⁶⁷ Optimization of processing conditions led to champion PCEs (AM 1.5) of 2.5 %⁶⁸ for MDMO-PPV (poly(2-methoxy-5-(3',7'-dimethyl-octyloxy-p-phenylene vinylene) : PCBM approaching 5 %^{12, 13} for P3HT : PCBM blends (Fig. 2-9). More significantly, the development of such blends first elucidated the unique dependence of blend nano-morphology (or D-A distribution and interaction) on

factors such as polymer-to-PCBM ratio, choice of solvent(s) and temperature annealing. The wealth of knowledge created revolutionized the way by which devices are fabricated today.

Blends of small molecules are achieved by co-subliming the donor and acceptor molecules from their respective sublimation boat sources in a thermal evaporator. The most successful small molecule networks are composed of C60 fullerene and copper (II) phthalocyanine (CuPc) and yield a PCE of 3.5 % (AM 1.5G).⁶⁹ A number of other interesting BHJ nano-structures tailored for better exciton harvest have also evolved. These include polymer or polymer-blend nano-spheres deposited from micro-emulsions of polymer nano-particles^{70, 71} and blends of polymer and cadmium selenide (CdSe) nanorod/tetrapod⁷²⁻⁷⁴ (Fig. 2-8). The progress in PCEs of several classes of solar cells is charted in Fig. 2-9. PCEs for various classes of dye-sensitized solar cells (conventional,⁷⁵⁻⁷⁸ solid-state⁷⁹⁻⁸² and quasi solid-state⁸³⁻⁸⁶) are included for the reader's interest although their working principles and development are beyond the scope of this thesis.

Although obvious improvements to exciton dissociation and device efficiencies have been realized, disordered BJHs suffer 2 main drawbacks from the architectural perspective. Firstly, in a disordered blend both the donor and acceptor molecules have access to the “wrong” electrode (*i.e.* donor contacts the metal cathode and acceptor contacts the ITO anode) resulting in shunt paths and reduced FF and Voc. Secondly, the non-continuous nature of the donor and acceptor domains leads to charge trapping such that even if free electrons and holes are efficiently generated, some cannot be transported to the electrodes. Bi-continuous charge percolation pathways to the electrodes are clearly required. Furthermore, the random

distribution of the donor and acceptor domains can result in incomplete photoluminescence (PL) quenching in areas where the donor is more than an exciton diffusion length away from an acceptor.

Figure 2-9

Progress in power conversion efficiency of various categories of excitonic and dyes-sensitized solar cells.

2.6 Ideal device geometry

A new device geometry (an ordered-BHJ) that addresses some of the above problems was proposed. First formalized in the year 2004,⁸⁷ the ideal architecture ensures most excitons are created within a diffusion length of a heterojunction and provides straight pathways to the electrodes to minimize charge transport time and the probability of back electron transfer (Fig. 2-10). The design allows for a tunable optical absorption length,

without compromising the exciton diffusion length and dissociation efficiency. In addition, the availability of electron- and hole-blocking layers prevents charge leakage and maximizes the shunt resistance (and thus V_{oc} and FF) of the device. Although more difficult to fabricate than disordered blends, ordered architectures could alleviate problems associated with charge recombination and low charge carrier mobility and result in devices with improved efficiency.

Figure 2-10

Design of an ideal ordered-BHJ device in which heterojunctions are readily available within the exciton diffusion length-scale for charge transfer and direct pathways to the electrodes are expected to facilitate charge transport and reduce the chances of back recombination.

2.6.1 Research efforts in all-organic solar cells

Research efforts towards all-organic blends with inter-digitated donor and acceptor domains have centered largely on self-ordering approaches. Arias *et al.*⁸⁸ showed that the use of viscous blend solutions (in isodurene) and slower evaporation rates after spin coating promoted vertical segregation in blends of poly(9,9'-dioctylfluorene-ci-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine (PFB, donor) and poly(9,9'-

octylfluorene-co-benzothiadiazole) (F8BT, acceptor). IPCEs of up to 14 %, 10 times higher than that of disordered BHJs were achieved as a result of enhanced charged transport. Sun *et al.*^{89, 90} proposed devices based on bridged D-A block copolymers that could in theory self-order into useful “secondary” and “ternary” geometries (Fig. 2-11a). The synthesis of discotic small molecules that self-stack forming columnar liquid crystalline structures has been highlighted as a promising route to highly efficient solar cells (Fig. 2-11b).⁹¹ However, the lack of homeotropic alignment (which impedes charge transport) and the extent of D-A phase separation with respect to the exciton diffusion length-scale have been identified as potential difficulties in this approach. More recently, several nano-patterning techniques such as nano-imprint lithography (500 – 700 nm period grating)⁹² and fabrication of nano-rods of photoactive polymers (diameter ~ 55 nm, height ~ 70 nm) by depositing into nanoporous templates⁹³ have evolved for better control over D-A separation and domain sizes. Although conceptually simple, further reduction in domain sizes for better exciton harvest is required and is technologically challenging. Also, there is a risk that if the acceptor material is solution-deposited onto the nano-patterned donor film, the solvent involved could destroy the nano-patterns or distort the active D-A interface. This could limit solvent choice and the methods by which the acceptor material can be deposited.

2.6.2 Hybrid organic-inorganic solar cells - why involve inorganic materials

An interesting development in the ideal ordered-BHJ system stems from replacing the organic acceptor material with an *n*-type inorganic semiconductor constituting hybrid organic-inorganic solar cells. Metal oxides such as ZnO and TiO₂ have been particularly

popular due to their transparency, high electron mobility and ease of processing. Other advantages of incorporating metal oxides are discussed below:

1) Mechanical stability – metal oxide films and nano-structures (*e.g.* nano-wire, nano-tube arrays) function as mechanically robust scaffolds for subsequent deposition/infiltration of polymer/small molecule. The active D-A interface is well-defined and remains so throughout the device fabrication process.

Figure 2-11

Self-assembly approaches towards all-organic inter-digitated donor and acceptor domains that involve

- self-ordering of bridge-donor-bridge-acceptor block copolymers forming stacked and columnar structures
- homeotropic alignment of donor and acceptor discotic small molecules resulting in alternating donor and acceptor columnar domains.

2) Electronic band structure matches that of most organic semiconductors – the conduction (LUMO) and valence (HOMO) band edges positioned at *ca.* 4.2 and 7.4 eV⁹⁴ respectively mean ZnO and TiO₂ are capable of accepting electrons from virtually all organic semiconductors.

3) Doping is possible – the HOMO and LUMO levels of metal oxides can be adjusted by doping. Mg doping for example, has been shown to shift the conduction band edge of ZnO towards vacuum, thereby increasing its band gap.²⁵ The increased band gap of ZnO translates to a larger effective band gap (Fig.2-6a) and consequently larger Voc and PCE in a device. Doping with Cd, S and N^{25, 95-97} on the other hand reduces the band gap of metal oxides and increases their photo-activity under visible light (pristine ZnO and TiO₂ absorb UV light). The enhanced absorption of visible light implies that these metal oxides not only accept and transport electrons, but also actively participate in photon absorption and contribute to exciton formation and charge generation.

4) The active interface between donor and metal oxide can be modified – the surface of TiO₂ in particular, provides an abundance of reactive sites for molecular attachment. Goh *et al.*⁹⁸ reported a band edge shift in TiO₂ films functionalized with a series of benzoic acid and substituted benzene carboxylic acid moieties resulting in a change in Voc. Interestingly, an increase in the exciton diffusion length (and hence lifetime) was observed in P3HT films deposited on certain surface-modified TiO₂ compared to pristine TiO₂. Lin *et al.*⁹⁹ reported enhanced Jsc, FF and PCE in anthracene-carboxylic-acid (ACA) functionalized TiO₂ nano-rods dispersed in P3HT over pristine nano-rods. The improvements to device performance was attributed to the ACA molecule 1) mediating charge transfer at the interface, 2) acting as a barrier preventing back electron recombination and, or 3) enhancing the interaction

between TiO₂ and P3HT as a result of better compatibility between the benzene and thiophene rings of ACA and P3HT respectively. The exact origin requires further investigation. Conversely the surface of polymer and small molecule films are difficult to modify due to the lack of anchoring sites.

2.6.3 Reported metal oxide nano-tube/ -rod based devices

Among the first devices based on ordered arrays of metal oxide nano-structures to be demonstrated were those composed of a) ZnO nano-rods and P3HT¹⁰⁰, b) TiO₂ nano-rods and MEH-PPV¹⁰¹ and c) TiO₂ nano-tubes and a blend of P3HT and PCBM¹⁰² respectively (Table 2-1). The key factor limiting the performance of device types a) and b) as proposed by the authors was the large inter-rod spacing leading to poor exciton dissociation efficiency. Also, the extra surface areas for charge separation and direct percolation pathways for charge transport provided by the TiO₂ nano-tube array in device type c) did not improve its efficiency further. Blends of P3HT and PCBM alone are already ~5 % efficient^{12, 13}.

Ordered arrays of TiO₂ nano-tubes protruding from substrates (the subject of interest) have conventionally been produced *via* hydrothermal growth¹⁰¹ and anodization of Ti.¹⁰³ While both are convenient single-step solution processes, hydrothermal growth offers little control over nano-tube/-rod dimensions, direction of growth (nano-rods/-tubes tend to branch out of the substrate in different directions) and spacing. TiO₂ nano-tubes resulting from anodizing Ti though vertically aligned are typically spaced very closely making it difficult to access and utilize the inter-tube surface areas. Also, the textured morphology of the nano-tube walls could impede subsequent infiltration of polymers or small molecules.

TABLE 2-1 Device characteristics of various metal oxide nano-rod/-tube arrays embedded in the donor material.

Device constituents	Jsc (mA/cm ²)	Voc (V)	FF	%PCE
P3HT and ZnO nano-rod array (by hydrothermal growth)	2.2	0.44	0.56	0.53
MEH-PPV and TiO ₂ nano-rod array (by hydrothermal growth)	0.95	0.88	0.47	0.39
P3HT:PCBM blend and TiO ₂ nano-tube array (by anodization of Ti)	12.4	0.64	0.51	4.1

2.6.4 Areas for further research

In order to achieve TiO₂ nano-tube arrays that are not only well-aligned and well-spaced but have tunable dimensions for systematic studies, we explore the use of nanoporous templates in directing the deposition of the arrays. Of the various templates available (*e.g.* track-etched polycarbonate^{104, 105} and block copolymer templates¹⁰⁶), the anodic alumina (AAO) template is highly favored and is also the material of our choice because the template formation process is straightforward and results in a high density of parallel pore channels (with tunable height and diameter) through which materials can be deposited.¹⁰⁷⁻¹¹² In general, the potential of metal oxide nano-structures fabricated *via* AAO-assisted deposition in hybrid solar cells as well as other opto-electronic applications remains largely unexplored due to the inability to stabilize the anodization of Al on ITO- and FTO- glass substrates.¹¹³ Reasons for the instability as well as means to overcome the problem require investigation

(Chapter 3). Furthermore, techniques to coat the AAO surfaces conformally with TiO_2 (generating TiO_2 nano-tubes after template removal) are currently limited to the conventional vapor-phase atomic layer deposition (ALD) process.^{111, 114} New and less energy-intensive solution-based deposition approaches could be useful to researchers who are interested in non-line-of-sight deposition of TiO_2 or other metal oxides films or nano-structures but have limited access to expensive ALD systems (Chapter 4). Finally, the device characteristics of resulting prototypes and more interestingly, the infiltration and orientation of the donor material in the nano-tube array as well as the charge transfer characteristics between donor and TiO_2 nano-tube await exploration (Chapter 5).

CHAPTER 3 FABRICATION OF STABLE AAO TEMPLATES ON ITO COATED GLASS ELECTRODE

3.1 Introduction

AAO templates prepared on transparent-conductive substrates such as ITO coated glass are especially useful for nano-material array syntheses for a variety of opto-electronic applications (*e.g.* in solar cell, photocatalytic and photonic devices).¹¹⁵⁻¹¹⁷ They are also a vital platform towards viable polymer/TiO₂ nano-tube based solar cell devices for this project. However, undesirable dissolution of ITO during the Al anodization process typically causes template delamination which has severely limited this research objective. Like many conductors (including Pt, Cu, and Ag), ITO undergoes undesirable dissolution and/or oxygen evolution reactions under typical anodization conditions,¹⁰⁸ resulting in the eventual delamination and destruction of the template. To date, only Chu *et al.*¹¹⁸ have successfully anodized Al on ITO coated glass. Their achievement could be attributed to the improved physical bonding of AAO to ITO as a result of depositing high-energy Al atoms on ITO coated glass by sputtering. However, sparks and gas evolution were reportedly observed as the anodization proceeded down to the Al/ITO interface due to isolated anodic dissolution of ITO.¹¹⁸⁻¹²⁰ Furthermore, if anodization was not terminated at the interval prescribed by the

authors,¹¹⁸⁻¹²⁰ the breakdown of ITO induced an increase in ITO sheet resistance to several thousands of ohms, which certainly would be detrimental to the performance of subsequent devices. Other researchers have attached free-standing AAO membranes on ITO using polymeric adhesives.^{121, 122} However, the use of insulating polymer inter-layers is undesirable, particularly in electronic applications, where they would hinder electrical charge transport.

This chapter describes the processing of stable AAO templates directly on ITO substrates without the aforementioned problems by utilizing an ultrathin (0.2 – 0.5 nm) adhesion/passivation layer of Ti between ITO and Al.¹¹³ The templates are robust and show excellent adhesion to ITO, while the pore channels are free of barrier layers (through connectivity to the ITO surface) after a pore widening procedure, making them highly suitable for subsequent nano-array synthesis. Precise Ti thickness control to <0.5 nm is critical, otherwise undesirably thick barrier layers at the bottom of the pore channels (Fig. 3-1c) would prevent pore connectivity to ITO. The complex correlation between the electrical conductivity of substrates and barrier layer formation is further elucidated in order to establish the criteria for successful barrier layer removal.

3.2 Principles of Al anodization

The anodization of aluminum and the mechanism of pore formation have been reported extensively.¹²³⁻¹²⁸ Briefly, when an Al-coated substrate (*e.g.*, Si, glass, Ti-coated substrates) is anodized opposite to an inert electrode (Fig. 3-1a) in the presence of acidic

electrolytes, the aluminum oxide formed at the anodizing front contains many surface irregularities where the electric field concentrates. This localized electric field enhances acidic dissolution of the oxide at the bottom of the pores while leaving the pore walls intact, resulting in pore formation (Fig. 3-1b). A thin inverted U-shaped barrier layer (with a void underneath) produced at the bottom of the pore channels¹²³ (Fig. 3-1c) is subsequently removed by immersion in dilute acid during which the pores are also enlarged.

Figure 3-1

Representation of the processes taking place during anodization (up to the Al-substrate interface) that result in pore formation. (a) Electric field E concentrates at the surface irregularities of the native aluminum oxide at the anodizing front. (b) Concentrated field enhances acidic dissolution of the oxide at the bottom of the pores, leading to pore channel formation. (c) A thin inverted-U shaped barrier layer is formed when anodization proceeds to and terminates at the substrate.

3.3 Experimental procedures

3.3.1 Template preparation on ITO coated glass

ITO coated glass substrates (with sheet resistance of $10.3 \Omega/\text{sq}$ obtained from Merck Display Technologies) were cleaned by:

- ultrasonicing in detergent (15 min), acetone (30 min), and IPA (30 min) respectively,
- drying with a stream of pressurized N_2 followed by
- cleaning in O_2 plasma for 5 min (10 sccm O_2 , RF power of 100W and pressure of 230 mTorr).

Pure Al (Super Conductor Materials 99.9999 %) films (100-200 nm thick) were deposited onto ITO coated glass by electron-beam evaporation (Edwards FL400) at a rate of 5 nm/s. Templates with Ti inter-layers of different thickness were prepared by evaporating 0.2-10 nm Ti (CERAC Specialty Inorganics 99.995 %) at a rate of 0.02-0.04 nm/s prior to Al evaporation without breaking chamber vacuum. AAO template formation involved:

- anodizing the Al coated substrates opposite to a platinum mesh counter electrode at 60 V in 0.3 M oxalic acid or 35 V in 0.2 M sulfuric acid, each maintained at 2 °C and,
- immersing the anodized films in 1 M (5 wt %) H_3PO_4 to adjust the pore diameter and simultaneously remove the barrier layer in a “pore widening treatment”.

3.3.2 Anodizing on other types of substrates

Several other types of semiconducting and insulating substrates with and without inter-layers (Table 3-1) were prepared to study the dependence of barrier layer formation on substrate conductivity. All substrates were cut to the same dimensions for fair comparison and were precleaned following procedures described above. TiO_2 layers on ITO coated glass

were spin coated from a solution produced from room temperature acid-catalyzed hydrolysis of titanium(IV) isopropoxide (TIP) in ethanol with a molar ratio of TIP/H₂O/ethanol/HNO₃ 1:1:50:0.2.¹²⁹ The films were then heated at 120 °C for 10 min, resulting in amorphous, insulating TiO₂, and/or annealed further at 500 °C for 2 h in air to obtain crystalline anatase, semiconducting TiO₂. Subsequently, the substrates described above were coated with Al and subjected to anodization.

TABLE 3-1 Details of the various insulation and semiconducting substrates and inter-layers prepared to compare barrier layer formation characteristics.

Substrate class	Details
Insulating	Plain glass
	50 nm amorphous TiO ₂ coated ITO coated glass
Semiconducting	Silicon wafer (p-type, [100]))
	50 nm anatase TiO ₂ coated ITO coated glass

3.3.3 Electrochemical deposition of Ni nano-rods in AAO templates prepared on ITO

To demonstrate that the AAO templates created were resilient enough to support subsequent deposition of nano-material arrays, Ni nano-rods were electrochemically deposited through the AAO template onto ITO coated glass by cathodically polarizing ITO at -0.75 V opposite a platinum mesh counter electrode in a standard three-electrode setup and a commercial Ni plating solution (Hiap Guan Electro-plating Materials). The estimated

deposition rate was *ca.* 10 nm/min. Hence the deposition was stopped just before the nano-rods overfilled the templates and formed a blanket Ni layer. The AAO template was subsequently etched away in 0.1 M KOH to expose the embedded Ni nano-rod array.

3.3.4 Characterization

The current/voltage characteristics during anodization were monitored on a Sorensen power meter. Morphological characterization included:

- field emission scanning electron microscopy (FESEM, JEOL 6700F with working voltage and distance of 5 kV and 6 mm respectively) to study the structures of the AAO template, barrier layer, and Ni nano-rod array. Samples for cross-sectional imaging were prepared by scribing a line at the back of the substrate with a diamond tipped scribe and cleaving the substrate at that line to ensure a clean and even break. The cleaved sample was mounted on a SEM sample holder (in cross-sectional configuration) and had a thin layer of Au sputtered (15s on the Fision SC650 sputterer) prior to sample loading to prevent charging during imaging.
- atomic force microscopy (AFM, Digital Instrument's Nanoscope III) to investigate the surface morphology of the various substrates employed and measure film thickness.

Sheet resistance measurements (of ITO coated glass) were taken on the SYS-301 resistivity probing system, Signatone Corporation. X-ray photoelectron spectroscopy (XPS) analyses were conducted on the VG ESCALAB 220I-XL imaging system equipped with a monochromatic Al- α source.

3.4 Anodizing Al on ITO coated glass

3.4.1 Anodization characteristics and breakdown

Figure 3-2 shows chronoamperic curves recorded during the anodization of Al on bare ITO and on ITO coated with thin (10 nm) and ultrathin (0.3 nm) Ti inter-layers. The anodization of Al on bare ITO was stable within the first 30 s. However, as the anodizing front approached the Al-ITO interface (beyond 30 s), there was a sudden surge in current, accompanied by sparks, vigorous gas evolution, and template delamination resulting from the anodic breakdown of ITO. This phenomenon could be attributed to three main reasons:^{118, 125, 126} (1) inadequate adhesion between Al films deposited by thermal or electron beam evaporation on ITO; (2) compressive forces in the template due to volume expansion as Al is converted to Al_2O_3 , which further weaken the template-to-substrate adhesion; and (3) inevitable pinhole defects that are either present intrinsically or are formed during anodization, through which the electrolyte diffuses to the ITO surface, causing localized anodic dissolution of ITO. The breakdown is so vigorous that sparking occurs and gas bubbles produced break through the template, exposing small areas of bare ITO. The dissolution reaction escalates as more areas of ITO are exposed, causing eventual delamination of AAO from ITO.

Figure 3-2

Anodization behavior of Al (~120 nm) coated on various substrates as indicated.

3.4.2 Passivation using Ti inter-layer and consequent formation of thick barrier layers

Several measures to overcome the above breakdown and delamination issues have been evaluated. These include 1) smoothing the ITO surface by a short chemical etch in dilute HNO_3 or KOH , or mechanical scrubbing with clean-room fabric and IPA, and 2) chemically modifying the ITO surface with a monolayer of TiO_x (prepared by immersing the ITO substrate in an anhydrous 1M TiCl_4 /toluene solution for chemisorption and subsequently rinsing with IPA). None of the above measures proved useful, suggesting that neither the surface roughness of ITO nor surface functionalization were critical factors governing the adhesion between AAO and ITO. The use of suitable inter-layers to enhance passivation and

adhesion was therefore contemplated. In particular, Ti and Cr films¹³⁰ have proven excellent as adhesion layers due to their high reactivity and ability to form oxides, nitrides or carbides with the adjacent layers. In practice, both materials are specifically used to bond gold and silicon which otherwise have little chemical affinity.¹³⁰

When a 2-10 nm Ti inter-layer was employed in our work, the anodization current was noticeably stabilized (Fig. 3-2), allowing anodization to proceed smoothly down to the substrate (indicated by the current proceeding to zero at 90 s). Unexpectedly, thick ~60 nm barrier layers at the bottom of the AAO pore channels were observed (Fig. 3-3b) after anodization followed by a 45 min pore widening treatment. Since the pore wall and barrier layer are comparable in thickness, prolonged immersion in H_3PO_4 to dissolve the barrier layer also dissolved the template completely. Thick barrier layers are highly undesirable as they render subsequent electro-deposition of materials difficult, if not impossible, and prevent ohmic contact between materials deposited by other vapor or solution techniques and the substrate. The latter is most detrimental to subsequent device integration using such nano-arrays. The formation of thick barrier layers (often as thick as the pore walls) resulting from the use of Ti and other “valve” metals as adhesion layers has been reported in several other publications,^{131, 132} but to date, there have been no explanations for the observed phenomenon. A number of methods from literature to thin or eliminate the barrier layer were attempted without success. For instance, Liang *et al.*¹³³ obtained through-hole AAO membranes using reactive ion etching (RIE) to remove the barrier layer, while more recently, Crouse *et al.*¹³⁴ introduced an *in situ* barrier layer removal procedure that involved stepping

up the voltage at the end of the anodization process (for a materials system involving Si substrate coated with Pt, Ti, and Al, respectively). When adopted in our work, the RIE treatment tended to be unstable and reduced the total template thickness more than the barrier layer thickness, while the latter approach proved ineffective for our ITO/Ti/Al materials combination.

Figure 3-3

(a) A plan view FESEM image of AAO templates typically produced on ITO coated with 0.3 – 10 nm Ti. (b) The cross section shows thick ~60 nm barrier layers that remained after a 45 minute pore widening process when a 10 nm Ti layer was used. (c) The barrier layers are significantly thinner (~20 nm, after a 20 minute pore widening process) when an ultra-thin (0.3 nm) Ti was employed. (d) The barrier layers in (c) were removed completely after an additional pore widening duration of 25 minutes. All templates were produced by anodizing in 0.3M oxalic acid at 60V. (e) A small area where AAO had delaminated from the ITO (bottom right corner) is visible in a template anodized at 40V. Those produced at 60V were defect free (f and g). Templates without barrier layers (g) are more transparent than those with barrier layers (f).

3.4.3 Successful barrier layer removal

We have discovered that significantly thinner barrier layers on the order of 20 nm could be achieved after anodization if the thickness of Ti was reduced to the subnano-meter (0.2-0.5 nm) level. Figures 3-3c,d show that the thin 20 nm barrier layers following 20 min of pore widening were completely dissolved after a further 25 min immersion (*i.e.*, a total pore widening procedure of 45 min), resulting in pore channels that extended through to the

ITO. From AFM (Fig. 3-4b), it is apparent that the 0.2-0.5 nm Ti evaporated was not a continuous layer but composed of Ti islands (*ca.* 7-9 nm in diameter) dispersed across the ITO surface. The chronoamperic characteristics (Fig. 3-2) were stable with no evidence of anodic breakdown of ITO or delamination problems. In addition, the anodization process did not deteriorate the electrical properties of ITO. For example, the ITO sheet resistance of 13.6 Ω/sq measured after anodization and template removal (by immersing in 0.1 M KOH for an hour) was marginally increased over that of a pristine ITO substrate (10.3 Ω/sq), compared to the sharp increase in resistance (by 2 orders of magnitude, if the anodization duration was not carefully controlled) reported elsewhere.¹²⁰ Ti appears to function remarkably as a passivation/ adhesion component, preventing direct contact between ITO and the electrolyte, which is vital to preventing anodic dissolution of ITO during anodization. To further demonstrate that the AAO templates are robust, show good adhesion to the ITO coated glass substrate, and are able to support subsequent growth of nano-material arrays, Ni was electrochemically deposited under DC bias into the templates with ITO as the working electrode using standard Ni plating apparatus. Straightforward electro-deposition under DC bias is a good indication that the AAO pore channels are unobstructed. We were unable to deposit Ni when templates with thick barrier layers (Fig. 3-3b) were employed. Figure 3-5a shows a plan view SEM image of a uniform array of Ni nano-rods after template removal, while the cross section (Fig. 3-5b) indicates that the nano-rods had overgrown the template slightly, resulting in a “nano-mushroom” array.

Figure 3-4

AFM morphology of (a) a blank ITO substrate and (b) an ITO substrate with 0.3 nm Ti evaporated.

The ultra-thin 0.3 nm Ti is not a continuous layer, but is composed of small Ti islands.

Figure 3-5

(a) Plan and (b) corresponding cross-sectional FESEM image of Ni nano-rods protruding from the ITO.

The procedures prescribed for successful barrier-layer-free template formation on ITO coated glass are generally repeatable across the anodization voltage range recommended for the various electrolyte systems (*i.e.*, 25-40 V for 0.2 M sulfuric acid and 40-80 V for 0.3 M oxalic acid). However, we propose the application of voltages that approach the upper limits of those voltage ranges. Small areas where the template had delaminated slightly from ITO were occasionally observed in templates produced using lower voltages (Fig. 3-3e). The delaminations appear to have manifested from localized breakdown of ITO as a result of the electrolyte diffusing through pinhole defects in the Al film to the ITO during anodization.

Increasing the applied voltage accelerates the pore formation process while suppressing defect formation, thereby enhancing the integrity of templates produced (Fig. 3-3f,g). 60V for oxalic and 35 V for sulfuric acids have proven effective in this regard.

3.5 Factors governing barrier layer thickness, morphology, and its subsequent removal

To further understand why irremovable barrier layers were observed with thicker (2-10 nm) Ti adhesion layers as opposed to ultrathin (0.2-0.5 nm), we compared the anodization characteristics and corresponding morphologies of AAO templates fabricated from several insulating (plain microscope glass and ITO coated glass coated with 50 nm of amorphous TiO₂) and semiconducting (Si and ITO coated glass coated with 50 nm of anatase TiO₂) substrates and inter-layers (Table 1). Ti-coated ITO substrates were also categorized under the class of substrates with an insulating inter-layer (Section 3.5.1). For better comparison, all substrates were coated with the same thickness of Al and were anodized under the same conditions. Interestingly, insulating substrates and substrates having insulating inter-layers yielded templates with thick barrier layers (Fig. 3-3b and 3-6a,b), while those produced on semiconductors were barrier-layer-free (Fig. 3-6c,d) after pore widening. Contrary to expectation, the chronoamperic curves recorded from all four substrates (Fig. 3-7) were similar in magnitude and shape, with little obvious differences to explain the trends gathered from FESEM (Fig. 3-6). More in-depth studies (*e.g.*, using the three-electrode setup) may be required to elucidate any correlation between barrier layer formation and the anodization

characteristics. Nevertheless, the FESEM images clearly support our hypothesis that barrier layer formation and morphology are governed by the conductivity of the underlying substrate.

It is known that the barrier layers in AAO produced on substrates typically adopt an inverted U-shape. According to Crouse *et al.*,¹²³ the inverted morphology results from the dissolution of alumina located between the barrier layer and the substrate to form voids (Fig. 3-1c). The more the alumina dissolves, the larger the voids and the thinner the barrier layer. The dissolution of alumina is catalyzed by a localized electric field at the template-to-substrate interface. We postulate that during anodization, this local field, vital for barrier layer reduction, was significantly reduced (or was even nonexistent) when insulating substrates or insulating inter-layers were used. Consequently, glass substrates (Fig. 3-6a) as well as ITO coated with 50 nm amorphous TiO₂ (Fig. 3-6b) and 2-10 nm Ti (Fig. 3-3b) resulted in templates with thick barrier layers. It was also apparent that the morphology of the barrier layer ranges from void (Fig. 3-3b) to void free (Fig. 3-6b), depending on the thickness of the insulating inter-layer. For example, thicker insulating layers require higher electric fields necessary for alumina dissolution while concurrently avoiding void formation. In contrast, their semiconducting counterparts supported a field that was large enough for effective barrier layer thinning. As the resulting barrier layers were sufficiently thin, they were successfully removed during subsequent pore widening (Fig. 3-6c,d). The above arguments also explain why templates produced on ITO coated with 0.2-0.5 nm Ti were barrier-layer-free (after pore widening). Being ultrathin, the Ti inter-layer had little influence over the electric field needed for barrier layer reduction.

Figure 3-6

Cross-sectional FESEM images of AAO templates produced on semiconducting (a) plain glass and (b) amorphous TiO₂-coated ITO, and insulating (c) Si and (d) anatase TiO₂-coated ITO. The spin coated TiO₂ layers in (b) and (d) are indicated by the white arrows. Barrier layers are evident in (a) and (b). All templates underwent a 45 minute pore widening etch. All scale bars reflect 150nm.

Figure 3-7

Anodization behavior of Al (~200nm) coated on various insulating and semiconducting substrates and inter-layers. All curves have been arbitrarily shifted for clarity.

3.5.1 Nature of the Ti inter-layer after anodization

XPS analysis of the 10 nm Ti inter-layer after anodization and template removal revealed that the layer had been converted to TiO_2 during anodization (Fig. 3-8). This observation is in agreement with several other reports where researchers demonstrated the emergence of amorphous TiO_2 nano-pillars from the bottom of the pore channels as the anodization proceeded down to and surpassed the Al-Ti interface (in this case the Ti layer was much thicker at 200nm).¹³⁵⁻¹³⁷ The corresponding plan-view SEM image (inset of Fig. 3-8) shows an array of TiO_2 nano-dots that had been formed just below the pore bottoms which is similar to those published.¹³⁵ TiO_2 is known to be highly insulating in its amorphous

form, but becomes semiconducting when crystallized. Therefore, Ti-coated ITO substrates were also categorized under the class of substrates with an insulating (amorphous) inter-layer.

Figure 3-8

XPS analysis of a 10nm Ti layer that was converted to TiO_2 during anodization. The inset shows a corresponding plan-view SEM image of a TiO_2 nano-dot array that had been formed just below the pore bottoms, which tallies with reported observations (Fig. 3g of Ref. 134).

3.6 Chapter summary

We have identified and demonstrated two key elements that are essential to the formation of robust AAO templates on ITO substrates: (1) an ultrathin (~ 0.3 nm) Ti adhesion layer that effectively prevent destructive anodic breakdown of ITO; and (2) an anodization voltage higher than conventionally applied that reduced defects in the templates. The templates had barrier layers that were thin enough to be eliminated *via* the usual pore-widening procedure and were resilient enough to support subsequent growth of Ni nano-rods

on ITO *via* standard DC electro-deposition. The evaporated Ti should be carefully confined within the subnano-meter (0.2-0.5 nm) regime, where Ti islands rather than continuous Ti layers are formed. Otherwise, thicker Ti, which is converted to amorphous and insulating TiO₂ during anodization, would deplete the electric field required for barrier layer thinning during anodization. When AAO templates fabricated on a series of insulating and semiconducting substrates and inter-layers were compared, insulating substrates and inter-layers were found to produce thick impenetrable barrier layers. Conversely, semiconducting substrates supported a larger local field that allowed for successful thinning of the barrier layer. The results and relationships established herein clearly emphasize the need for careful substrate selection when template formation by Al anodization is involved. In cases where insulating substrates or inter-layers are required, other template-forming techniques (*e.g.*, lithography) could be more appropriate.

CHAPTER 4 TEMPLATE-DIRECTED “LIQUID-ALD”

GROWTH OF TiO₂ NANO-TUBE ARRAYS

4.1 Introduction

Well-ordered and vertically-aligned TiO₂ nano-tube arrays on substrates are highly sought after for photovoltaic^{102, 103}, sensor¹³⁸, and photocatalytic^{139, 140} applications primarily due to their directionality, high surface-to-volume ratios, and the ability to control their properties by varying nano-tube dimensions. Fabrication routes to such arrays can be broadly categorized into self-directed and template-assisted approaches. Although self-assembly (including anodization of Ti¹⁴¹ and hydrothermal growth procedures¹⁴²) provides a more direct means to the arrays, template-assisted approaches^{114, 119} could prove better for a more consistent control over nano-tube dimensions as well as inter-tube spacings, that are required in OPV application.

Atomic Layer Deposition (ALD) and sol-gel techniques are commonly used to deposit TiO₂ in AAO templates. ALD^{111, 114, 143-147} is a vapor phase non-line-of-sight technique capable of producing highly conformal coatings even on substrates with complex features. However, like many vapor deposition techniques, ALD generally requires

expensive equipment and high running costs incurred for vacuum conditions. To avoid contamination issues, ALD systems are often dedicated to just a handful of deposition materials. Hence, the choice of precursor, oxidant and temperature is restricted. The sol-gel approach is an attractive wet processing technique that provides wide area film coverage with simple and inexpensive apparatus. Chu, *et al.*¹¹⁹ produced TiO₂ nano-tube arrays by immersing the templates (prepared on indium-tin-oxide (ITO)-glass) in TiO₂ sol for several minutes to fill the pore channels with sol particles. Although straightforward, the segregation of large gel particles during sol-gel transition and removal of large amounts of organic solvents during annealing often lead to high shrinkage, rendering conformal and crack-free nano-tubes difficult¹⁴⁸. Problems such as poor tube-to-substrate adhesion and variation in particle sizes over the height of the tubes were also identified¹¹⁹. Kunitake *et al.* developed a surface sol-gel (SSG) process^{149, 150} that has found several interesting applications such as nano-precision replication of natural objects,^{151, 152} creation of defect-free dielectric films¹⁴⁸ and more recently, replication of AAO through-hole membranes creating unsupported TiO₂/polymer composite nano-tubings in which a polymer was used as a binder to enhance mechanical properties.¹⁵³ Notably however, ALD has often been the choice technique to deposit TiO₂ nano-tube arrays on substrates for reasons discussed above. Therefore, a more versatile and scalable method for nano-tube array deposition could be desirable in proliferating the study of their materials properties and the exploration of their potential applications.

Liquid-phase procedures that confer ALD-like conformal metal oxide coatings and yet circumvent the use of vacuum systems should bring significant benefits to the research

community. In this work, we demonstrate the deposition of well-aligned TiO₂ nano-tube arrays extending from Si and ITO-glass substrates by precise “liquid-ALD (LALD)”¹⁵⁴ replication (Fig. 4-1a) of AAO templates fabricated directly on the substrates. We term our procedure “liquid-ALD” for we find the deposition rates and resulting films and nano-structures produced are strikingly similar to those from conventional gas-phase ALD, unachievable via sol-gel processes. Our intention is to develop a new facile LALD process that has the advantages of being more flexible, versatile, automatable and scalable. We show that the rate of deposition has a direct influence on thin film morphology which also dictates the ability to control the thickness and roughness of the nano-tube walls. There are additional challenges in order to achieve uniform LALD deposition inside the nano-channels of the AAO templates on substrate where the bottom ends are closed. Furthermore, we demonstrate the possibility of doping of TiO₂ films and nano-tubes by incorporating vanadia (V) oxytripropoxide (VTP, 98% Aldrich) during LALD assembly. Doping alters the band gap and optical absorption wavelength range of TiO₂ films^{95, 96} and nano-tube arrays, making them useful in optoelectronic applications requiring deeper-UV or visible-light absorption properties.

Figure 4-1

Schematics of a) the sequential and repeated chemisorption/hydrolysis reactions in a typical LALD cycle and b) two routes to in-situ doping: on left - chemisorption in pre-mixed precursor solutions containing TIP and a different metal (M) alkoxide; on right - chemisorbing M alkoxide after every few TIP cycles. c) to f) Formation of TiO₂ nano-tubes by depositing in AAO templates prepared on substrates.

4.2 Experimental details

4.2.1 Preparation of substrates for TiO₂ deposition

AAO templates on Si and ITO coated glass substrates were fabricated by anodizing Al films on the substrates, following procedures prescribed in Section 3.3.1. While Al (150 nm to 300 nm)-coated Si wafers were obtained commercially from Evaporated Coatings, Inc., those on ITO coated glass were deposited by electron-beam evaporation (Section 3.3.1). The coated substrates were anodized opposite to a platinum mesh counter electrode in 0.3 M oxalic acid maintained at 2 °C, at voltages ranging from 40-60 V depending on the desired pore dimensions and spacing. They were then immersed in 1.0 M (5 wt%) H₃PO₄ for 30-75 min to remove the thin barrier layer at the bottom of the pore channels¹⁰⁹ and simultaneously adjust the pore diameter. Figure 4-5a shows a template on Si that had undergone a 40V anodization and a 30 min pore widening process, resulting in an average pore diameter of 60 – 70 nm and inter-pore centre-to-centre spacing of ~ 150nm.

The kinetics of LALD assembly was monitored by recording the frequency change on a quartz crystal microbalance (QCM) after each deposition cycle. Gold resonators for QCM studies were degreased in acetone, rinsed with de-ionized (DI) water, immersed in Piranha solution (H₂SO₄:H₂O₂ = 3:1 by volume) and rinsed again with DI water. After drying with a N₂ blowgun, the resonators were left overnight in mercaptoethanol (10 mM in toluene) to functionalize the gold surface with reactive hydroxyl groups (Fig. 4-1), rinsed with ethanol and dried with the N₂ blowgun again. TiO₂ films were also deposited on Si substrates for morphological studies by Atomic Force Microscopy (AFM). The Si substrates were cleaned

the same way as the gold resonators, but without the need for the mercaptoethanol functionalization step.

4.2.2 TiO₂ thin film and nano-tube array deposition

In a typical thin film deposition cycle, QCM resonators or Si substrates were immersed in 100 mM of TIP (97 % Aldrich) dissolved in anhydrous toluene for 3 min for the chemisorption reaction (Fig. 4-1a), followed by immediate sonication in isopropanol (IPA) to remove unreacted species. They were then immersed in de-ionized (DI) water for 1 min to effect hydrolysis of the chemisorbed propoxide groups and dried with a N₂ gun. The above steps were repeated to obtain the desired film thickness. All reactions were performed under ambient conditions. To minimize the effects of humidity on the experiment, fresh TIP-toluene precursor solutions were used after every 10 deposition cycles.

TiO₂ nano-tube arrays were formed by subjecting the AAO template (prepared on Si and ITO coated glass substrates, Fig. 4-1b) to the above chemisorption, rinsing and hydrolysis steps, with 3 adjustments:

- 1) the templates were sonicated lightly for the first 5 – 10 s of the 3 min chemisorption reaction,
- 2) hydrolysis was carried out under sonication in ethanol containing 10 % DI water by volume, and
- 3) the templates were heated at 90 °C for 5 min before the next deposition cycle.

The first modification expelled entrapped air and allowed TIP to access the confined AAO pore channels; the second ensured consistent water penetration and hydrolysis reaction in the

channels; while the third enhanced the removal of excess moisture from the templates. Before the template could be chemically etched away to reveal the embedded nano-tubes, it must be exposed by removing the over-layer of TiO_2 deposited on top of the AAO template (Fig. 4-1c). This was accomplished by a short reactive-ion etch using a gas mixture of 55 sccm CHF_3 and 5 sccm O_2 , RF power of 175 W and pressure of 55 mTorr in an Oxford Plasmalab®80Plus etcher. The AAO template was dissolved by immersing in aqueous 0.01M KOH for an hour (Fig. 4-1e) to leave behind the TiO_2 nano-tube arrays extending from the substrate surface.

4.2.3 TiO_2 nano-tube and thin film characterization

The TiO_2 nano-tube arrays were characterized by field-emission scanning electron microscopy (FESEM, JEOL 6700F) at an acceleration voltage of 5 kV. X-ray diffraction (XRD, Bruker General Area Detector Diffraction System (GADDs)) was performed to probe the crystal structure of the arrays. The GADDs system employs a $\text{Cu K}\alpha$ target and has a 2D detector that allows for simultaneous data collection of the user-defined 2θ range without sample or detector movement. Parameters employed for the scans were a voltage of 40kV, current of 40 mA, a 2θ angle range of $20 - 54^\circ$ and scan duration of 10 min. Individual nano-tubes were studied by a transmission electron microscope (TEM, JEOL 2010 LaB6, with point resolution of 1.9 Å and spherical aberration of 0.5 nm) operated at an acceleration voltage of 200 kV and filament current of 103 μA . Samples for TEM were prepared by gently scraping the substrates and dispersing the detached nano-tubes in ethanol by ultrasonication. The suspension was then dispensed drop-wise onto a TEM carbon grid and dried

for observation. QCM data was recorded on the Princeton Applied Research QCM 917 and AFM images (in tapping mode) were collected on Digital Instrument's Nanoscope III.

4.3 Results and discussions

4.3.1 Kinetics and morphology of LALD deposition

The kinetics of LALD deposition was monitored in real-time by subjecting a gold-coated QCM resonator to the sequential chemisorption/hydrolysis reactions. The thickness change (d) per deposition cycle was calculated using a derivative of the Sauerbrey equation,^{149, 150} where ΔF is the frequency change observed and ρ is the density of TiO_2 powder (typically 1.7 g/cm^3)^{149, 150}:

$$2d (\text{\AA}) = -\Delta F (\text{Hz}) / 1.83\rho (\text{g/cm}^3) \quad (1)$$

AFM images of thin films deposited on Si under similar experimental conditions were collected to correlate the rate of film growth to the resultant morphology. Immediate rinsing of substrates after chemisorption in TIP with minimal exposure to humidity resulted in an almost constant growth rate of $2.4 \text{ \AA/cycle}$ (evident from the linearity of the QCM trend in Fig. 4-2a), and rendered films that were smooth and particulate-free at the sub-nanometer scale (Fig. 4-2b). Conversely deliberate prolonged exposure to the ambient generated films of inferior morphology (Fig. 4-2c). While a stable (but higher, $7.9 \text{ \AA/cycle}$) growth rate (beyond 11 cycles, see arrow in Fig. 4-2a) could still be achieved, premature hydrolysis of excess reactants on the substrate resulted in the formation of large TiO_2 gel particles 15-20 nm in diameter across the substrate surface. Such observations suggest that with higher deposition rates, the deposition can no longer be considered a true ALD assembly but instead

approaches a typical sol-gel process. If translated to the nano-channels of the AAO template, premature hydrolysis would result in non-uniform nano-tube wall thickness, which becomes an issue especially in a regime where size-dependent effects on the tube electronic structure are observed.¹¹⁴ Moreover, the mass transport and loss of connectivity between the nano-particles during crystallization¹⁵⁵ become significant and could impede charge transport in subsequent opto-electronic devices. The achieved deposition rate of $2.4 \text{ \AA cycle}^{-1}$ suggests an ALD-precise deposition. TEM analysis on the nano-tubes leads to the same conclusion which is discussed in detail later.

Figure 4-2

a) QCM frequency shifts ($-\Delta F$) as a function of the number of LALD deposition cycles. b) and c) 3-dimensional AFM images of films deposited by 10 LALD cycles on Si substrates where b) is a conformal film deposited with minimum exposure to the ambient and c) is a film composed of particulates resulting from poor control over deposition conditions.

4.3.2 Optimizing the LALD process for nano-tube deposition

The deposition procedures employed on flat feature-less substrates had to be adjusted in order to ensure the repeatability of LALD in the confined AAO pore channels. The experimental variables that were critical to successful deposition of TiO₂ nano-tubes are summarised in Table 4-1. The concentration of the TIP-toluene solution and duration of immersion of templates for chemisorption to proceed, were not critical to the success of deposition. Concentrations of 0.01 M, 0.03 M and 100 mM and durations of 3, 5 and 10 min were each capable of producing nano-tubes. The 100 mM solution was notably less moisture-sensitive than its less concentrated counterparts when exposed to the atmosphere and was therefore employed for the rest of this study.

TABLE 4-1 Experimental variables and their effects on deposition.

Variables	Experimental Conditions	Criticality
Concentration of TIP-toluene solution	0.01M, 0.03M & 100mM	None observed
Duration of immersion in TIP-toluene solution for chemisorption	3, 5 & 10 minutes	None observed
Humidity	-	Critical
Rinsing solvent	Anhydrous toluene & IPA	Critical
Chemical composition of hydrolysis bath	Water (100 %) & 10 vol% water in ethanol	Critical

Ultrasonication in IPA following immersion in TIP was indispensable for array formation. This is because IPA dissolves both residual TIP as well as $\text{Ti}(\text{OH})_4$ precipitates, preventing the formation of TiO_2 over-layers (Fig. 4-3). Rinsing with anhydrous toluene (which is difficult to keep dry and does not dissolve away $\text{Ti}(\text{OH})_4$) increased the risk of over-layer formation.

Figure 4-3

Plan view FESEM image showing presence of TiO_2 over-layer.

The chemical composition of the hydrolysis bath was found to be an important variable influencing array formation. Given its high surface tension, it was practically impossible for pure water to penetrate all the pore channels of the template to hydrolyze the chemisorbed alkoxide even with the help of ultrasonication. This resulted in nano-tubes with varied wall thicknesses. Successful penetration saw the sequential deposition of tubes with thicker walls that were left standing on substrate after template removal. Tubes with thinner

walls (due to inconsistent water penetration and hydrolysis), were weak and broke off from the substrate, leaving behind empty spaces amid clusters of standing tubes (Fig. 4-4). Ethanol has a much lower surface tension than water and can penetrate the pore channels more easily. A mixed solvent system was therefore used to tune the surface tension of the hydrolyzing medium. It was found that the use of ethanol hydrated with 10 % water by volume for the hydrolysis step produced an array of tubes that was uniform across the substrate (Figure 4-5c,d).

Figure 4-4

Plan view SEM image showing non-uniform nano-tube array.

4.3.3 Morphology and crystal structure in LALD-derived TiO_2 nano-tube arrays

Fig. 4-5a,b show plan-view FESEM images of AAO templates on Si before and after deposition respectively. The pore openings are visibly smaller after deposition but remain clear of debris, demonstrating the non-line-of-sight capability of the LALD technique. Dense

and well-aligned arrays of nano-tubes become apparent after process optimization and template removal (Fig.4-5c,d). XPS scans (not shown here) indicated complete dissolution of AAO and also no traces of K^+ contamination from the KOH etchant. The nano-tube dimensions can be tuned, with most robust structures being 150 – 400 nm tall, 60-70 nm in diameter with 5 – 20 nm thick walls. Nano-tubes resulting from 30 deposition cycles have a wall thickness of ~ 5 nm (estimated from TEM), implying a deposition rate of approximately $1.6 \text{ \AA/cycle}$. This value is similar to those published for conventional ALD in AAO templates ($1.5 - 1.8 \text{ \AA cycle}^{-1}$).¹¹⁴ The TEM image at low magnification (Fig. 4-5e) shows that the nano-tube walls are relatively smooth, with no apparent segregation of large TiO_2 crystallites. The walls are also uniform in thickness along the length of the nano-tube. A cluster of nano-tubes with tube openings positioned parallel to the electron beam is shown in Fig. 4-5f.

Figure 4-5

Plan view FESEM images of the AAO template a) before and b) after LALD deposition. c) and d) show plan view images of TiO₂ nano-tube arrays on Si substrate after template removal. The nano-tubes are ~150 nm tall, with an outer diameter of ~60-70 nm and wall thickness of ~5 nm. d) A cluster of dislodged nano-tubes reveals the height of the tubes, the hollow tube channels and the closed nano-tube ends. e) and f)

Low-magnification TEM images showing e) the full height of a cluster of TiO₂ nano-tubes oriented perpendicular to the electron beam and f) a cluster of nano-tube openings positioned parallel to the beam.

While XRD results (Fig. 4-6i) suggest that the as-deposited nano-tubes are amorphous, we have discovered through closer inspection by high resolution TEM (at a suitably thin region near the nano-tube opening, Fig. 4-6a) that they were in fact of a “pseudo-crystalline” nature in which there was already some degree of molecular ordering. The corresponding selected area diffraction (SAD) pattern (Fig. 4-6b) is clearly different from that characteristic of a truly-amorphous TEM holey-carbon film (inset of Fig. 4-6b) and reveals faint traces of ring-like halos. The observed “pseudo-crystallinity” may be interpreted as evidence that LALD is indeed capable of producing molecularly-precise films *via* completely wet layer-by-layer assembly. The degree of crystallinity in the arrays was found to increase with increasing nano-tube wall thickness, in agreement with observations from the literature that crystallization in TiO_2 begins at a threshold thickness of 5 nm.¹⁵⁶ The XRD peaks and SAD ring pattern for nano-tubes with wall thickness < 5 nm (Fig. 4-6d and i) are poorly resolved with lattice fringes in small 2-3 nm domains that are barely detectable (see circled area in Fig. 4-6c). The crystallinity in nano-tubes with 10 nm walls was improved with obvious lattice fringes extending over the length of the nano-tubes (Fig. 4-6e). The lattice spacing of 3.5 Å corresponds to the distance between the primary anatase (101) crystal planes. Nano-tubes with ~20 nm walls were fully crystalline and resulted in distinct SAD spots as well as XRD peaks (Fig. 4-6h and i respectively). The lattice fringe images shown in Figures 3e and g indicate that single-crystal-like TiO_2 nanotubes were deposited. It is noted that the sol-gel derived TiO_2 is usually polycrystalline. Therefore, we believe the resultant single-crystal-like morphology should be a key attribute of LALD because such structure has not been reported in TiO_2 nano-structures prepared *via* sol-gel processes.

Figure 4-6

High resolution TEM images of a) a pristine nano-tube displaying “pseudo-crystallinity” and its corresponding SAD pattern in b). The degree of crystallinity increases with nano-tube wall thickness with lattice fringes becoming progressively more prominent from c) 5 nm to e) 10 nm and g) 20 nm thick walls. The SAD pattern also progresses from d) faint to f) distinct rings and finally h) distinct spots. The increase in crystallinity is also evident from XRD analysis shown in i).

4.3.4 Connectivity between nano-tube and substrate

For device application, the nano-tube array has to be electrically connected to the underlying ITO electrode. The conductive-AFM setup was used to examine this connectivity with the ITO electrode biased and the AFM receiving tip (Pt coated) grounded. The I-V measurement on a single LALD-derived TiO_2 nano-tube on ITO (Fig. 4-7) shows a sharp breakdown under negative bias (~ -0.5 V) and only a small current in the forward bias. Analysis of the corresponding energy band diagram (inset of Fig. 4-7) shows indeed that only a small negative bias needs to be applied for electrons to be injected into TiO_2 . On the contrary, a significant positive bias would have to be applied to cause a similar breakdown under forward bias. These observations provide evidence that the tube is well connected to ITO and also that it conducts only electrons (*i.e.* *n*-type behavior).

Figure 4-7

I-V curve of a single TiO_2 nano-tube on ITO coated glass recorded by conductive-AFM. The inset shows the corresponding energy band diagram of the configuration employed.

4.3.5 In-situ vanadia doping- preliminary findings

We expand further on the capabilities of the LALD technique by presenting preliminary evidence that doping of LALD-derived TiO_2 films and nano-tubes can be accomplished by incorporating vanadia (V) oxytripropoxide (VTP, 98 % Aldrich) during LALD assembly. To our knowledge, in-situ doping of films *via* liquid-phase layer-by-layer assembly has not been reported so far. We propose that doping can be achieved by 1) immersing substrates in pre-mixed precursor solutions of TIP containing various amounts of VTP dopant for chemisorption or 2) chemisorbing VTP after every few TIP cycles (Fig. 4-1b, right). The inset of Fig. 4-8 shows that films of vanadia can be deposited *via* the usual LALD procedures and that the rate of deposition is slower than for TiO_2 . Fig. 4-8 shows UV-vis absorption spectrum of films deposited *via* the latter approach where 3TV represents 3 layers of TIP followed by a layer of VTP and so forth. Clearly, the absorption wavelength range of V-doped films is broadened with red shifting of the absorption edge (and hence optical band gap) into the visible region. We postulate that the slight blue shift of the absorption peak at 300 nm from pure TiO_2 to doped films could be due to quantum effects originating from slight differences in the thickness of films deposited.¹¹⁴ Since the deposition rates of TIP and VTP are different, we could not achieve exactly the same thickness across all samples. Although distinctly different UV-vis spectra were recorded, the actual amount of doping and also the doping states could not be detected by XPS probably because the level of doping was lower than the detection limit of the XPS equipment. Thicker films have to be prepared or more VTP incorporated for more conclusive studies. Nevertheless, the doped films and nano-tubes prepared here are promising for photovoltaic and photocatalytic applications requiring visible light absorption. Further investigations to

elucidate the actual amount of doping and also the electronic properties (e.g. band structure and charge carrier mobility) of these materials are encouraged.

Figure 4-8

UV-vis absorption spectrum of LALD-derived pure TiO₂ and vanadia films prepared on glass substrates together with vanadia-doped (3TV, 4TV and 9TV) films. 3TV represents 3 layers of TIP before a layer of VTP and so forth. The red shift in absorption over pristine TiO₂ is evident in all doped films. The top inset compares QCM frequency shifts for LALD-assembled pure TiO₂ and vanadia films where the rate of deposition is slower for VTP.

4.4 Chapter summary

In summary, we have demonstrated the practical feasibility of a liquid ALD (LALD) technique in preparing robust arrays of TiO₂ nano-tubes extending from various substrates by the careful reaction of TiO₂ precursors on AAO templates. The process presents a facile,

Chapter 4

flexible automatable and scalable liquid-phase alternative to vapor phase ALD. The methodology can be readily extended to other metal oxide systems or desired materials combination as seen from the example of doping. The potential of LALD-derived TiO₂ nano-tube arrays in photovoltaic devices is explored in Chapter 5.

CHAPTER 5 MODEL PHOTOVOLTAIC DEVICES BASED ON P3HT AND ARRAYS OF TiO₂ NANO- TUBES

5.1 Introduction

In this chapter, the potential of LALD-derived arrays of TiO₂ nano-tubes as an electron acceptor and conductor in ordered-BHJ solar cells is explored. To reiterate, an ideal order-BHJ geometry⁸⁷ would provide sufficient D-A interfaces within the exciton diffusion length-scale (3 – 20 nm)^{54, 55} for dissociation of the majority of excitons generated and straight percolation pathways to the electrodes to prevent geminate recombination and minimize charge transport time. The advantages of incorporating nano-tube/wire arrays of an *n*-type inorganic semiconductor in place of the organic acceptor material have been discussed in Section 2.6. The devices presented in this chapter are known as inverted solar cells as the ITO and Ag electrodes operate in reverse polarity from the norm (Section 2.4.2) (*i.e.* ITO functions as cathode and Ag as anode).

Several research groups have demonstrated devices with arrays of TiO₂ or ZnO nano-wires embedded in P3HT or MEH-PPV that were 0.4 - 0.5 % efficient.^{101, 157, 158} The 3 to 4-fold improvement over benchmark bi-layered devices (fabricated from featureless TiO₂ films) was largely attributed to enhanced electron transport through the directional nano-wires.

However, the champion PCE (0.5 %) remains significantly lower than the current state-of-the-art (7.4 %)¹⁴ and also the theoretical limit (31 %).⁷ Suggestions for further improvements have been centered on engineering nano-array dimensions to better match the exciton diffusion length-scale of the donor material. This chapter discusses model devices composed of P3HT and LALD-derived TiO₂ nano-tube arrays. P3HT was chosen as the donor material mainly for its good solubility in common solvents, ability to orientate (π -stack) upon thermal treatment and the availability of polymer fractions of various molecular weights (from Rieke Metals and BASF) for systematic studies.

At this juncture, it may be interesting to the reader that the structure/dimension of the AAO/LALD -derived TiO₂ nano-array is correlated to that of the ideal case (Fig. 2-10) and preliminary speculation on how resulting devices may perform is discussed. Based on the literature, a theoretically ideal configuration which dissociates excitons efficiently may be perceived schematically as shown in Fig. 5-1a. The actual array dimensions adopted in this thesis (Fig. 4-7b, 5-4 and 5-6) were derived from optimized AAO template forming procedures (Chapter 3) and were slightly larger (Fig. 5-2b). Nevertheless, one must realize that the *ideal* working dimensions that allow for both efficient exciton dissociation as well as charge collection have yet to be fully established, otherwise resultant efficiency values would not be limited to just ~0.5 %. For example, it is widely assume in the literature that the large metal oxide inter-tube/rod spacing in ordered-BHJ devices is the root cause for the low efficiencies garnered. However, the work presented in this chapter offers and quantifies a different perspective, that the low efficiencies are likely due to P3HT coiling under nano-confinement, which results in an appreciable reduction in hole-mobility through the device.

The understanding established herein should provide insights into future design and materials selection for better-performing ordered nano-array BHJ solar cells.”

Figure 5-1

Ordering of nano-tubes (in plan view) in a) the ideal and b) experimental configurations.

5.2 Experimental procedures

5.2.1 Device fabrication and characterization

All device fabrication and testing procedures were carried out in an N₂ filled glovebox (MBraun). Procedures for the formation of stable AAO templates on ITO coated glass and for LALD were described in Chapters 3 and 4 respectively. The nano-tube arrays employed in devices were 150 nm tall, ~75 nm in outer diameter with 10 nm thick walls and spaced ~75 nm apart (wall-to-wall distance) (Fig. 5-4a and inset of 5-7a). The arrays were calcined in air at 500 °C for 2 hours to convert the amorphous as-deposited nano-tubes to the crystalline anatase phase. Subsequently, a layer of P3HT (molecular weight of 55 – 60k, Rieke Metals) was spin-coated on the arrays from chlorobenzene and an 80 nm layer of Ag

(the anode) was evaporated. The final device configuration (Fig. 2-10) also included a dense 40 nm hole-blocking TiO_2 layer between ITO coated glass and the arrays. The arrays remained robust, surviving P3HT spin coating and other device fabrication procedures (Fig. 5-4b and c). Both ITO coated glass and Ag electrodes were patterned to give pixel areas of ca. 0.14 cm^2 . Completed devices were annealed further at 100°C for 1 hour to improve the Ag-to-P3HT contact.

I-V characteristics of the devices were recorded on a Keithley 2400 sourcemeter as the devices were subjected to AM 1.5G simulated illumination from a KH Steuernagel solar simulator (channeled to the device through a quartz window in the glovebox). The intensity of the simulator was adjusted with an NREL AM 1.5G-calibrated Si photodiode to address any mismatch between the spectral output of the simulator and the true terrestrial AM 1.5G solar insolation.²³ For IPCE measurements, white light from a Newport-Oriel 150W Xenon lamp was focused into a Cornerstone 130 1/8m monochromator and the monochromatic output channeled into the glovebox and onto the device through an optic fibre. A mechanical chopper wheel was placed between the Xe lamp and monochromator to modulate the light in square pulses at 237 Hz and a Stanford Research 830 lock-in amplifier programmed to lock on to that frequency and measure the voltage signal due only to the monochromatic light.

5.2.2 Optical characterization

UV-vis absorption spectroscopy was carried out on the Shimadzu 2501-PC. PL quenching, conducted to study the charge transfer behavior between P3HT and TiO_2 , was measured on the Perkin-Elmer LS50B spectrofluorimeter.

5.2.3 Charge mobility studies by photo-CELIV

A technique known as photoinduced charge extraction by linearly increasing voltage (Photo-CELIV)^{159, 160} was employed to further understand the correlation between P3HT chain orientation and charge mobility.

5.2.3.1 The technique

Photo-CELIV is an emerging technique that can characterize charge mobility in a device in the μs to ms time-scale. It rivals time-of-flight (TOF) and field-effect transistor (FET) techniques because the device can be tested in its as-fabricated configuration and the mobility measured is in the direction of charge transport inherent to the device. In essence, free charges that are generated in a solar cell after excitation from a laser are extracted by linearly increasing voltage. Under normal operating conditions, photo-excited charges either undergo recombination at the D-A interface or are collected at their respective electrodes by the built-in potential (*i.e.* electrons to ITO coated glass and holes to Ag). In photo-CELIV, an offset bias (U_{offset} , Fig. 5-2) is applied to push the Fermi levels of the electrodes back to open-circuit condition (Fig. 5-10b inset) to ensure the photo-excited charges remain within the active region. A short triangular voltage pulse (*i.e.* linearly increasing voltage, Fig. 5-2) is then applied in *opposite polarity* (ITO and Ag to positive and negative terminals respectively) after a short time delay (t_{del}) to extract the charges before they undergo recombination. t_{del} is necessary to prevent extra contributions from the large initial flux of free charges (immediately after laser excitation) overwhelming the actual response of the device. The pulse sequence and schematic response of the technique are shown in Fig. 5-2. In the dark, the response is a square pulse (shaded gray in Fig. 5-2) and the plateau value

corresponds to the capacitive displacement current ($j(0)$) of the dielectric layer. The extraction current is negligible because the intrinsic charge carrier density is so small it cannot be detected. When excited by the laser, a hump (shaded blue) appears following the extraction of the extra laser-excited charges. The mobility of a device is computed using Fig. 5-2 and the equation:

$$\mu = \frac{3d^2}{At_{max}^2 (1 + 0.36 (\Delta j / j(0)))}$$

where d is the thickness of P3HT and $A = dU/dt$

5.2.3.2 The equipment

The devices were illuminated by a <5 ns pulse of laser (Litron Nd: YAG) of 532 nm wavelength. After a pre-set delay time (t_{del}), the triangular voltage pulse was applied by a digital function generator (Stanford Research DS 345). The delay time between laser illumination and onset of extraction was varied by a pulse generator (Stanford Research DG 535). The current transients were recorded by a digital oscilloscope (Agilent Infinium 1GHz) using a load resistance of 100Ω.

Figure 5-2

Schematic of the triangular voltage pulse and corresponding current transient response from a typical photo-CELIV experiment.

5.3 Results - Key findings from initial devices fabricated

We adopted the melt-infiltration technique (used by Coakley, *et al.* to fill P3HT into the channels of mesoporous TiO_2 ^{161, 162} and empty AAO templates¹⁶³) to promote filling of P3HT into the nano-tube arrays. Melt-infiltration involves depositing a layer of P3HT on the arrays and annealing at high temperatures (before metallization) to drive the polymer in under gravitational force. The PCEs of devices (with a 380 nm layer of P3HT) annealed at temperatures ranging from 100 – 220 °C for 10 min are summarized in Fig. 5-3. In agreement with observations from the literature, an annealing temperature of 200 °C resulted in devices with the highest efficiency. However, cross-sectional FESEM analyses (Fig. 5-

4b,c)) show that P3HT was only partially infiltrated and resided mostly on top of the arrays. The improvement to PCE could at best be attributed to better crystallinity and morphology and also more intimate contacts forming between P3HT and the top-end of the nano-tubes with increased annealing temperature. A number of modifications to device fabrication procedures were evaluated without further success to polymer filling. These include 1) prolonged annealing at 200 °C and 220 °C for up to 6 hours, 2) soaking the nano-tube arrays in pristine chlorobenzene and spinning dry prior to dispensing the P3HT solution, 3) dispensing and leaving the P3HT solution on the arrays for 1 min before spinning dry and 4) functionalizing the surface of the arrays with a monolayer of octyltrichlorosilane (OTS) to convert the super-hydrophilic nature of the nano-tubes to a hydrophobic one. OTS treatment was expected to improve the compatibility between P3HT and the nano-tubes (both now of hydrophobic nature). Nevertheless, arrays with partially-infiltrated P3HT were further explored for device fabrication to better understand their potential for energy conversion.

Figure 5-3

PCE of devices annealed (prior to metallization) at various temperatures to promote P3HT infiltration into the arrays. At temperatures above 160 °C, nano-tube-based devices begin to overtake the PCE of their bi-layered counterparts as a result of better contacts between P3HT and the nano-tubes forming. The error bars were collated from 20 devices.

Figure 5-4

a) The nano-tubes employed for device fabrication were 150 nm tall, ~75 nm in diameter, spaced ~75 nm apart (wall-to-wall), had a wall thickness of ~10 nm and were deposited on a 40 nm dense TiO₂ hole-blocking layer. Despite up to 6 hours of melt infiltration at 200 °C, P3HT failed to infiltrate fully into the array as the cross-sectional FESEM images in b) and c) show.

The I-V characteristics and key efficiency factors of devices with varied thicknesses of partially-infiltrated P3HT are presented in Fig. 5-5 and Table 5-1. As expected, the J_{sc} , FF and thus PCE improved with reduced P3HT thickness (adjusted by varying the concentration of P3HT in chlorobenzene and/or spin coating speed) in tandem with reduced series resistance in the device. More significantly, over all thicknesses of P3HT, the J_{sc}

resulting from nano-tube arrays was higher than those from benchmark bi-layered architectures based on featureless TiO₂ films (Table 5-1, within parentheses). Such result is encouraging for 2 reasons. Firstly, despite having approximately only half the D-A interfacial area of a bi-layered device (as estimated from FESEM images), the higher J_{sc} achieved demonstrates that the LALD-derived nano-tubes are superior to feature-less TiO₂ for electron transport. Secondly, the champion PCE of 0.3 % (with partially infiltrated P3HT) is already of the same order of magnitude as similar published devices (0.4 – 0.5 %),^{101, 158} where the authors claimed P3HT infiltration had not been an issue. The low overall efficiency values achieved for the batch of devices with P3HT partially filled (Fig. 5-3, 5-5 and Table 5-1) may be attributed to the small area of contact between P3HT and the nano-arrays. Consequently, the D-A interfacial area for exciton splitting is also much lower than it should be in the ideal situation (Fig. 2-10) where the donor and acceptor domains are interdigitated. Hence, it is anticipated that higher efficiencies (even surpassing those from the literature) could be realized by improving P3HT filling and maximizing the D-A interfacial area. Ideally, both the inner and outer walls of the nano-tubes should be fully utilized. We estimate (again from FESEM images) that the D-A interfacial area available in arrays with P3HT fully infiltrated would be 5 and 10 times that in their bi-layered and partially-infiltrated counterparts, respectively.

Figure 5-5

I-V curves of devices composed of TiO_2 nano-tube arrays with various amounts of P3HT deposited on top.

TABLE 5-1 Detailed efficiency factors of devices based on LALD-derived TiO₂ nano-tube arrays and benchmark featureless films (within parentheses)

P3HT thickness	Voc (V)	Jsc (mA/cm ²)	FF	%PCE
380 nm (40 mg/ml, 1000 rpm)	0.73 (0.73)	0.39 (0.27)	0.37 (0.45)	0.11 (0.089)
230 nm (40 mg/ml, 1500 rpm)	0.65 (0.77)	0.41 (0.21)	0.47 (0.35)	0.15 (0.057)
200 nm (40 mg/ml, 2000 rpm)	0.65 (0.65)	0.58 (0.39)	0.52 (0.56)	0.20 (0.14)
180 nm (30 mg/ml, 1000 rpm)	0.65 (0.65)	0.82 (0.40)	0.50 (0.54)	0.30 (0.14)

5.4 Devices with P3HT fully infiltrated

It became obvious that gravity alone was not enough to drive P3HT into the nano-tube arrays. To achieve infiltration, we subjected samples with partially infiltrated P3HT (Fig. 5-4b,c) to vacuum-assisted melt-infiltration in a vacuum oven programmed at 200 °C and 5 mBar for 8 hours, similar to the approach used by Baek *et al.* to fill P3HT into the pores of AAO templates.¹⁶⁴ P3HT is drawn into the arrays by capillary force as the applied vacuum removes air pockets from the unfilled arrays (arrows in Fig. 5-6a, left). Cross-sectional field-emission scanning electron microscopy (FESEM) confirms that P3HT filled both the nano-tube channels as well as the inter-tube spaces (Fig 5-5c).

Figure 5-6

a) Under vacuum-assisted melt-infiltration, P3HT is drawn into the arrays as the applied vacuum removes air from the arrays (black arrows). b) and c) are cross-sectional FESEM images showing P3HT partially-infiltration and complete infiltration respectively. The inset in c) shows in broken nano-tube in which the infiltrated P3HT is visible. All scale bars indicated 150 nm.

Contrary to expectation, devices with P3HT fully infiltrated were an order of magnitude less efficient despite the larger interfacial area available for exciton dissociation. The sharp reductions in J_{sc} and IPCE values suggest problems related to either exciton dissociation due to the larger nano-array spacing (Fig. 5-1) and/or charge transport to the electrodes. Despite the increase in D-A interfacial area and enhanced percolation pathways

conferred by the improved P3HT filling, such limitations would reduce the performance of a device significantly. Such factors were explored in Section 2.4.3.2.

Figure 5-7

a) I-V curves of devices fabricated with P3HT of various molecular weights, infiltrated and partially-infiltrated. The inset is a plan-view FESEM image the TiO₂ nano-tubes employed in the devices. b) Corresponding IPCE curves of the respective devices.

TABLE 5-2 Detailed efficiency factors of devices from Fig. 5-7 with values for the bi-layered device (with high Mw P3HT) within parentheses

Device description		V _{oc} (V)	J _{sc} (mA/cm ²)	FF	%PCE
High Mw P3HT (Rieke Metals 4002-E) Mw = 55 – 60k RR = 90-93%	Partially-infiltrated	0.51 (0.57)	0.82 (0.35)	0.43 (0.45)	0.20 (0.12)
	Infiltrated	0.53	0.20	0.45	0.05
Low Mw P3HT (BASF P200 Sepiolid) Mw = 21.3k RR = 98%	Partially-infiltrated	0.31	1.54	0.42	0.20
	Infiltrated	0.35	0.20	0.48	0.03

5.4.1 PL quenching – a study of charge transfer characteristics at the D-A interface

To determine the factor(s) responsible for the sharp decline in device performance, the charge transfer characteristics at the active interface were investigated by PL studies. It is evident from Fig. 5-8 that the PL from devices with P3HT infiltrated was quenched significantly (~90 %). Successful PL quenching is clear indication of a highly efficient charge separation process occurring at the interface. The remnant unquenched PL could be attributed to the ~25 nm P3HT over-layer that remained on top of the arrays after infiltration (necessary to prevent shorts in a device) as well as excitons generated inside the arrays that did not reach an interface in time to dissociate. Although higher efficiencies were obtained from devices with partially infiltrated P3HT (Table 5-2), the degree of PL quenching was significantly less (~60 %) than in those with P3HT infiltrated. These results imply that the interface between P3HT and LALD-deposited TiO₂ is ideal for charge transfer. Also the dimensions of the arrays (nano-tube diameter and inter-tube distance of ~75 nm), although larger than the exciton diffusion length-scale (3 – 20 nm), were not the key bottleneck limiting device performance.

Figure 5-8

PL spectra from the various devices as labeled.

5.4.2 UV-vis spectroscopy – elucidating the morphology of P3HT in devices

We next profiled the orientation of P3HT in the respective devices using UV-vis spectroscopy. In order to collect only data from P3HT confined in the arrays and reduce contributions from the over-layer, we deposited thinner P3HT layers (~90 nm from 10 mg/ml chlorobenzene solutions) on the arrays. Devices with P3HT infiltrated were short-circuited, further proof that little or no over-layer remained on top of the arrays. The absorption spectra of P3HT on the arrays were blue-shifted with respect to that of pristine P3HT (also annealed at 200 °C), with confined (*i.e.* infiltrated) P3HT exhibiting a larger blue-shift (Fig. 5-9, solid lines). The vibronic shoulders at 600, 550 and 525 nm were less prominent with infiltration. Such observations are characteristic of a rod-like-to-coil-like transition in the

P3HT chains.^{102, 161} The lack of conjugation and π - π inter-chain interactions in coiled P3HT would be detrimental to hole transport in a device (Section 2.6.1).

We have observed that the infiltrated P3HT chains were so tightly coiled that they were not amenable to further post-infiltration thermal annealing (between 220 °C to 250 °C) in attempts to uncoil and realign the chains (*i.e.* no further changes to device efficiency and efficiency factors). We have also fabricated and characterized devices with P3HT of lower molecular weight (Mw) and higher regio-regularity (RR) with the assumption that shorter polymer chains may crystallize better in the nano-tube arrays. However similar trends in device (Table 5-2) and UV-vis (Fig. 5-9, dashed curves) results were observed. We postulate that the chains employed in this lower Mw P3HT were still not short enough to prevent coiling and effect significantly better orientation. Nevertheless, the reduction in the extent of blue shift in lower Mw P3HT (dashed lines) compared to that of the higher Mw P3HT (solid lines, Fig. 5-9) suggests the degree of orientation from lower Mw chains has improved to some extent. However, we caution using P3HT of even lower Mw or derivatives of thiophene oligomers without first investigating their HOMO, LUMO and band gap values and their compatibility with TiO₂. It is evident from Fig. 5-9 that the lower Mw P3HT employed in this work has a smaller band gap than its higher Mw counterpart (*i.e.* dashed lines are more red shifted than solid lines) which inevitably leads to a smaller effective band gap (Fig. 2-6a), a lower Voc and a lower ultimate efficiency.

Figure 5-9

Normalized UV-vis spectra from the various devices as labeled.

5.4.3 Charge mobility studies by photo-CELIV

The photoinduced charge extraction by linearly increasing voltage (Photo-CELIV, described in Section 5.2.3) technique^{159, 160} was employed to elucidate the correlation between P3HT chain orientation and its resultant charge mobility. When the hump (following the extraction of the extra laser-excited charges, shaded blue in Fig. 5-2) is on a reasonably long time-scale of 10 - 100 μ s, it is convention to assign it to the hole-mobility in P3HT and assume the electrons in TiO_2 are extracted so fast that they do not show up on that time-scale. The hole-mobilities as well as illuminated and dark current transient responses of the respective devices are shown in Fig. 5-10a and b. As hypothesized, the efficiency of

devices with P3HT infiltrated into the arrays was limited largely by the poor hole-mobility in P3HT ($1.5 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, an order of magnitude lower than in other devices) as a result of the polymer chains coiling under nano-confinement (Fig. 5-9). The time taken to extract all photo-excited charges was >5 times longer ($>100 \mu\text{s}$) than for all other device (Fig. 5-10a, *i.e.* time taken for the curves to return to plateau condition). Hole-mobilities in bi-layered and partially infiltrated devices were slightly lower than in pristine P3HT probably due to slight differences in morphology at the P3HT-TiO₂ interface. For example, the blue-shift in UV-vis spectra for arrays with partially infiltrated P3HT indicates that the polymer chains directly adjacent to the arrays were more disordered than in a pristine P3HT film (Fig. 5-9). The low hole-mobilities inherent to bi-layered and partially infiltrated devices (7.9×10^{-5} and $7.3 \times 10^{-5} \text{ cm}^2/\text{Vs}$ respectively) probably also explain the low overall efficiency (the highest achieved thus far is 0.3 %).

Another interesting observation is the humps in the dark transients particularly for devices with P3HT infiltrated (Fig. 5-10b). As mentioned, the current transient in the dark is normally a hump-less square response. Such phenomenon may be explained as follows. The Ag-P3HT and ITO-TiO₂ contacts are slightly injecting¹⁶⁰ due to the proximity of their respective energy levels (*i.e.* Fermi level of Ag to HOMO of P3HT; Fermi level of ITO to LUMO of TiO₂), more so at the Ag-P3HT contact (inset of Fig. 5-10b). As a result, holes are being injected into P3HT and electrons to TiO₂ even in the dark. These injected charges migrate to the D-A interface where they are driven by the band energy offset to undergo recombination. Application of the linearly increasing voltage arrests and extracts these charges before they recombine. The dark extraction current is highest in devices with P3HT

infiltrated as the D-A interfacial area is the highest among all devices characterized. This is further proof that P3HT was well infiltrated and formed intimate D-A interfaces following our prescribed vacuum-assisted melt-infiltration procedures. A hump is also noticeable in bi-layered devices where the interfacial area is second highest. In contrast, humps did not manifest in pristine P3HT (where D-A interfaces do not exist) and in devices with partially infiltrated P3HT (where the interfacial area was significantly less). The time-scale of extraction is again longer in devices with P3HT infiltrated than in other devices due to the low hole-mobility as discussed before.

Figure 5-10

Experimental a) illuminated and b) dark responses from photo-CELIV experiments. The inset in b) shows the energy band diagram of a device under open-circuit condition.

5.5 Chapter summary

In summary, by using these model devices, we have investigated the electrical and physical properties of P3HT partially- and fully- confined in ordered arrays of TiO₂ nanotubes. While simple melt-infiltration annealing resulted in partial P3HT infiltration into the arrays, vacuum-assisted melt-infiltration was essential to promote complete filling. Cross-sectional FESEM analyses as well as dark photo-CELIV transients suggest that P3HT permeated the

arrays well following the prescribed vacuum-assisted procedure. Contrary to the expectation that the larger D-A interfacial area would result in enhanced device efficiencies in tandem with improved photoluminescence quenching, devices with P3HT fully infiltrated were 4-6 times less efficient than their counterparts with partial P3HT filling, with particular impact on device J_{sc} . PL studies show that the charge transfer process at the P3HT-TiO₂ interface was highly efficient when P3HT was fully infiltrated. However, the blue shift in UV-vis absorption spectra suggests that the P3HT chains adopted a coiled configuration when confined in the nanotube arrays. We believe that such nano-confinement effect was responsible for the low hole-mobility in confined P3HT ($1.5 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, about 5 times lower than its partially-confined counterparts). This was in turn responsible for the unexpected low efficiency in the device where P3HT is fully infiltrated. We have shown that photo-CELIV is an effective tool to directly and quantitatively probe the electronic properties of the polymer under confinement at the nano-scale. It is anticipated that such an understanding of the behavior of semiconductor polymer chains confined in nano-sized domains resulting from this work would further proliferate the development of better-performing devices with the widely coveted *ideal* ordered-BHJ structure. Strategies for further improvement include: 1) optimizing the array dimensions (diameter and inter-tube distance) to one where P3HT chain coiling can be arrested and orientation improved and, 2) exploring the use of small molecules and/or oligomers, which may address orientation issues that affect hole-transport. Initial work in these areas is detailed in Chapter 6.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

6.1 Conclusions

The work presented in this thesis was conducted in pursuit of robust and functional arrays of TiO₂ nano-tubes ideal for application in ordered bulk heterojunction solar cells. This has entailed understanding and overcoming persistent instability issues to produce stable AAO templates on the ITO electrode and developing a new and less-energy-demanding solution route to deposit TiO₂ in the templates. Furthermore the potential of the arrays in actual device prototypes was demonstrated, and a major bottleneck to higher efficiencies identified. The key findings and contributions from this project are summarized below:

- 1. The origin of the bottlenecks in preparing AAO templates on ITO coated glass was identified and surmounted.**

Robust AAO templates on ITO coated glass were the basic foundation without which the objectives of this project would be difficult to fulfill. Like many conductors (including Pt, Ag and Cu), pristine ITO coated glass undergoes spontaneous dissolution and out-gassing under typical Al anodizing conditions. Therefore, when the anodization front approaches the Al-ITO interface, the AAO template delaminates from the ITO surface. Stabilization of the anodization process requires 1) the use of an ultra-thin Ti (0.2 – 0.5 nm) adhesion and

passivation layer between Al and ITO that simultaneously prevents thick impenetrable barrier layers from forming, as well as 2) the application of a voltage higher than normally applied to accelerate the anodization process and prevent defects forming and propagating. The above breakthroughs should encourage the deposition of a wide range of other nano-structured materials on ITO coated glass for a variety of other opto-electronic applications.

2. The correlation between substrate conductivity and barrier-layer morphology was elucidated.

Insulating substrates (including glass, amorphous TiO_2 inter-layer, and ITO coated glass coated with thicker (2 – 10 nm) Ti) were found to deplete the local electric field essential for barrier layer thinning at the bottom of the pore channels. Thick barrier layers (as thick as the AAO pore walls) were formed as a result. In contrast, semiconducting substrates (including Si, anatase TiO_2 inter-layer and ITO coated glass coated with ultra-thin Ti) supported a larger electric field that thinned the barrier layers sufficiently for them to be completely removed after subsequent pore widening procedures. These findings provide clearer insight into the types of substrates that would be compatible with template formation by anodization of Al.

3. A new “liquid-ALD” technique to coat the AAO templates with TiO_2 was established.

The process generates smooth conformal nano-tube walls comparable to those produced by conventional vapor-phase ALD and surpassing those achieved by sol-gel and Ti anodization routes. Yet, the high running costs incurred for the vacuum environment critical to the latter is avoided and contamination is also less of an issue as the glass apparatus involved can be

cleaned or replaced easily. Proper control over the deposition conditions with minimal exposure of the reactants and substrates to the ambient resulted in thin films that were smooth and particulate-free at the subnano-meter scale. A modified hydrolysis solution (ethanol/H₂O mixture) and thorough drying of substrates at 90 °C before the next deposition cycle ensured that the same precise LALD process could be repeated in the confined pore channels of the AAO templates. Conductive-AFM results showed that the LALD-derived TiO₂ nano-tube arrays were electrically connected to the underlying ITO and were also electron-conducting (*n*-type, as anticipated), further indication of their potential in subsequent photovoltaic devices. The LALD procedures prescribed herein can be extended to other metal oxides (subject to the availability of suitable reactants and rinsing solvents) and are scalable and automatable for the convenience of interested researchers.

4. Preliminary evidence of doping of TiO₂ by modified LALD procedures was discussed.

To expand further on the versatility of the LALD process, the possibility of doping the TiO₂ films and nano-tubes by incorporating a vanadia precursor during LALD assembly was explored. In particular, the UV-vis spectra of doped films produced by chemisorbing a layer of VTP after every few layers of TIP were clearly red-shifted with respect to that of pristine TiO₂. Although the actual amount of doping could not be determined as yet (the level of doping was too low to be detected by XPS), the implications of these preliminary results are interesting for device studies. For example, the effects of doping on optical absorption, band gap engineering and charge carrier mobility await investigation.

5. Actual model device prototypes composed of LALD-derived TiO₂ nano-tube arrays and P3HT were demonstrated and a key factor limiting efficiency was identified.

The device characteristics of arrays with P3HT partially and fully infiltrated were compared. Despite residing mostly on top of the arrays and having only half the D-A interfacial area available in a bi-layer for charge separation, devices with partially infiltrated P3HT were already two times more efficient than their bi-layered counterparts. This improvement was interpreted as proof of good electron mobility through the nano-tubes. Devices with P3HT well infiltrated were unexpectedly an order of magnitude less efficient, with an obvious reduction in J_{sc} . Nearly complete PL quenching excluded poor charge transfer at the D-A interface as a cause for the reduction and suggested slow hole-transport in P3HT was the next probable limiting factor. As postulated, UV-vis results and corresponding hole-mobility studies by photo-CELIV determined that the efficiency of such devices was ultimately limited by poor hole-mobility as a result of the P3HT chains losing their ability to π -stack and instead, coiling under nano-confinement.

6.2 Recommendations for further work

Based on the above conclusions, the following research directions are proposed with some preliminary experiments detailed:

6.2.1 Modify the surface of TiO₂ with molecules suitable to guide the alignment of P3HT chains in the nano-tube arrays

Organic thin-film transistor (OTFT) studies have shown that thiophene-based polymers can be made to π -stack in the direction parallel to the Si substrate by functionalizing the SiO₂ dielectric layer with a small molecule (most often OTS).¹⁶⁵ The hydrophobic nature of OTS preferentially “attracts” the alkyl side chains of the thiophene-based polymer to the dielectric layer, causing the thiophene rings to stack together. Hole-transport between source and drain (in the lateral direction) is thereby improved. If the walls of the TiO₂ nano-tubes (which are perpendicular to the ITO coated glass substrate) are functionalized similarly, it may be possible to π -stack the P3HT chains in the direction perpendicular to the substrate, that is, in the direction of charge transport in the usual device configuration. Although this option has not been investigated fully, PL results show that OTS prevents exciton dissociation at the D-A interface in agreement with recent literature that the Si-O bond is highly electrically insulating,¹⁶⁶ and is therefore unsuitable in the above circumstance. Other hydrophobic molecules which also serve to mediate charge transfer would be useful.

6.2.2 Solvent vapor annealing to infiltrate and control the orientation of P3HT

Solvent vapor annealing^{97, 167, 168} involves confining the spin-deposited P3HT film in an environment saturated with solvent vapor (such as under a glass petri dish), thereby delaying the total time needed for the film to dry completely. This negates the need for thermal treatments at high temperature, whilst giving the polymer more time to flow and orientate. Such approach has yet to be evaluated in hybrid ordered-BHJ systems and is

therefore recommended as a potential alternative to the melt-infiltration and vacuum-assisted melt-infiltration processes explored in this thesis.

6.2.3 Employ a different class of donor materials in place of P3HT

6.2.3.1 *Small molecules*

Unlike polymers, small molecules do not coil and may improve the hole-transport when confined to small spaces. Several conditions when considering the use of such compounds include: 1) an energy band structure matching that of TiO_2 in order for excitons to successfully dissociate into free charges at the interface, 2) a band gap between 1.6 – 1.8 eV to capture the majority of incident photon flux (Section 2.5) and 3) π -stacking in the direction of charge transport in a device (discotic molecules, for example, have the inherent ability to self-stack perpendicular to the underlying substrate (Section 2.6.1). Some groundwork in this research direction has been started as described below.

CuPc is an interesting candidate for the above objective as it has a band structure matching that of TiO_2 , a band gap of 1.6eV (Fig. 6-1 inset) and is stable in air. Its optical absorption profile is shown in comparison to that of P3HT in Fig. 6-1. Since CuPc is practically insoluble in common solvents, it is usually deposited *via* vacuum sublimation. In a conventional sublimation chamber, substrates are mounted on a sample wheel (above the source boat) which is rotated during sublimation to ensure uniform deposition. However, pore filling is difficult to achieve since the sublimed CuPc molecules travel in all directions and may eventually obstruct the tube channel openings. To collimate the path of the molecules and attempt to guide them into the nano-channels of the TiO_2 nano-tube arrays, we

employed a plastic cone in the modified configuration shown in Fig. 6-2a, where the substrate is placed directly on top of the cone. It is evident from Fig. 6-2b that partial pore filling (in an AAO template) could be achieved and arrays of CuPc nano-pillars were resulted after template dissolution (Fig. 6-2b). However, the technique requires further optimization with more precise alignment of the cone and leveling of the substrate on top of the cone to improve filling. Pore filling could not be achieved in instances where the cone was slightly misaligned (Fig. 6-2c). The positioning of the cone and substrate here was to the discretion of the individual researcher. Permanent fixtures for precise alignment should be contemplated for further work in this area.

Figure 6-1

Normalized UV-vis spectra of CuPc and P3HT as indicated with the band structure of CuPc shown in the inset.

Figure 6-2

a) Illustration of the setup used in the collimated evaporation of CuPc. The arrows indicate the path of the CuPc molecules with molecules of straight travel paths allowed through to the substrate and the strays arrested at the walls of the cone. b) shows partial pore filling with arrays of nano-pillars resulting after template removal (c), while misalignment of the cone and substrate leads to non-infiltration (d).

A second route to deposit CuPc in the TiO₂ nano-tube arrays was also investigated preliminarily. By electrophoretic deposition, Xu *et al.* demonstrated complete filling of AAO templates producing CuPc nanowires after template removal.¹⁶⁹ In our work, a negative DC bias (15 – 40V) was applied to the arrays that were placed opposite to an inert Pt electrode in an electrolyte containing 0.46 mg CuPc, 40 ml chloroform and 0.5 ml

trifluoroacetic acid. CuPc molecules undergo protonation in the trifluoroacetic acid (the nitrogen atoms as acidic centers) and are attracted to the negatively-charged arrays. Fig. 6-3 shows an array of nano-tubes a) before and b and c) after deposition. Application of voltages $\geq 30\text{V}$ tended to result in non-infiltration with the appearance of large area networks of CuPc micro-belts residing on top of the arrays (Fig. 6-3b). Slowing the rate of deposition by reducing the voltage to 15V has resulted in improved filling (Fig. 6-3c), the uniformity of which could be enhanced by reducing the voltage further. Also, the rate of film growth and the ability to fill both the tube channels require further experimentation. Compared to vacuum sublimation, electrophoretic deposition negates the use of vacuum and reduces wastage of CuPc since only what is needed is taken up by the arrays. This approach should be an interesting endeavor.

Figure 6-3

Plan-view FESEM images of a) a pristine nano-tube array and the morphology of CuPc deposited at b) 30V and c) 15V respectively. All scale bars indicate 200 nm.

Another proposed research direction is the use of solution-processable small molecules. This requires further collaborations with chemists in designing and synthesizing molecules that are suitable for this purpose. Brief work was carried out with an in-house synthesized molecule 4T1B (Fig. 6-4),^{170, 171} which is soluble in chloroform. Unfortunately, the uniformity of spin-coated films was poor as observed by the naked eye and under an optical microscope, ultimately causing shorts in the device. Other soluble discotic or dendrimeric molecules may be more appropriate.

Figure 6-4

Molecular structures of 4T1B (4 thiophene and 1 benzothiadiazole) and other in-house synthesized thiophene-benzothiadiazole derivatives.

6.2.4 Explore doped nano-tubes for various opto-electronic applications

As elaborated in Chapter 4, the inclusion of VTP during LALD resulted in TiO₂ coatings with various degrees of red-shifting in optical absorption. Visible-light-absorbing properties are attractive particularly for photovoltaic and photocatalytic applications. Before incorporating into device prototypes, the actual amount of doping, doping states and electrical properties should first be determined. Other dopants (*e.g.* Mg, Fe, Sn) can also be explored.

REFERENCES

1. P. Sheehan, R. N. Jones, A. Jolley, B. L. Preston, M. Clarke, P. J. Durack, S. M. N. Islam, P. H. Whetton, Climate change and the new world economy: Implications for the nature and timing of policy responses, *Global Environmental Change-Human and Policy Dimensions* **2008**, 18, 380-396.
2. S. E. Shaheen, D. S. Ginley, G. E. Jabbour, Organic-based photovoltaics. toward lowm-cost power generation, *MRS Bull.* **2005**, 30, 10-19.
3. K. Kurokawa, K. Komoto, P. Vleuten, D. Faiman, *Energy from the desert: Practical proposals for very large scale photovoltaic systems*, 2nd edn., James and James (Science Publishers) Ltd, 2007.
4. P. V. Kamat, Meeting the clean energy demand: Nanostructure architectures for solar energy conversion, *Journal of Physical Chemistry C* **2007**, 111, 2834-2860.
5. R. W. Miles, G. Zoppi, I. Forbes, Inorganic photovoltaic cells, *Mater. Today* **2007**, 10, 20-27.
6. B. A. Gregg, The photoconversion mechanism of excitonic solar cells, *MRS Bull.* **2005**, 30, 20-22.
7. W. Shockley, Quiesser, H.J., Detailed balance limit of efficiency of p-n junction solar cells, *J. Appl. Phys.* **1961**, 32, 510-519.
8. M. A. Green, 1st International Workshop on Nanostructures in Photovoltaics, Dresden, Germany, 2001.
9. M. A. Green, 3rd World Conference on Photovoltaic Energy Conversion, Osaka, JAPAN, 2003.
10. G. Conibeer, Third-generation photovoltaics, *Mater. Today* **2007**, 10, 42-50.
11. C. W. Tang, 2-Layer Organic Photovoltaic Cell, *Appl. Phys. Lett.* **1986**, 48, 183-185.
12. M. Reyes-Reyes, K. Kim, D. L. Carroll, High-efficiency photovoltaic devices based on annealed poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C-61 blends, *Appl. Phys. Lett.* **2005**, 87
13. W. L. Ma, C. Y. Yang, X. Gong, K. Lee, A. J. Heeger, Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology, *Adv. Funct. Mater.* **2005**, 15, 1617-1622.
14. Y. Liang, Z. Xu, J. Xia, S.T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, For the bright future - bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%, *Adv. Mater.* **2010**, DOI: 10.1002/adma20093528.
15. N. S. Sariciftci, Plastic photovoltaic devices, *Mater. Today* **2004**, 36-40.
16. H. A. M. van Mullekom, J. Vekemans, E. E. Havinga, E. W. Meijer, Developments in the chemistry and band gap engineering of donor-acceptor substituted conjugated polymers, *Materials Science & Engineering R-Reports* **2001**, 32, 1-40.
17. R. Kersting, U. Lemmer, M. Deussen, H. J. Bakker, R. F. Mahrt, H. Kurz, V. I. Arkhipov, H. Bassler, E. O. Gobel, Ultrafast field-induced dissociation of excitons in conjugated polymers, *Phys. Rev. Lett.* **1994**, 73, 1440-1443.

18. I. G. Hill, A. Kahn, Z. G. Soos, R. A. Pascal, Charge-separation energy in films of pi-conjugated organic molecules, *Chem. Phys. Lett.* **2000**, 327, 181-188.
19. S. F. Alvarado, P. F. Seidler, D. G. Lidzey, D. D. C. Bradley, Direct determination of the exciton binding energy of conjugated polymers using a scanning tunneling microscope, *Phys. Rev. Lett.* **1998**, 81, 1082-1085.
20. S. E. Gledhill, B. Scott, B. A. Gregg, Organic and nano-structured composite photovoltaics: An overview, *J. Mater. Res.* **2005**, 20, 3167-3179.
21. B. A. Gregg, M. C. Hanna, Comparing organic to inorganic photovoltaic cells: Theory, experiment, and simulation, *J. Appl. Phys.* **2003**, 93, 3605-3614.
22. S. M. Sze, *Physics of semiconductor devices*, John Wiley & Sons, 1981.
23. V. Shrotriya, G. Li, Y. Yao, T. Moriarty, K. Emery, Y. Yang, Accurate measurement and characterization of organic solar cells, *Advanced Functional Materials* **2006**, 16, 2016-2023.
24. C. J. Brabec, Organic photovoltaics: technology and market, *Sol. Energy Mater. Sol. Cells* **2004**, 83, 273-292.
25. D. C. Olson, S. E. Shaheen, M. S. White, W. J. Mitchell, M. van Hest, R. T. Collins, D. S. Ginley, Band-offset engineering for enhanced open-circuit voltage in polymer-oxide hybrid solar cells, *Adv. Funct. Mater.* **2007**, 17, 264-269.
26. M. C. Scharber, D. Wuhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. L. Brabec, Design rules for donors in bulk-heterojunction solar cells - Towards 10 % energy-conversion efficiency, *Advanced Materials* **2006**, 18, 789-+.
27. F. B. Kooistra, J. Knol, F. Kastenberger, L. M. Popescu, W. J. H. Verhees, J. M. Kroon, J. C. Hummelen, Increasing the open circuit voltage of bulk-heterojunction solar cells by raising the LUMO level of the acceptor, *Org. Lett.* **2007**, 9, 551-554.
28. N. Karst, J. C. Bernede, On the improvement of the open circuit voltage of plastic solar cells by the presence of a thin aluminium oxide layer at the interface organic/aluminium, *Physica Status Solidi a-Applications and Materials Science* **2006**, 203, R70-R72.
29. Y. Kinoshita, R. Takenaka, H. Murata, Independent control of open-circuit voltage of organic solar cells by changing film thickness of MoO₃ buffer layer, *Appl. Phys. Lett.* **2008**, 92.
30. V. D. Mihaileti, P. W. M. Blom, J. C. Hummelen, M. T. Rispens, Cathode dependence of the open-circuit voltage of polymer : fullerene bulk heterojunction solar cells, *J. Appl. Phys.* **2003**, 94, 6849-6854.
31. G. Dennler, N. S. Sariciftci, Flexible conjugated polymer-based plastic solar cells: From basics to applications, *Proceedings of the Ieee* **2005**, 93, 1429-1439.
32. H. Hoppe, N. Arnold, D. Meissner, N. S. Sariciftci, Symposium on Thin Film and Nano-Structured Materials for Photovoltaics, Strasbourg, FRANCE, 2003.
33. H. Hoppe, N. Arnold, N. S. Sariciftci, D. Meissner, Modeling the optical absorption within conjugated polymer/fullerene-based bulk-heterojunction organic solar cells, *Sol. Energy Mater. Sol. Cells* **2003**, 80, 105-113.
34. H. Hoppe, N. S. Sariciftci, D. Meissner, Optical constants of conjugated polymer/fullerene based bulk-heterojunction organic solar cells, *Molecular Crystals and Liquid Crystals* **2002**, 385, 233-239.
35. L. A. A. Pettersson, L. S. Roman, O. Inganäs, Modeling photocurrent action spectra of photovoltaic devices based on organic thin films, *J. Appl. Phys.* **1999**, 86, 487-496.

36. J. Y. Kim, S. H. Kim, H. H. Lee, K. Lee, W. L. Ma, X. Gong, A. J. Heeger, New architecture for high-efficiency polymer photovoltaic cells using solution-based titanium oxide as an optical spacer, *Adv. Mater.* **2006**, 18, 572-+.
37. V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, Elastomeric transistor stamps: Reversible probing of charge transport in organic crystals, *Science* **2004**, 303, 1644-1646.
38. I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. Macdonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. M. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, M. F. Toney, Liquid-crystalline semiconducting polymers with high charge-carrier mobility, *Nature Materials* **2006**, 5, 328-333.
39. T. D. Anthopoulos, B. Singh, N. Marjanovic, N. S. Sariciftci, A. M. Ramil, H. Sitter, M. Colle, D. M. de Leeuw, High performance n-channel organic field-effect transistors and ring oscillators based on C-60 fullerene films, *Appl. Phys. Lett.* **2006**, 89
40. D. J. Gundlach, K. P. Pernstich, G. Wilckens, M. Gruter, S. Haas, B. Batlogg, High mobility n-channel organic thin-film transistors and complementary inverters, *J. Appl. Phys.* **2005**, 98
41. B. S. Ong, Y. L. Wu, P. Liu, Design of high-performance regioregular polythiophenes for organic thin-film transistors, *Proceedings of the Ieee* **2005**, 93, 1412-1419.
42. B. S. Ong, Y. L. Wu, P. Liu, S. Gardner, Structurally ordered polythiophene nanoparticles for high-performance organic thin-film transistors, *Adv. Mater.* **2005**, 17, 1141-+.
43. L. Schmidt-Mende, M. Watson, K. Mullen, R. H. Friend, International Conference on Discotic Liquid Crystals, Trieste, Italy, 2002.
44. W. W. H. Wong, D. J. Jones, C. Yan, S. E. Watkins, S. King, S. A. Haque, X. M. Wen, K. P. Ghiggino, A. B. Holmes, Synthesis, Photophysical, and Device Properties of Novel Dendrimers Based on a Fluorene-Hexabenzocoronene (FHBC) Core, *Org. Lett.* **2009**, 11, 975-978.
45. F. C. Grozema, L. D. A. Siebbeles, Mechanism of charge transport in self-organizing organic materials, *Int. Rev. Phys. Chem.* **2008**, 27, 87-138.
46. D. M. Gupta, S.; Narayan, K. S., Fill factor in organic solar cells, *Sol. Energy Mater. Sol. Cells* **2008**
47. S. Gunes, H. Neugebauer, N. S. Sariciftci, Conjugated polymer-based organic solar cells, *Chem. Rev.* **2007**, 107, 1324-1338.
48. N. Blouin, A. Michaud, M. Leclerc, A low-bandgap poly(2,7-carbazole) derivative for use in high-performance solar cells, *Adv. Mater.* **2007**, 19, 2295-+.
49. C. P. Chen, S. H. Chan, T. C. Chao, C. Ting, B. T. Ko, Low-bandgap poly(thiophene-phenylene-thiophene) derivatives with broaden absorption spectra for use in high-performance bulk-heterojunction polymer solar cells, *J. Am. Chem. Soc.* **2008**, 130, 12828-12833.
50. R. Kroon, M. Lenes, J. C. Hummelen, P. W. M. Blom, B. De Boer, Small bandgap polymers for organic solar cells (polymer material development in the last 5 years), *Polymer Reviews* **2008**, 48, 531-582.
51. J. Roncali, Molecular engineering of the band gap of pi-conjugated systems: Facing technological applications, *Macromol. Rapid Commun.* **2007**, 28, 1761-1775.

52. L. J. A. Koster, V. D. Mihailetschi, P. W. M. Blom, Ultimate efficiency of polymer/fullerene bulk heterojunction solar cells, *Appl. Phys. Lett.* **2006**, 88
53. S. R. Forrest, The limits to organic photovoltaic cell efficiency, *MRS Bull.* **2005**, 30, 28-32.
54. A. C. Mayer, S. R. Scully, B. E. Hardin, M. W. Rowell, M. D. McGehee, Polymer-based solar cells, *Mater. Today* **2007**, 10, 28-33.
55. G. Yu, A. J. Heeger, Charge separation and photovoltaic conversion in polymer composites with internal donor-acceptor heterojunctions, *J. Appl. Phys.* **1995**, 78, 4510-4515.
56. J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, Efficient photodiodes from interpenetrating polymer networks, *Nature* **1995**, 376, 498-500.
57. M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson, R. H. Friend, Laminated fabrication of polymeric photovoltaic diodes, *Nature* **1998**, 395, 257-260.
58. A. J. Mozer, N. S. Sariciftci, 15th International Conference on Photochemical Conversion and Storage of Solar Energy, Paris, FRANCE, 2004.
59. P. W. M. Blom, V. D. Mihailetschi, L. J. A. Koster, D. E. Markov, Device physics of polymer : fullerene bulk heterojunction solar cells, *Adv. Mater.* **2007**, 19, 1551-1566.
60. H. Hoppe, N. S. Sariciftci, Organic solar cells: An overview, *J. Mater. Res.* **2004**, 19, 1924-1945.
61. M. T. Lloyd, J. E. Anthony, G. G. Malliaras, Photovoltaics from soluble small molecules, *Mater. Today* **2007**, 10, 34-41.
62. R. A. J. Janssen, J. C. Hummelen, N. S. Sariciftci, Polymer-fullerene bulk heterojunction solar cells, *MRS Bull.* **2005**, 30, 33-36.
63. N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, Semiconducting polymers (as donors) and buckminsterfullerene (as acceptor) - photoinduced electron-transfer and heterojunction devices, *Synth. Met.* **1993**, 59, 333-352.
64. S. C. J. Meskers, P. A. van Hal, A. J. H. Spiering, J. C. Hummelen, A. F. G. van der Meer, R. A. J. Janssen, Time-resolved infrared-absorption study of photoinduced charge transfer in a polythiophene-methanofullerene composite film, *Physical Review B* **2000**, 61, 9917-9920.
65. C. J. Brabec, G. Zerza, G. Cerullo, S. De Silvestri, S. Luzzati, J. C. Hummelen, N. S. Sariciftci, Tracing photoinduced electron transfer process in conjugated polymer/fullerene bulk heterojunctions in real time, *Chem. Phys. Lett.* **2001**, 340, 232-236.
66. B. Kraabel, D. McBranch, N. S. Sariciftci, D. Moses, A. J. Heeger, Ultrafast spectroscopic studies of photoinduced electron-transfer from semiconducting polymers to C-60, *Physical Review B* **1994**, 50, 18543-18552.
67. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Polymer photovoltaic cells - enhanced efficiencies via a network of internal donor-acceptor heterojunctions, *Science* **1995**, 270, 1789-1791.
68. S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, 2.5% efficient organic plastic solar cells, *Appl. Phys. Lett.* **2001**, 78, 841-843.

69. S. Uchida, J. G. Xue, B. P. Rand, S. R. Forrest, Organic small molecule solar cells with a homogeneously mixed copper phthalocyanine: C-60 active layer, *Appl. Phys. Lett.* **2004**, 84, 4218-4220.
70. T. Kietzke, D. Neher, M. Kumke, O. Ghazy, U. Ziener, K. Landfester, Phase separation of binary blends in polymer nanoparticles, *Small* **2007**, 3, 1041-1048.
71. T. Kietzke, D. Neher, M. Kumke, R. Montenegro, K. Landfester, U. Scherf, A nanoparticle approach to control the phase separation in polyfluorene photovoltaic devices, *Macromolecules* **2004**, 37, 4882-4890.
72. A. P. Alivisatos, Semiconductor clusters, nanocrystals, and quantum dots, *Science* **1996**, 271, 933-937.
73. W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, Hybrid nanorod-polymer solar cells, *Science* **2002**, 295, 2425-2427.
74. D. J. Milliron, I. Gur, A. P. Alivisatos, Hybrid organic - Nanocrystal solar cells, *MRS Bull.* **2005**, 30, 41-44.
75. Y. Chiba, A. Islam, R. Komiya, N. Koide, L. Y. Han, Conversion efficiency of 10.8% by a dye-sensitized solar cell using a TiO₂ electrode with high haze, *Appl. Phys. Lett.* **2006**, 88
76. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrybaker, E. Muller, P. Liska, N. Vlachopoulos, M. Gratzel, Conversion of light to electricity by CIS-X2BIS(2,2'-BIPYRIDYL-4,4'-DICARBOXYLATE)RUTHENIUM(II) charge-transfer sensitizers (X = CL-, BR-, I-, CN-, AND SCN-) on nanocrystalline TiO₂ electrodes, *J. Am. Chem. Soc.* **1993**, 115, 6382-6390.
77. M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Gratzel, Engineering of efficient panchromatic sensitizers for nanocrystalline TiO₂-based solar cells, *J. Am. Chem. Soc.* **2001**, 123, 1613-1624.
78. B. Oregan, M. Gratzel, A Low-Cost, High-Efficiency Solar-Cell Based on Dye-Sensitized Colloidal TiO₂ Films, *Nature* **1991**, 353, 737-740.
79. J. Kruger, R. Plass, M. Gratzel, H. J. Matthieu, Improvement of the photovoltaic performance of solid-state dye-sensitized device by silver complexation of the sensitizer cis-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato) ruthenium(II), *Appl. Phys. Lett.* **2002**, 81, 367-369.
80. Q. B. Meng, K. Takahashi, X. T. Zhang, I. Sutanto, T. N. Rao, O. Sato, A. Fujishima, H. Watanabe, T. Nakamori, M. Uragami, Fabrication of an efficient solid-state dye-sensitized solar cell, *Langmuir* **2003**, 19, 3572-3574.
81. B. O'Regan, D. T. Schwartz, S. M. Zakeeruddin, M. Gratzel, Electrodeposited nanocomposite n-p heterojunctions for solid-state dye-sensitized photovoltaics, *Adv. Mater.* **2000**, 12, 1263-+.
82. L. Schmidt-Mende, S. M. Zakeeruddin, M. Gratzel, Efficiency improvement in solid-state-dye-sensitized photovoltaics with an amphiphilic Ruthenium-dye, *Appl. Phys. Lett.* **2005**, 86
83. D. B. Kuang, C. Klein, Z. P. Zhang, S. Ito, J. E. Moser, S. M. Zakeeruddin, M. Gratzel, Stable, high-efficiency ionic-liquid-based mesoscopic dye-sensitized solar cells, *Small* **2007**, 3, 2094-2102.

84. E. Stathatos, P. Lianos, U. Lavrencic-Stangar, B. Orel, A high-performance solid-state dye-sensitized photoelectrochemical cell employing a nanocomposite gel electrolyte made by the sol-gel route, *Adv. Mater.* **2002**, 14, 354-357.
85. L. Wang, S. B. Fang, Y. Lin, X. W. Zhou, M. Y. Li, A 7.72% efficient dye sensitized solar cell based on novel necklace-like polymer gel electrolyte containing latent chemically cross-linked gel electrolyte precursors, *Chem. Commun.* **2005**, 5687-5689.
86. P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Gratzel, A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte, *Nature Materials* **2003**, 2, 402-407.
87. K. M. Coakley, M. D. McGehee, Conjugated polymer photovoltaic cells, *Chem. Mater.* **2004**, 16, 4533-4542.
88. A. C. Arias, N. Corcoran, M. Banach, R. H. Friend, J. D. MacKenzie, W. T. S. Huck, Vertically segregated polymer-blend photovoltaic thin-film structures through surface-mediated solution processing, *Appl. Phys. Lett.* **2002**, 80, 1695-1697.
89. S. S. Sun, C. Zhang, A. Ledbetter, S. Choi, K. Seo, C. E. Bonner, M. Drees, N. S. Sariciftci, Photovoltaic enhancement of organic solar cells by a bridged donor-acceptor block copolymer approach, *Appl. Phys. Lett.* **2007**, 90
90. S. S. Sun, Design of a block copolymer solar cell, *Sol. Energy Mater. Sol. Cells* **2003**, 79, 257-264.
91. S. Sergeyev, W. Pisula, Y. H. Geerts, Discotic liquid crystals: A new generation of organic semiconductors, *Chem. Soc. Rev.* **2007**, 36, 1902-1929.
92. M. S. Kim, J. S. Kim, J. C. Cho, M. Shtein, L. J. Guo, J. Kim, Flexible conjugated polymer photovoltaic cells with controlled heterojunctions fabricated using nanoimprint lithography, *Appl. Phys. Lett.* **2007**, 90
93. S. P. Baek, J. B.; Lee, W.; Han, S-H.; Lee, J.; Lee, S-H., A facile method to prepare regioregular poly(3-hexylthiophene) nanorod arrays using anodized aluminium oxide templates and capillary force, *New J. Chem.* **2009**, ASAP
94. Y. Xu, M. A. A. Schoonen, The absolute energy positions of conduction and valence bands of selected semiconducting minerals, *Am. Mineral.* **2000**, 85, 543-556.
95. H. Irie, Y. Watanabe, K. Hashimoto, Nitrogen-concentration dependence on photocatalytic activity of $\text{TiO}_2\text{-xN}_x$ powders, *J. Phys. Chem. B* **2003**, 107, 5483-5486.
96. T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, S. Sugihara, Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping, *Applied Catalysis B-Environmental* **2003**, 42, 403-409.
97. Y. Zhao, Z. Y. Xie, Y. Qu, Y. H. Geng, L. X. Wang, Solvent-vapor treatment induced performance enhancement of poly(3-hexylthiophene): methanofullerene bulk-heterojunction photovoltaic cells, *Applied Physics Letters* **2007**, 90
98. C. Goh, S. R. Scully, M. D. McGehee, Effects of molecular interface modification in hybrid organic-inorganic photovoltaic cells, *J. Appl. Phys.* **2007**, 101
99. Y. Y. Lin, T. H. Chu, C. W. Chen, W. F. Su, Improved performance of polymer/ TiO_2 nanorod bulk heterojunction photovoltaic devices by interface modification, *Appl. Phys. Lett.* **2008**, 92
100. D. C. Olson, J. Piris, R. T. Collins, S. E. Shaheen, D. S. Ginley, 4th International Symposium on Transparent Oxide Thin Films for Electronics and Optics, Tokyo, JAPAN, 2005.

101. Q. S. Wei, K. Hirota, K. Tajima, K. Hashimoto, Design and synthesis of TiO₂ nanorod assemblies and their application for photovoltaic devices, *Chem. Mater.* **2006**, 18, 5080-5087.
102. G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, C. A. Grimes, High efficiency double heterojunction polymer photovoltaic cells using highly ordered TiO₂ nanotube arrays, *Appl. Phys. Lett.* **2007**, 91
103. G. K. Mor, O. K. Varghese, M. Paulose, K. Shankar, C. A. Grimes, A review on highly ordered, vertically oriented TiO₂ nanotube arrays: Fabrication, material properties, and solar energy applications, *Sol. Energy Mater. Sol. Cells* **2006**, 90, 2011-2075.
104. S. Dubois, J. Colin, J. L. Duvail, L. Piroux, Evidence for strong magnetoelastic effects in Ni nanowires embedded in polycarbonate membranes, *Physical Review B* **2000**, 61, 14315-14318.
105. Z. X. Ye, H. Zhang, H. D. Liu, W. H. Wu, Z. P. Luo, Observation of superconductivity in single crystalline Bi nanowires, *Nanotechnology* **2008**, 19
106. E. J. W. Crossland, S. Ludwigs, M. A. Hillmyer, U. Steiner, Freestanding nanowire arrays from soft-etch block copolymer templates, *Soft Matter* **2007**, 3, 94-98.
107. B. B. Lakshmi, C. J. Patrissi, C. R. Martin, Sol-gel template synthesis of semiconductor oxide micro- and nanostructures, *Chem. Mater.* **1997**, 9, 2544-2550.
108. O. Rabin, P. R. Herz, Y. M. Lin, A. I. Akinwande, S. B. Cronin, M. S. Dresselhaus, Formation of thick porous anodic alumina films and nanowire arrays on silicon wafers and glass, *Adv. Funct. Mater.* **2003**, 13, 631-638.
109. M. S. Sander, L. S. Tan, Nanoparticle arrays on surfaces fabricated using anodic alumina films as templates, *Adv. Funct. Mater.* **2003**, 13, 393-397.
110. S. Shingubara, O. Okino, Y. Sayama, H. Sakaue, T. Takahagi, Two-dimensional nanowire array formation on Si substrate using self-organized nanoholes of anodically oxidized aluminum, *Solid-State Electronics* **1999**, 43, 1143-1146.
111. L. K. Tan, M. A. S. Chong, H. Gao, Free-standing porous anodic alumina templates for atomic layer deposition of highly ordered TiO₂ nanotube arrays on various substrates, *Journal of Physical Chemistry C* **2008**, 112, 69-73.
112. B. Yao, D. Fleming, M. A. Morris, S. E. Lawrence, Structural control of mesoporous silica nanowire arrays in porous alumina membranes, *Chem. Mater.* **2004**, 16, 4851-+.
113. T. R. B. Foong, A. Sellinger, X. Hu, Origin of the bottlenecks in preparing anodized aluminum oxide (AAO) templates on ITO glass, *ACS Nano* **2008**, 2, 2250-2256.
114. M. S. Sander, M. J. Cote, W. Gu, B. M. Kile, C. P. Tripp, Template-assisted fabrication of dense, aligned arrays of titania nanotubes with well-controlled dimensions on substrates, *Adv. Mater.* **2004**, 16, 2052-+.
115. S. S. Kim, C. Chun, J. C. Hong, D. Y. Kim, Well-ordered TiO₂ nanostructures fabricated using surface relief gratings on polymer films, *J. Mater. Chem.* **2006**, 16, 370-375.
116. J. J. Shyue, R. E. Cochran, N. P. Padture, Transparent-conducting, gas-sensing nanostructures (nanotubes, nanowires, and thin films) of titanium oxide synthesized at near-ambient conditions, *J. Mater. Res.* **2006**, 21, 2894-2903.
117. L. K. Teh, V. Furin, A. Martucci, M. Guglielmi, C. C. Wong, F. Romanato, Electrodeposition of CdSe on nanopatterned pillar arrays for photonic and photovoltaic applications, *Thin Solid Films* **2007**, 515, 5787-5791.

118. S. Z. Chu, K. Wada, S. Inoue, S. Todoroki, Formation and microstructures of anodic alumina films from aluminum sputtered on glass substrate, *J. Electrochem. Soc.* **2002**, 149, B321-B327.
119. S. Z. Chu, K. Wada, S. Inoue, S. Todoroki, Synthesis and characterization of titania nanostructures on glass by Al anodization and sol-gel process, *Chem. Mater.* **2002**, 14, 266-272.
120. S. Z. Chu, K. Wada, S. Inoue, S. Todoroki, Fabrication and characteristics of nanostructures on glass by Al anodization and electrodeposition, *Electrochim. Acta* **2003**, 48, 3147-3153.
121. S. J. Limmer, T. P. Chou, G. Z. Cao, A study on the growth of TiO₂ nanorods using sol electrophoresis, *Journal of Materials Science* **2004**, 39, 895-901.
122. L. Liu, Y. M. Zhao, N. Q. Jia, Q. Zhou, C. J. Zhao, M. M. Yan, Z. Y. Jiang, Electrochemical fabrication and electronic behavior of polypyrrole nano-fiber array devices, *Thin Solid Films* **2006**, 503, 241-245.
123. D. Crouse, Y. H. Lo, A. E. Miller, M. Crouse, Self-ordered pore structure of anodized aluminum on silicon and pattern transfer, *Applied Physics Letters* **2000**, 76, 49-51.
124. O. Jessensky, F. Muller, U. Gosele, Self-organized formation of hexagonal pore arrays in anodic alumina, *Applied Physics Letters* **1998**, 72, 1173-1175.
125. A. P. Li, F. Muller, A. Birner, K. Nielsch, U. Gosele, Hexagonal pore arrays with a 50-420 nm interpore distance formed by self-organization in anodic alumina, *J. Appl. Phys.* **1998**, 84, 6023-6026.
126. F. Y. Li, L. Zhang, R. M. Metzger, On the growth of highly ordered pores in anodized aluminum oxide, *Chemistry of Materials* **1998**, 10, 2470-2480.
127. H. Masuda, K. Yasui, Y. Sakamoto, M. Nakao, T. Tamamura, K. Nishio, Ideally ordered anodic porous alumina mask prepared by imprinting of vacuum-evaporated Al on Si, *Japanese Journal of Applied Physics Part 2-Letters* **2001**, 40, L1267-L1269.
128. J. P. O'Sullivan, G. C. Wood, The morphology and mechanism of formation of porous anodic films on aluminium, *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **1970**, 317, 511-543.
129. W. X. Que, A. Uddin, X. Hu, Thin film TiO₂ electrodes derived by sol-gel process for photovoltaic applications, *J. Power Sources* **2006**, 159, 353-356.
130. S. Franssila, *Introduction to Microfabrication*, John Wiley and Sons, 2004.
131. A. L. Cai, H. Y. Zhang, H. Hua, Z. B. Zhang, Direct formation of self-assembled nanoporous aluminium oxide on SiO₂ and Si substrates, *Nanotechnology* **2002**, 13, 627-630.
132. M. L. Tian, S. Y. Xu, J. G. Wang, N. Kumar, E. Wertz, Q. Li, P. M. Campbell, M. H. W. Chan, T. E. Mallouk, Penetrating the oxide barrier in situ and separating freestanding porous anodic alumina films in one step, *Nano Lett.* **2005**, 5, 697-703.
133. J. Y. Liang, H. Chik, A. J. Yin, J. Xu, Two-dimensional lateral superlattices of nanostructures: Nonlithographic formation by anodic membrane template, *J. Appl. Phys.* **2002**, 91, 2544-2546.
134. M. M. Crouse, A. E. Miller, D. T. Crouse, A. A. Ikram, Nanoporous alumina template with in situ barrier oxide removal, synthesized from a multilayer thin film precursor, *J. Electrochem. Soc.* **2005**, 152, D167-D172.

135. A. Mozalev, M. Sakairi, I. Saeki, H. Takahashi, Nucleation and growth of the nanostructured anodic oxides on tantalum and niobium under the porous alumina film, *Electrochim. Acta* **2003**, 48, 3155-3170.
136. A. Mozalev, M. Sakairi, H. Takahashi, Structure, morphology, and dielectric properties of nanocomposite oxide films formed by anodizing of sputter-deposited Ta-Al bilayers, *J. Electrochem. Soc.* **2004**, 151, F257-F268.
137. A. I. Vorobyova, E. A. Outkina, Study of pillar microstructure formation with anodic oxides, *Thin Solid Films* **1998**, 324, 1-10.
138. M. Paulose, O. K. Varghese, G. K. Mor, C. A. Grimes, K. G. Ong, Unprecedented ultra-high hydrogen gas sensitivity in undoped titania nanotubes, *Nanotechnology* **2006**, 17, 398-402.
139. Y. K. Lai, L. Sun, Y. C. Chen, H. F. Zhuang, C. J. Lin, J. W. Chin, Effects of the structure of TiO₂ nanotube array on Ti substrate on its photocatalytic activity, *J. Electrochem. Soc.* **2006**, 153, D123-D127.
140. J. M. Macak, M. Zlamal, J. Krysa, P. Schmuki, Self-organized TiO₂ nanotube layers as highly efficient photocatalysts, *Small* **2007**, 3, 300-304.
141. C. A. Grimes, Synthesis and application of highly ordered arrays of TiO₂ nanotubes, *J. Mater. Chem.* **2007**, 17, 1451-1457.
142. Z. R. R. Tian, J. A. Voigt, J. Liu, B. McKenzie, H. F. Xu, Large oriented arrays and continuous films of TiO₂-based nanotubes, *J. Am. Chem. Soc.* **2003**, 125, 12384-12385.
143. M. Ritala, M. Leskela, Atomic layer epitaxy - a valuable tool for nanotechnology?, *Nanotechnology* **1999**, 10, 19-24.
144. J. Aarik, A. Aidla, H. Mandar, V. Sammelselg, Anomalous effect of temperature on atomic layer deposition of titanium dioxide, *J. Cryst. Growth* **2000**, 220, 531-537.
145. J. Aarik, A. Aidla, H. Mandar, T. Uustare, M. Schuisky, A. Harsta, Atomic layer growth of epitaxial TiO₂ thin films from TiCl₄ and H₂O on alpha-Al₂O₃ substrates, *J. Cryst. Growth* **2002**, 242, 189-198.
146. J. Aarik, A. Aidla, T. Uustare, V. Sammelselg, Morphology and Structure of TiO₂ Thin-Films Grown by Atomic Layer Deposition, *J. Cryst. Growth* **1995**, 148, 268-275.
147. M. A. Cameron, I. P. Gartland, J. A. Smith, S. F. Diaz, S. M. George, Atomic layer deposition of SiO₂ and TiO₂ in alumina tubular membranes: Pore reduction and effect of surface species on gas transport, *Langmuir* **2000**, 16, 7435-7444.
148. Y. Aoki, T. Kunitake, A. Nakao, Sol-gel fabrication of dielectric HfO₂ nano-films; Formation of uniform, void-free layers and their superior electrical properties, *Chem. Mater.* **2005**, 17, 450-458.
149. I. Ichinose, H. Senzu, T. Kunitake, A surface sol-gel process of TiO₂ and other metal oxide films with molecular precision, *Chem. Mater.* **1997**, 9, 1296-&.
150. I. Ichinose, H. Senzu, T. Kunitake, Stepwise adsorption of metal alkoxides on hydrolyzed surfaces: A surface sol-gel process, *Chem. Lett.* **1996**, 831-832.
151. R. A. Caruso, Micrometer-to-manometer replication of hierarchical structures by using a surface sol-gel process, *Angewandte Chemie-International Edition* **2004**, 43, 2746-2748.
152. J. G. Huang, T. Kunitake, Nano-precision replication of natural cellulosic substances by metal oxides, *J. Am. Chem. Soc.* **2003**, 125, 11834-11835.

153. J. Huang, T. Kunitake, Nanotubings of titania/polymer composite: template synthesis and nanoparticle inclusion, *J. Mater. Chem.* **2006**, 16, 4257-4264.
154. T. R. B. Foong, Shen, Y., Hu, X. and Sellinger, A., Template-directed liquid ALD growth of TiO₂ nanotube arrays: properties and potential in photovoltaic devices, *Adv. Funct. Mater.*, **2010**, 20, 1390 - 1396.
155. B. Smarsly, D. Grosso, T. Brezesinski, N. Pinna, C. Boissiere, M. Antonietti, C. Sanchez, Highly crystalline cubic mesoporous TiO₂ with 10-nm pore diameter made with a new block copolymer template, *Chem. Mater.* **2004**, 16, 2948-2952.
156. L. E. Greene, M. Law, B. D. Yuhas, P. D. Yang, ZnO-TiO₂ core-shell nanorod/P3HT solar cells, *Journal of Physical Chemistry C* **2007**, 111, 18451-18456.
157. D. C. Olson, J. Piris, R. T. Collins, S. E. Shaheen, D. S. Ginley, Hybrid photovoltaic devices of polymer and ZnO nanofiber composites, *Thin Solid Films* **2006**, 496, 26-29.
158. C. Y. Kuo, W. C. Tang, C. Gau, T. F. Guo, D. Z. Jeng, Ordered bulk heterojunction solar cells with vertically aligned TiO₂ nanorods embedded in a conjugated polymer, *Appl. Phys. Lett.* **2008**, 93
159. G. Dennler, A. J. Mozer, G. Juska, A. Pivrikas, R. Osterbacka, A. Fuchsbaue, N. S. Sariciftci, Charge carrier mobility and lifetime versus composition of conjugated polymer/fullerene bulk-heterojunction solar cells, *Org. Electron.* **2006**, 7, 229-234.
160. A. J. Mozer, N. S. Sariciftci, L. Lutsen, D. Vanderzande, R. Osterbacka, M. Westerling, G. Juska, Charge transport and recombination in bulk heterojunction solar cells studied by the photoinduced charge extraction in linearly increasing voltage technique, *Appl. Phys. Lett.* **2005**, 86
161. K. M. Coakley, Y. X. Liu, M. D. McGehee, K. L. Frindell, G. D. Stucky, Infiltrating semiconducting polymers into self-assembled mesoporous titania films for photovoltaic applications, *Advanced Functional Materials* **2003**, 13, 301-306.
162. K. M. Coakley, M. D. McGehee, Photovoltaic cells made from conjugated polymers infiltrated into mesoporous titania, *Appl. Phys. Lett.* **2003**, 83, 3380-3382.
163. K. M. Coakley, B. S. Srinivasan, J. M. Ziebarth, C. Goh, Y. X. Liu, M. D. McGehee, Enhanced hole mobility in regioregular polythiophene infiltrated in straight nanopores, *Adv. Funct. Mater.* **2005**, 15, 1927-1932.
164. S. Baek, J. B. Park, W. Lee, S. H. Han, J. Lee, S. H. Lee, A facile method to prepare regioregular poly(3-hexylthiophene) nanorod arrays using anodic aluminium oxide templates and capillary force, *New J. Chem.* **2009**, 33, 986-990.
165. B. S. Ong, Y. L. Wu, Y. N. Li, P. Liu, H. L. Pan, Thiophene polymer semiconductors for organic thin-film transistors, *Chemistry-a European Journal* **2008**, 14, 4766-4778.
166. M. H. Yoon, A. Facchetti, T. J. Marks, sigma-pi molecular dielectric multilayers for low-voltage organic thin-film transistors, *Proceedings of the National Academy of Sciences of the United States of America* **2005**, 102, 4678-4682.
167. M. Campoy-Quiles, T. Ferenczi, T. Agostinelli, P. G. Etchegoin, Y. Kim, T. D. Anthopoulos, P. N. Stavrinou, D. D. C. Bradley, J. Nelson, Morphology evolution via self-organization and lateral and vertical diffusion in polymer: fullerene solar cell blends, *Nature Materials* **2008**, 7, 158-164.
168. G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang, Y. Yang, "Solvent annealing" effect in polymer solar cells based on poly(3-hexylthiophene) and methanofullerenes, *Advanced Functional Materials* **2007**, 17, 1636-1644.

169. H. B. Xu, H. Z. Chen, W. J. Xu, M. Wang, Fabrication of organic copper phthalocyanine nanowire arrays via a simple AAO template-based electrophoretic deposition, *Chem. Phys. Lett.* **2005**, 412, 294-298.
170. P. Sonar, S. P. Singh, P. Leclerc, M. Surin, R. Lazzaroni, T. T. Lin, A. Dodabalapur, A. Sellinger, Synthesis, characterization and comparative study of thiophene-benzothiadiazole based donor-acceptor-donor (D-A-D) materials, *J. Mater. Chem.* **2009**, 19, 3228-3237.
171. P. Sonar, S. P. Singh, S. Sudhakar, A. Dodabalapur, A. Sellinger, High-mobility organic thin film transistors based on benzothiadiazole-sandwiched dihexylquaterthiophenes, *Chem. Mater.* **2008**, 20, 3184-3190.