

Solution-Processed Inorganic Semiconductors in Hybrid Photovoltaics: Mechanisms of Charge Separation and Effects of Interface Structure

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Abstract

Nanocrystalline inorganic semiconductors have emerged as attractive alternatives to molecular dyes as photosensitisers for mesoporous metal oxide-based semiconductor-sensitised solar cells (SSSCs). In this configuration, Sb_2S_3 has shown particular promise, yielding impressive power conversion efficiencies. At the operational heart of these devices, there are a series of interfacial electron transfer reactions that act to separate photogenerated charges. The delicate balance between charge separation and recombination plays an important part in defining device efficiency, but the mechanism by which charge separation occurs in Sb_2S_3 -based systems has been relatively poorly understood. In the first part of this work, transient absorption spectroscopy is used to probe interfacial electron and hole transfer in mesoporous $\text{TiO}_2/\text{Sb}_2\text{S}_3$ -based photovoltaic assemblies. The reported observations point to the importance of the hole transfer reaction not simply as a means of regenerating the sensitiser, but rather as an integral part of the charge separation process.

Inspired by these results, a novel device architecture and processing route is developed in which the structural, optical and electrical properties of the sensitised TiO_2 film are encompassed in a single component; namely a mesoporous Sb_2S_3 photoanode. The resulting high surface area is shown to allow for efficient charge transfer to a polymeric hole acceptor, whilst electron transport through the Sb_2S_3 layer is demonstrated by the fabrication of functioning photovoltaic devices.

In order to consider the role of mesostructure in Sb_2S_3 -based solar cells, devices based on a flat Sb_2S_3 /hole transport material (HTM) interface are developed and compared to SSSC analogues. It is found that although these two classes of device are structurally very different, overall performance is remarkably similar. This highlights the impressive performance of the thin-film assembly, but also draws into question the importance of meso-scale morphological control. Through a combination of transient absorption spectroscopy and transient photovoltage measurements, it is determined that structural limitations to interfacial charge separation can be overcome in these systems by the action of an electric field.

Understanding the role of mesostructure is a particularly pertinent challenge in the context of organic lead halide perovskite absorbers, with which very high efficiencies have been achieved in a range of structured and non-structured device architectures. Here, it is shown that the presence of a mesostructured electron acceptor to rapidly quench the perovskite excited state enhances the stability of interfacial charge separation and significantly increases innate tolerance to environmental processing conditions. This work highlights a significant advantage of retaining mesoscale morphological control in the preparation of efficient, low cost and stable hybrid photovoltaics.

Declaration of Originality

Except where specific reference is made to the contributions of others, this thesis represents my own work. No part of it has been submitted to satisfy the requirements of any other degree at this or any other university.

Flannan T. F. O'Mahony

April 2014

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List of Publications

The Importance of Photoexcited Electron Extraction for Sustained Organic Lead Halide Perovskite Photovoltaic Performance O'Mahony, F. T. F.; Lee, Y. H.; Jellett, C.; Gratzel, M.; O'Regan, B. C.; Nazeeruddin, M. K.; Haque, S. A.; *To be submitted to Nature Communications* **2014**

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Solution Processed Polymer–Inorganic Semiconductor Solar Cells Employing Sb₂S₃ as a Light Harvesting and Electron Transporting Material Bansal, N.; O'Mahony, F. T. F.; Lutz, T.; Haque, S. A. *Advanced Energy Materials* **2013**, 3, 986

Solution-Processed Mesoscopic Bi₂S₃:Polymer Photoactive Layers MacLachlan, A. J.; O'Mahony, F. T. F.; Sudlow, A. L.; Hill, M. S.; Molloy, K. C.; Nelson, J.; Haque, S. A. *ChemPhysChem* **2014**, Available Online

Energy Level Alignment in TiO₂/Metal Sulfide/Polymer Interfaces for Solar Cell Applications Lindblad, R.; Cappel, U. B.; O'Mahony, F. T. F.; Siegbahn, H.; Johansson, E. M. J.; Haque, S. A.; Rensmo, H. *Physical Chemistry Chemical Physics* **2014** Submitted

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1 Introduction

As a planet, we are in the midst of one of the greatest periods of change in terms of how we source, produce, trade and consume energy since the Industrial Revolution. Some of the very foundations upon which our global energy economy has been built are being uprooted and re-established: traditionally importing countries are becoming exporters, exporters are becoming importers, new and valuable global trade routes are developing and novel technologies are revolutionising the scale of natural resources available to us. At the same time, our demand for energy continues its near exponential growth. Whilst global growth is currently being led by China, India is expected to take over its chief driver by 2020. Elsewhere, the United States is moving towards self-sufficiency following the shale gas revolution; Brazil is to become the world's number one oil exporter by 2015; Canada, rather than sending energy commodities south of the border, is exporting to China; Japan and Germany are all but dismantling their reliance on nuclear power following the Fukushima disaster; the UAE is even importing natural gas from the USA.¹

An important implication of these wholesale and monumental shifts is that the price of energy is fluctuating, and most significantly, it is doing so in different ways in different regions of the world. Whilst cheap and abundant natural gas is driving prices down in the USA, with China and Latin America expecting similar trends as they begin to exploit their own unconventional gas resources, costs in Japan and the European Union are expected to soar. This discrepancy could seriously challenge international competitiveness in energy intensive industries, with major and far-reaching economic consequences.

At the same time, some familiar and obstinate pillars of the old world stand unmoved amongst these revolutionary winds of change. Firstly, worldwide fossil-fuel subsidies continue to increase. Secondly, and by no means independently, CO₂ emissions are still rising. If we continue to augment the emission of greenhouse gases at the same rate, we are on track for a long-term 3.6 °C rise in average global temperature,¹ which is significantly in excess of the 2 °C target agreed by the United Nations. The implications of such an overshoot would be catastrophic and irreparable. Thirdly, but firmly at odds with the previous points, fuel poverty remains brutally widespread and there are currently 1.3 billion people in the world without access to electricity. Double that; namely 25 % of the world's population, are still only able to cook using traditional biomass. How can we address these vital and seemingly conflicting issues? How do we balance our moral responsibility to ensure universal access to secure and reliable sources of energy without destroying the long-term future of our environment and our species?

At the heart of any serious attempt to meet this challenge must be a diversification of the energy mix to include more green and renewable energy sources, such as solar, wind, hydropower and biofuel. Although a certain degree of progress is being made on this front – the recent BP Energy Outlook 2035 predicts that the global electricity market share of renewables will rise from its current value of 5 % to 14 % by 2035 –² we are clearly not advancing as quickly as we need to. Indeed, there are indications that progress may even be stalling, with the Bloomberg New Energy Finance research group reporting that total investment in clean energy has fallen successively in 2012 and 2013, largely as a result of subsidy cuts in EU countries.³

Ultimately, wholesale changes in fuel diversity will be driven by relative prices. Even for the aforementioned BP renewables scenario to be realised, reductions in policy support must be counterbalanced by continued improvements in the energy efficiency of alternative technologies and reductions in the costs of materials, processing and infrastructure. This is especially true for photovoltaic (PV) technologies. The magnitude of solar energy incident upon the Earth makes the Sun an undoubtedly attractive and almost infinitely promising power resource. However, comprehensive and effective energy market penetration of solar conversion systems has been hindered by the significant expense of producing and installing suitably efficient modules. Whilst this imbalance may have been masked recently by an artificially low price induced by the alleged dumping of Chinese-made PV on European and US markets, the introduction of trade regulations and reductions in government subsidies are likely to act as further deterrents to investment. Furthermore, there is a strong argument to suggest that subsidisation does little economical or environmental good in the long term, as it encourages companies to sell established but limited technologies rather than taking on the risk of investing in innovation. In Germany for example, the government has committed €100bn to subsidising solar energy over the next 20 years, to achieve an anticipated 0.7 % fulfilment of primary energy consumption.⁴ Meanwhile, the *Energiewende* policy – the decisive and proactive shift from fossil fuels and nuclear to renewables – has contributed to an escalation of domestic fuel poverty and significant export losses in the manufacturing sector.⁵ Without the development of cheaper and more efficient technologies, even the best intentions may be doomed to failure.

For silicon-based solar cells, which have thus far represented the most commercially viable photovoltaic option, the scope for increasing efficiency without causing costs to skyrocket is limited. On this basis, the investigation of cheaper materials and processing routes and the design of modules with lower balance-of-system costs is a more auspicious means of readdressing the cost-efficiency trade-off.

One way to reduce the cost of producing photovoltaics is to move away from our reliance on expensive and energy intensive vacuum deposition processes and towards cheaper and more versatile solution-based methods. This motivation has led to the study and development of solar cells based on

materials such as organic polymers, molecular dyes and solution-processable inorganic semiconductors. However, the use of these materials creates new challenges for the design of photovoltaic systems and efficiencies are yet to compete with more traditional technologies. In order to overcome this performance gap, continued efforts to improve understanding of how this new generation of devices might work and the factors that limit their performance are vital, as are as the design of novel device architectures and the continued investigation of new materials. This thesis aims to address some of these issues, specifically with respect to the application of solution-processed inorganic semiconductors in hybrid photovoltaics and the factors that may govern device performance.

1.1 References

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- (2) *BP Energy Outlook 2035*, BP, 2014.
- (3) *Press Release - Global Trends in Clean Energy Investment*, Bloomberg New Energy Finance, 2014, <http://about.bnef.com/>.
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2 Background, Theory and Motivations

2.1 Semiconductors – Discrete Orbitals to Continuous Bands

On an atomic level, electrons exist in discrete quantum energy levels, or atomic orbitals. When two atoms combine to form a molecule, the energy levels rearrange, or split, to form a pair of molecular orbitals, one of which exists at a slightly lower energy than the original atomic levels and the other at a slightly higher energy. These are the bonding and antibonding molecular orbitals, respectively, and are illustrated in Figure 1a for a simple diatomic molecule. As increasingly more atoms are combined to form larger and more complex molecules, the discrete molecular orbitals begin to overlap. In a crystal, this happens to such an extent that the molecular orbitals behave as though no longer discrete from one another and form continuous bands of energy levels (Figure 1b).

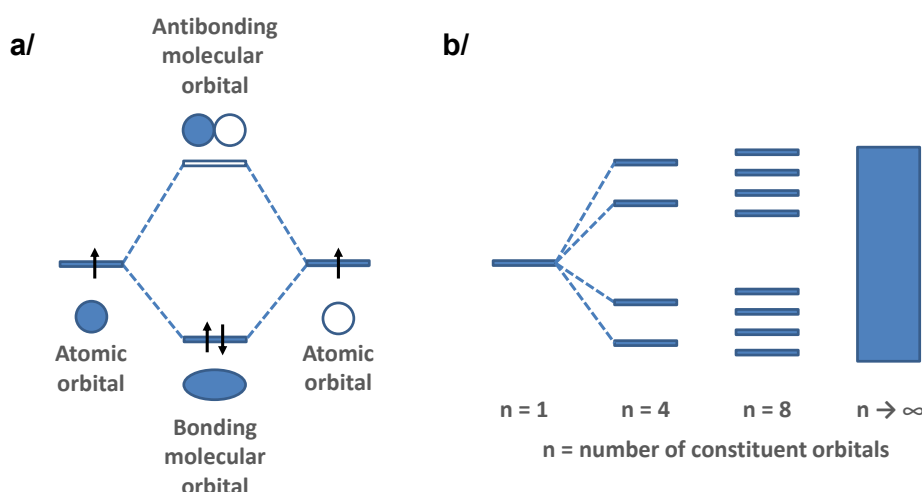


Figure 1 - Illustrations to show a/ the formation of bonding and antibonding molecular orbitals for a diatomic system and b/ the formation of continuous bands from molecular orbitals.

The highest energy band that is occupied with electrons is the valence band, whilst the lowest energy band vacant at absolute zero is the conduction band. Within the conduction band, electrons are no longer directly involved in bonding and are free to move through the material. The same is true of the holes of positive charge that remain in the valence band and the material is able to conduct electricity. For a metal, the valence and conduction band overlap energetically, such that excitation to the unoccupied band occurs readily (Figure 2) and the material behaves intrinsically as a conductor. If an energy gap or bandgap (ΔE_G) exists between the valence band and the conduction band, the material

will either behave as an insulator (if $\Delta E_G > \sim 3 \text{ eV}$) or a semiconductor (if ΔE_G falls within the approximate range of 0.5 - 3 eV). For an insulator, the difficulty in providing the energy required to excite an electron from the valence band to the conduction band is sufficient to critically inhibit the possibility of electrical conduction. Similarly, for a semiconductor in the dark at low temperature, limited conductivity is observed as very few electrons in the valence band possess sufficient kinetic energy to traverse the bandgap. However, provision of this energy through external means such as heat or light allows the material to conduct charge. This intrinsic conductivity decreases with increasing bandgap.

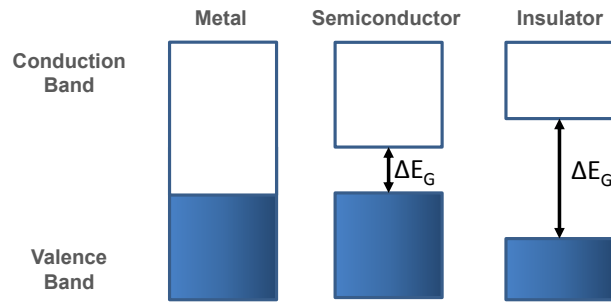


Figure 2 – Illustration of the band structure of a metal, a semiconductor and an insulator.

At absolute zero, electrons possess no kinetic energy and thus occupy the lowest energy levels available to them. The electrochemical potential of these electrons defined the Fermi level E_F . As the temperature is increased, electrons can be excited into states of higher energy. At thermal equilibrium, the probability of electron occupation at a given energy E at temperature T is given by the Fermi-Dirac distribution:

$$f(E, E_F, T) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \quad (2.1)$$

and the number density of electrons $n(E)$ in the energy range of E to $E + dE$ for a distribution of states $g(E)$ is given by:

$$n(E)dE = g(E)f(E, E_F, T)dE \quad (2.2)$$

In a semiconductor, the occupied valence band and the vacant conduction band are separated by an energy gap containing no available electronic states and the Fermi level sits within the bandgap. At room temperature, the density of electrons in the conduction band of a perfect and unmodified semiconductor crystal will be relatively low and the material will only be weakly conducting. However, the conductivity of the semiconductor can be modified by the introduction of electron or

hole donating impurities into the crystal lattice. Doping the material in this manner introduces extra states into bandgap of the material from which electrons (or holes) are more readily freed from bonding to conduct charge (Figure 3). This also changes the electrochemical potential of electrons in the system and therefore the Fermi level shifts, with the direction of movement depending upon the nature of the dopant; if an electron deficient dopant is introduced, electrons are withdrawn from the conduction band and the Fermi level shifts towards the valence band (p-type doping) whereas the introduction of excess electrons causes the Fermi level to move towards the conduction band (n-type doping).

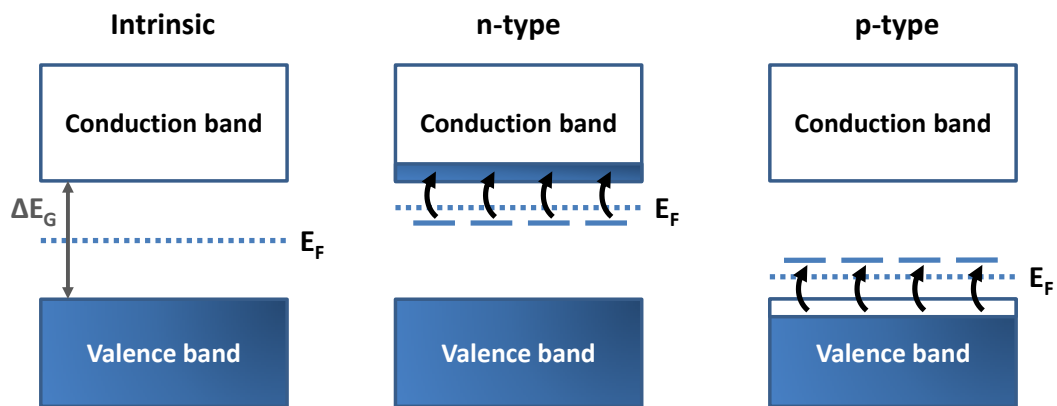


Figure 3 – Illustration of semiconductor inter-bandgap states introduced by n-type and p-type doping.

The presence of spatially localised energy states within the bandgap of a semiconductor, whether introduced intentionally by doping or unintentionally, for example as a result of surface or bulk defects or at grain boundaries between adjacent crystals, can trap charge carriers and potentially act as recombination centres, as well as influencing the distribution of electric field at an interface with another material.¹ The influence of surface traps becomes increasingly relevant as the physical dimensions of the semiconductor are reduced and the surface-to-volume ratio increases, whilst solution processing often increases the probability of finding bulk defects within the semiconductor crystal.

2.2 Semiconductor Junctions and Inorganic Photovoltaics

Photoconductivity is realised in a semiconductor by the promotion of valence electrons to the conduction band by absorption of photons with energy greater than the bandgap. This is the first step towards photovoltaic energy conversion. In a working solar cell, these photogenerated electrons and holes (the corresponding units of positive charge left behind in the valence band) must be separated from one another and transported through the material to external contacts before they recombine and are wasted. For this to happen, some kind of driving force is required. In photosynthesis, charges are spatially separated by a series of electron transfer reactions, which are driven by differences in the free energy of adjacent electron donor and acceptor sites. Alternatively, charge separation and transport can be achieved by introducing an inherent asymmetry to the device through the combination of electronically heterogeneous materials and the generation of an electric field. This situation is most simply represented by considering the interaction between a semiconductor and a metal and the formation of a Schottky junction. When the two materials are brought together, electrons flow from the lower to the higher work function material until thermal equilibrium is achieved and the Fermi levels equilibrate. As a result of this redistribution of charge, a layer of positive local electrostatic potential energy exists in the material that has donated its electrons, with an equal and opposite amount of negative charge transferred to the accepting material. This causes an electric field to develop near the junction. Figure 4 illustrates this behaviour for an n-type semiconductor and a metal, where the work function of the metal is greater than that of the semiconductor ($WF_m > WF_n$).

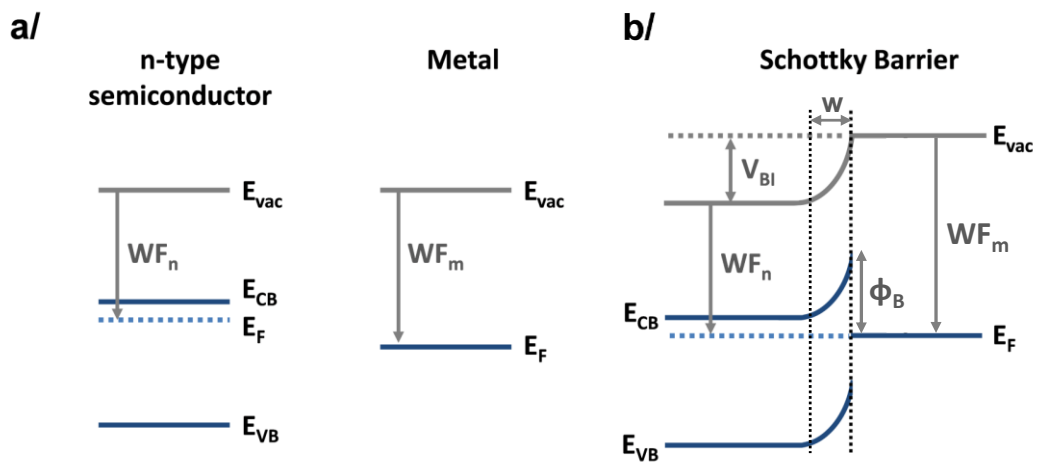


Figure 4 – Illustration of the formation of a Schottky barrier between an n-type semiconductor and a metal.

Upon contact of the materials described in Figure 4, electrons flow from the semiconductor to the metal, the Fermi level equilibrates throughout the composite and an electric field develops across the

junction. The bandgap of the semiconductor and its electron affinity remain constant, as does the work function of the metal and change in the electrostatic potential energy is represented by a change in the vacuum energy E_{vac} and the strength of the electric field is represented by the gradient of E_{vac} . In each material, the region in which the field drops is termed the space charge region or the depletion layer, whose width w is related to the dielectric permittivity of the material ϵ , the size of the built in potential difference V_{BI} and the free charge density (the doping density in a semiconductor) N_A :

$$w = \left(\frac{2\epsilon V_{BI}}{qN_A} \right)^{1/2} \quad (2.3)$$

where q is the elementary charge. As metals contain a very high concentration of free charge carriers, the field drop within the metal occurs in extremely close proximity to the interface. In the semiconductor, the width of the space charge region, which contains the immobile positive charges left behind following electron migration to the metal (if the semiconductor is n-type), is more significant. As such, a macroscopic asymmetry develops in the form of a difference in electrostatic potential in the bulk of the material and in the interface region. The direction of the associated electric field depends upon the respective Fermi levels of the isolated materials. For the example shown in Figure 4, a Schottky Barrier of height Φ_B has been formed whereby the field has introduced an increased resistance to the motion of electrons from the bulk of the semiconductor to the interface but a path of lower resistance for holes. In the dark, such a system would operate as a diode; electron flow from the semiconductor to the metal would only take place when the height of the Schottky barrier was reduced by applied voltage. Current flow in the other direction would be limited by the low concentration of mobile holes in the n-type semiconductor.[†]

Under illumination, the space charge layer can cause photogenerated electrons and holes to separate from one another before they can recombine, with electrons being pushed towards the bulk of the semiconductor and holes being collected by the metal. The build-up of negative charge in the semiconductor layer and positive charge in the metal causes the Fermi level to split and a photovoltage is generated. The requirements of both charge generation and separation are satisfied, and providing the charges can be extracted, the system functions as a solar cell.

[†] A similar but reverse effect would be observed if an equivalent p-type semiconductor-metal junction was formed, whereby the Schottky barrier would drive electrons in the semiconductor towards the metal and holes towards the bulk. When a semiconductor (n- or p-type) –metal junction is formed and the work function of the semiconductor is greater than that of the metal, an Ohmic contact is formed.

Whilst the Schottky barrier heterojunction is a simple example of a photovoltaic system, the amount of photovoltage that can be generated is somewhat limited.¹ Far greater success can be achieved by using the junction between two differently doped regions of a semiconductor to separate and transport photogenerated charges as in a p-n homojunction. In this configuration, the absence of a physical material boundary has the advantage of eliminating losses associated with undesirable interface states that can develop at a heterojunction. This was the strategy employed by the early PV researchers at the Bell Laboratories in New Jersey in the 1950s, who developed the first practical solar cells. It is also one that underpins many of the most efficient modern devices.

When semiconductors with different doping levels are brought into contact with one another, electrons flow from the p-type material to the n-type until the Fermi levels equilibrate and a depletion region forms at the interface (Figure 5). The opposing layers of fixed counter-charge that remain on either side of the junction following ionisation of the dopant atoms cause an electric field to develop across the interface. This is represented in Figure 5 by a shift in the vacuum level. The junction region provides a barrier to majority carriers and the device behaves as a diode. Unlike at a semiconductor-metal interface, the depletion region effectively extends into each component, which when the cell is illuminated can allow photogenerated minority carriers (electrons in the p-type material and holes in the n-type) on both sides to be swept across the junction. Again, the depth to which the depletion region extends into each material depends on the respective doping densities and dielectric permittivities. When the assembly is illuminated, electron-hole pairs are created in the depletion region, where they are separated by the electric field, but also within the neutral bulk of each material. In the latter case, minority carriers must diffuse to the depletion region before they can be separated. Given that for a solar cell optical thickness must ideally exceed the absorption depth to ensure that no incident light is wasted, minority carrier diffusion can become a limiting factor in the photocurrent generation process. For crystalline silicon – probably the most commonly used material in p-n junction photovoltaics – this imposes the expensive requirement for very high standards of crystal purity. The intrinsic defects of polycrystalline and amorphous materials increase the number of carrier traps and recombination sites and thus reduce minority carrier diffusion lengths.

When minority carrier diffusion lengths are short, for example when the use of less pure materials is desired, one approach to avoiding the issues associated with photogenerated charges not reaching the depletion region is to introduce an intrinsic (non-doped) semiconductor region in between the p- and n-type layers. In such a p-i-n junction configuration, the same built-in potential develops as for the equivalent p-n junction, but the electric field extends through the depth of the intrinsic semiconductor layer (Figure 6). In this case, a much higher proportion of photogenerated charges experience the separating effect of the electric field, although series resistance in the device is typically increased.

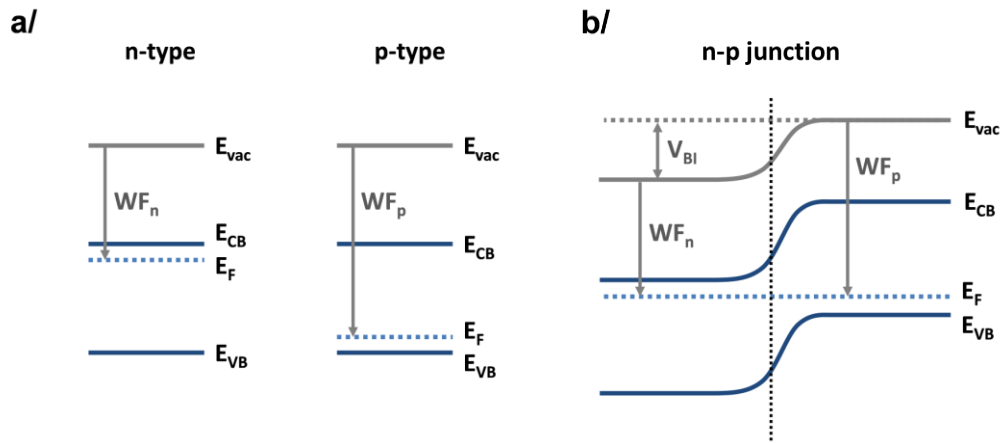


Figure 5 – Illustration of the formation of a p-n junction between an n-type and a p-type semiconductor.

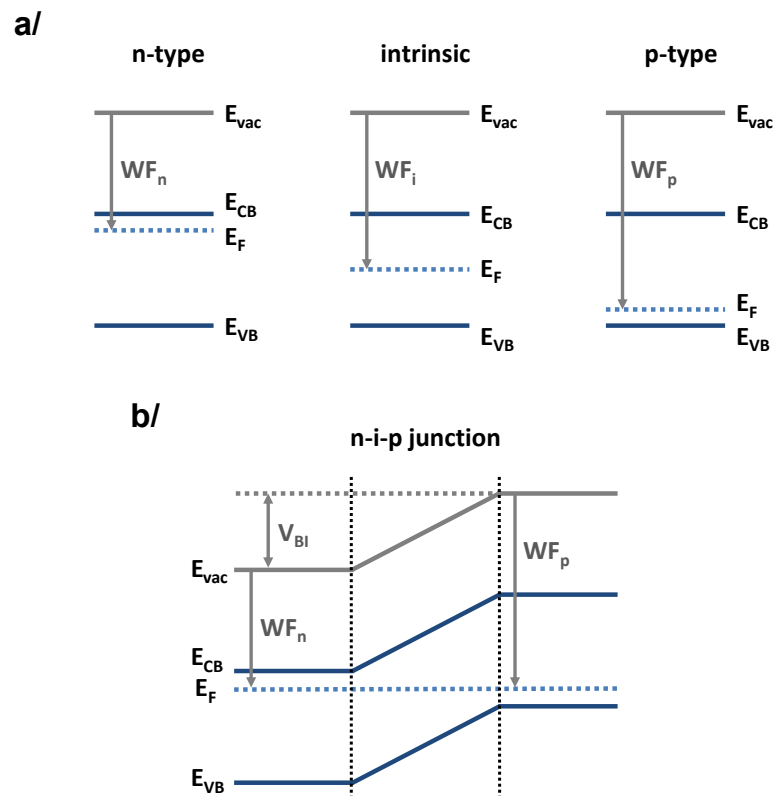


Figure 6 - Illustration of the formation of a p-i-n junction between an n-type, an intrinsic and a p-type semiconductor.

2.3 Excitonic Photovoltaics

When light is absorbed in an inorganic semiconductor, the high dielectric constants ensure that photogenerated electron and hole are only loosely bound to one another by coulombic forces. Conversely in molecular semiconductors, such as certain organic polymers and small molecules (which typically have much lower dielectric constants), photogenerated charges exist as tightly bound electron-hole pairs, or excitons. In these instances, the electrostatic fields resulting from differences in work function are rarely strong enough to break the strong coulombic coupling and radiative recombination occurs rapidly. However, by careful design, the offset of energy at a heterojunction between two materials can provide the driving force required to split the coupled charges. The distance that an exciton can travel before recombination occurs is the exciton diffusion length, and this is often only on the scale of tens of nanometres. Meanwhile, hundreds of nanometres of optical depth are required to ensure effective light harvesting. One way of addressing these conflicting requirements is by controlling the morphology of the interface, such that excitons are always generated in close proximity to the heterojunction but continuous pathways still exist for transport of the separated charges to the contacts. This can be achieved by using a two-component blend of donor and acceptor materials, such as in a bulk-heterojunction solar cell.² In these systems, charge transport is driven by the electrostatic potential difference between the two electrodes, in similar manner to a p-i-n junction. An alternative strategy involves the decoupling of light absorption and charge transport, such as in a dye sensitised solar cell (DSSC).

2.3.1 Dye Sensitised Solar Cells

In a dye sensitised solar cell, a thin layer of photosensitive dye is sandwiched between electron and hole conducting media. Typically, a wide bandgap, n-type metal oxide such as TiO_2 is used as the electron acceptor, while the hole conductor can either be a redox active liquid electrolyte or a solid-state hole transport material (HTM). For most applications, the development of all solid-state devices is hugely preferable in view of the challenges associated with effectively sealing a volatile solvent within the device. The use of a thin absorber layer ensures that photon absorption always occurs in close proximity to an interface, eliminating the requirement for exciton diffusion to an interface. High optical absorption is achieved by mesostructuring the TiO_2 electrode, which can increase effective surface area by several orders of magnitude.³

Under illumination, the separation of excitons in the sensitizer is initiated by ultrafast electron injection to the electron acceptor, followed by ground state regeneration through hole transfer to the hole conductor.⁴ The interfacial separation of charge causes the quasi-Fermi levels of electrons and hole in the system to split and a photovoltage is generated. The separated charges are transported through the electron and hole transporting materials to selective contacts to produce current. Recombination of photogenerated charges, either within the sensitizer layer or between interfacially separated electrons and holes, competes kinetically with the separation and transport processes, and the balance between these forward and reverse reactions largely defines the performance of the device. For photocurrent to be extracted from the device, it is clearly necessary that the rates of charge separation and transport exceed those of the respective competing recombination processes. For example, the injection of photoexcited electrons from the sensitizer to the TiO_2 must occur before the excited state relaxes to ground, while electrons in the TiO_2 and holes in the hole transported must be transported to a contact before they are able to recombine with an opposing carrier. Under open-circuit conditions, where no current is extracted from the device, the rates of the forward and reverse reactions are equal and a steady-state population of separated charge exists within the device. The point at which this occurs (as well as the inherent energetics of the device) defines the open-circuit voltage V_{OC} .

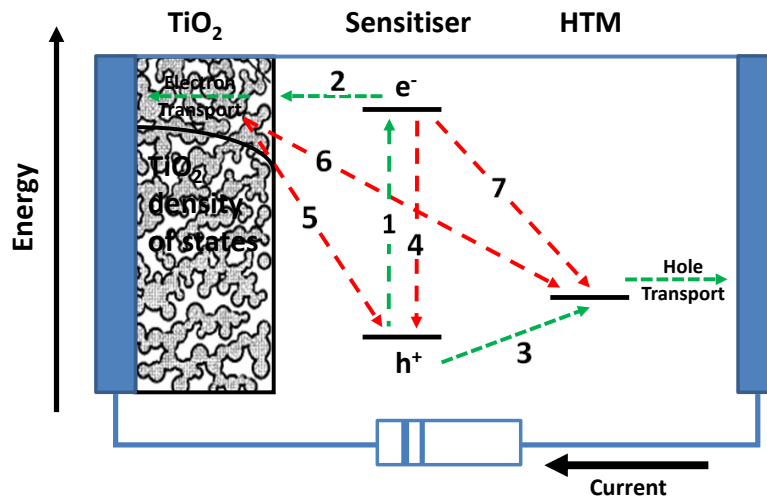


Figure 7 – Schematic to illustrate charge photogeneration, separation and recombination in a sensitised solar cell. Details of these processes are provided in the main text.

The fundamental operational mechanism of a sensitised solar cell is illustrated in Figure 7, where the following charge separation and recombination processes are represented:

1. Absorption of light induces photoexcitation
2. Electron injection from the sensitiser to the metal oxide
3. Hole transfer to the HTM
4. Relaxation of the sensitiser excited state
5. Interfacial recombination of injected electrons with holes in the sensitiser
6. Interfacial recombination of injected electrons with holes transferred to the HTM
7. Recombination of electrons in the sensitiser with holes in the HTM

2.3.2 Semiconductor Sensitised Solar Cells

Nanocrystalline inorganic semiconductors are attractive alternatives to molecular dyes for sensitising mesoporous TiO_2 .^{5,6} Not only do many of these materials possess high extinction coefficients and the capability for multiple exciton generation (where a single photon could be used to generate more than one charge carrier), but also quantum confinement effects allow the absorption onset to be tuned by variation of particle size and thus present the option of tailoring photoresponse to suit a specific application. Briefly, these changes in electronic structure occur when the physical dimensions of a semiconductor crystal (in 1, 2 or 3 dimensions) are smaller than the exciton Bohr radius. Confinement of the wavefunction in this manner causes the electronic structure at the band edges to shift from a continuum of states to discrete energy levels. Within the regime of quantum confinement (typically $< \sim 10$ nm for cadmium chalcogenides, or ~ 50 nm for lead chalcogenides),⁷ reduction in the dimensions of the crystal cause the bandgap to increase in energy and therefore the absorption onset to blue-shift. For a detailed theoretical treatment of quantum confinement effects, the reader is encouraged to consult an excellent review by Bawendi *et al.*⁸

A range of metal chalcogenides have been considered as nanocrystalline sensitisers, including CdS, PbS, InP, Sb_2S_3 and CdSe. To coat the metal oxide surface, nanocrystals can either be pre-synthesised as discrete quantum dots (*ex-situ*) and then attached to the metal oxide by virtue of a bi-functional molecular linker, or grown directly on the surface (*in-situ*) by solution, vapour, or electrochemical means. Whilst the former approach allows for better definition of nanocrystal size and shape as well as enhanced control of surface passivation, the latter affords ease of processing and typically results in a more intimate contact between the absorber layer and the surface of the metal oxide. Currently, the record efficiency for an *ex-situ* quantum dot-sensitised solar cell (QDSSC) is 6.8 % and was achieved using mesoporous TiO_2 , CdTe/CdSe core/shell quantum dots and a liquid polysulfide electrolyte.⁹ However, solid-state devices prepared in this configuration have generally proven to be much less efficient. In contrast, devices consisting of a mesoporous TiO_2 electrode coated *in-situ* with Sb_2S_3 via chemical bath deposition and infiltrated with a solid organic polymer hole conductor have achieved a record 7.5 % efficiency.¹⁰ It is noted that *in-situ* deposited absorber layers rarely resemble monolayer arrays of discrete quantum dots, but rather exist as a thin polycrystalline layer that may or may not display quantum confinement effects. For this reason, such systems are often referred to as extremely thin absorber (ETA) solar cells.

In a similar manner to the conventional DSSC, device performance of the semiconductor-sensitised analogue is largely defined by the delicate kinetic balance between charge separation, transport and recombination. For the dye-cell, many years of research have informed a relatively comprehensive

understanding of these processes and thus helped elucidate the structure-function relationships and design rules required for the reliable preparation of high-performance devices and the informed selection of novel materials. However, the replacement of a molecular dye with an inorganic nanocrystal absorber can introduce significant changes to the way in which the device operates, due to factors such as differences in surface coverage, the prevalence of inter-bandgap states at the nanocrystal surfaces that can mediate charge separation and recombination, the possibility of charge accumulation within the semiconductor sensitiser layer and the potential ability of nanocrystals to conduct charge themselves.¹¹ As such, new studies that focus specifically on semiconductor-sensitised systems are of crucial importance. For example, whilst it is often desirable to extend the photoresponse of a nanocrystalline sensitiser towards the infrared by reducing particle size, it has been shown that the loss of driving force for electron injection associated with lowering the energy of the sensitiser conduction band can retard interfacial separation, thus allowing recombination to become increasingly competitive and reducing overall yield.¹²⁻¹⁴ For a more detailed discussion of progress in the understanding of the factors influencing charge separation and recombination in SSSCs, the reader is referred to recent reviews by Rhee *et al.*,¹⁵ Selenski *et al.*,¹⁶ and Roelofs *et al.*,¹⁷ as well as slightly older but valuable contributions from Mora-Seró and Bisquerts,¹⁸ and Kamat.¹⁹

Very recently, a new class of solution-processable inorganic absorbers have been used to achieve extremely high efficiencies in a wide range of solid-state device architectures (with PCEs of up to 16 %), including when used as a sensitiser for mesoporous TiO₂.²⁰⁻²² These organic lead halide perovskites form the focus of Chapter 7 and will be discussed in greater detail therein.

2.3.3 Colloidal Quantum Dot Solar Cells

When nanocrystalline semiconductors were first introduced into photovoltaics as sensitisers for mesoporous metal oxides, it was thought that only a thin absorber layer could be used if efficient charge separation was to be achieved. On this basis, a mesostructured interface would be required for the film to absorb sufficient light. The development of efficient flat-junction colloidal quantum dot (CQD) solar cells suggests that this may not always be the case.^{5,23} In the depleted heterojunction configuration, a dense film of photosensitive p-type quantum dots is deposited on the surface of a flat transparent FTO/TiO₂ electrode and the resulting built-in field is used to separate photogenerated charges. In these systems, where the CQD layer acts as both light absorber and hole conductor, photocurrents exceeding 20 mA cm⁻² can be extracted from 400 - 500 nm thick layers of PbS²⁴ or CdTe.²⁵ Interestingly, when the flat metal oxide is replaced with a mesostructured electrode, enhanced interfacial recombination inhibits V_{OC} and overall performance suffers.²⁶

2.3.4 Hybrid Solar Cells

Another way of exploiting the charge transport and absorption properties of nanocrystals is by blending them with an organic polymer to act as alternative electron acceptor/transport materials to fullerene derivatives,²⁷ which display only limited absorption and contribute to instability.^{28,29} The intention of developing these hybrid solar cells is to combine the favourable properties of both components, such as stability, strong and tuneable absorption and high charge mobilities of the inorganic material with the ease of processing, flexibility and low-cost of organic polymers whilst also substantially expanding the library of potential material combinations and broadening photoresponse. Most commonly, these devices are based on a bulk heterojunction (BHJ)-type architecture where the electron donor and acceptor materials are intimately mixed on the nanoscale to form a thin blended film sandwiched between selective contacts.³⁰⁻³² Ideally, light is absorbed by both components and photogenerated carriers are separated at the heterojunction, before being transported out of the film through a continuous channel of either polymer or inorganic (most commonly for holes and electrons, respectively). A key challenge to the development of these systems revolves around the question of how best to physically integrate the inorganic material into the polymer film without compromising charge separation or transport.³³ As such, control of nanoscale morphology has been shown to be vital to the achievement of high internal conversion efficiencies.³⁴⁻³⁶ One approach to this, which also circumvents the requirement for labour intensive synthesis and surface modification of colloidal quantum dots,³⁰ involves the *in-situ* decomposition of a precursor to the inorganic component in a polymer film to yield an interconnected network of nanocrystals whose surfaces are passivated by the polymer itself. This strategy has successfully been applied to the preparation of devices consisting of networks of ZnO,³⁷ TiO₂,³⁸ CdS,^{39,40} CuInS₂⁴¹ and Sb₂S₃⁴² nanocrystals within a conducting polymer matrix.

2.3.5 Sb₂S₃–based Photovoltaics

Table 1 details the record device parameters and material composition for various device architectures where nanocrystalline metal chalcogenides are employed as light absorbers, thus highlighting the architectural versatility of this class of materials. For a number of years, crystalline Sb₂S₃ (stibnite) has led the class of ETA-type cells and shown exceptional promise with a range of solid-state hole conductors, including *spiro*-OMeTAD,⁴³ CuSCN⁴⁴⁻⁴⁶ and semiconducting polymers such as P3HT^{47,48} and PCPDTBT.^{10,49} However, at the time of commencing this project, understanding of the mechanisms of charge photogeneration was limited and few design rules existed to aid the development of new and increasingly efficient devices. As a result, the introduction of Sb₂S₃ to alternative hybrid device configurations had not been extensively explored, despite reportedly high electron and hole mobilities.⁵⁰⁻⁵²

Device Type	Material composition	J _{SC} / mA cm ⁻²	V _{OC} / V	FF	PCE / %	Ref.
QDSSC	mp-TiO ₂ / <u>CdTe</u> / polysulfide electrolyte	19.6	0.61	0.57	6.8	9
ETASC	mp-TiO ₂ / <u>Sb₂S₃</u> /PCPDTBT	16.1	0.67	0.65	7.5	10
CQDSC	flat TiO ₂ / <u>PbS</u>	22.7	0.62	0.61	8.5	24
Hybrid Blend	<u>PbS_xSe_{1-x}</u> /PDTPBT	14.7	0.57	0.66	5.5	35
Hybrid Blend (<i>in situ</i>)	<u>CIS</u> /PSiF-DBT	10.3	0.54	0.50	2.8	41

Table 1 – Record efficiencies, associated parameters and material configurations for various device architectures utilising nanocrystalline metal chalcogenide absorbers. In each case, the light harvesting nanocrystalline component has been underlined. The abbreviation ‘mp’ describes a mesoporous electrode structure.

In the meantime, a range of studies have appeared in the literature that have helped to address questions regarding how the Sb₂S₃-based ETA devices work, the factors that affect interfacial charge transfer and recombination, and potential limitations of the system. Amongst these, it has been shown that hole transfer can take place even when electron injection is inhibited and that the former reaction may thus play an integral role in the charge photogeneration process.⁵³ These results are presented in Chapter 4. In subsequent work, Kamat and co-workers suggest that on the basis of ultrafast transient absorption measurements, interfacial hole transfer is mediated by the trapping of holes as sulphur radicals within the Sb₂S₃ lattice.^{52,54} The trapping process is believed to occur on the picosecond timescale, thus disrupting the non-radiative recombination of photogenerated electrons and holes in

the absorber and allowing time for the hole to diffuse to the interface with the hole conductor. Depending on the thickness of the film, either hole diffusion or interfacial transfer can act as the rate limiting step for hole transfer. The strong link between hole transfer efficiency and the efficiency of charge extraction may explain why Im *et al.* found internal conversion efficiency to be highly sensitive to the choice of polymeric hole conductor, with improved performance achieved when a chemical interaction exists between the polymer HTM backbone and the Sb_2S_3 crystal.⁴⁹

Despite the impressive performance achieved with Sb_2S_3 -based ETA cells compared to other metal chalcogenide analogues, even the maximum reported open-circuit voltage of 670 mV represents very significant losses with respect to the bandgap of the absorber (~ 1.7 eV)⁵⁵. Boix *et al.*, have used electrochemical impedance spectroscopy to confirm that fast charge carrier recombination is dramatically limiting V_{OC} , and propose that this effect is likely to be associated with the presence of surface states in the Sb_2S_3 .^{56,57} Lee *et al.* have built on these observations to experimentally confirm the presence of defect states at the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface using deep-level transient spectroscopy,⁵⁸ whilst Darga *et al.* identify an exponentially decaying continuum of Sb_2S_3 bandgap states below the conduction band edge that is believed to contribute to enhanced recombination, but the authors attribute these states to the presence of vacancies and substitutional defects within the bulk of the absorber. Very recently, Choi *et al.* have shown that the elimination of interband defect states through surface sulphurisation can lead to an increase in V_{OC} and improved device performance.¹⁰

Studies such as these have contributed to a significantly enhanced understanding in recent years of the fundamentals of how Sb_2S_3 -based ETA cells work, thus revealing some of the design-rules and structure-function relationships required for the continued evolution of device efficiency. Furthermore, this knowledge has facilitated the informed design of novel photovoltaic architectures based on Sb_2S_3 absorbers,⁵⁹ as well as the targeted introduction of Sb_2S_3 into more familiar hybrid device architectures such as thin film bilayers,⁶⁰ coated-nanowire arrays^{61,62} and bulk-heterojunction-type blends.⁴² The development of some of these systems is described in Chapters 5 and 6.

2.3.6 Solution Processing of Sb_2S_3

Early investigations into the use of Sb_2S_3 in semiconductor devices, such as photoconducting targets for video camera tubes,⁶³ electronic switches⁶⁴ and photodetectors,⁶⁵⁻⁶⁷ involved the preparation of films by thermal evaporation of the powdered metal sulfide. More recently, cheaper and more accessible solution-based processes have taken precedence. The most common of these is chemical bath deposition (CBD), where a substrate is immersed in a reacting solution containing a source of antimony ions (e.g. SbCl_3 , $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2$) and of sulphur ions (Na_2S , $\text{Na}_2\text{S}_2\text{O}_3$). This allows an amorphous layer of the metal sulfide to grow on the substrate surface, with subsequent thermal annealing yielding the crystalline stibnite phase.^{50,68} The most efficient Sb_2S_3 -based photovoltaic devices have been prepared according to this method,¹⁰ but disadvantages include the large quantities of starting materials required (relative to the amount of Sb_2S_3 deposited on the substrate surface), the sensitivity of deposition rate to small fluctuations in temperature and the associated requirement that the reaction solution be kept at a low temperature, and the difficulties in scaling up the process for industrial application. Alternative routes to the preparation of Sb_2S_3 films for photovoltaics, such as spray pyrolysis⁶⁹ and atomic layer deposition⁷⁰ suffer from problems of significant material wastage, high temperatures and the safety challenges associated with vapour deposition in the former case, and the need for advanced and expensive equipment in the latter. Furthermore, efficiencies of the resulting devices are consistently lower than CBD-prepared analogues. As such, the continued development of novel, facile and scalable processing techniques for the preparation of Sb_2S_3 is an important challenge.

The thermal decomposition of solution-processable single-source precursors, such as metal alkylthiocarbonates (metal xanthates) and related complexes, represents a versatile route to the preparation of a wide variety of nanocrystalline metal chalcogenide semiconductors.^{71,72} In the context of photovoltaics, metal xanthates have principally been used to grow interconnected networks of conducting nanocrystals within organic polymer films in the bulk-heterojunction configuration.³⁹ Cadmium sulfide-based systems produced in this manner has been studied extensively,^{34,39,40,73,74} but the ease with which these precursors can be synthesised and processed and the scope of materials available make the xanthate decomposition route an attractive means of introducing other metal sulfides, such as Sb_2S_3 , into a range of device architectures. For these reasons, antimony xanthates have recently been used to grow Sb_2S_3 :P3HT hybrid blends,⁴² ETA layers to sensitise mesoporous TiO_2 ,^{60,75} mesoporous films of Sb_2S_3 for use as solar cell photoanodes⁵⁹ and flat thin films for hybrid bilayer devices.⁶⁰

2.4 Current-Voltage Measurements

The most common way of characterising the performance of a solar cell is to measure the current that flows as a function of applied voltage. In the dark, the device should behave as a diode, allowing current to flow in forward bias, but not in reverse. When the cell is illuminated, photogenerated carriers deliver photocurrent and/or photovoltage, both of which scale with light intensity. Typical current-voltage curves, in the dark and under illumination, are illustrated in Figure 8. At open circuit conditions, the rates of charge separation and recombination are equal, no net current flows and the cell achieves its maximum photovoltage V_{OC} . The amount of photocurrent produced under short-circuit conditions, where by definition no photovoltage is produced, is defined as the short-circuit current J_{SC} . In between V_{OC} and J_{SC} , the device generates power. The maximum power P_{max} can be described by the sum of J_{SC} and V_{OC} , multiplied by the fill factor FF, which quantifies the ratio between the voltage and current at the maximum power point (V_{mpp} and J_{mpp}) and the theoretical maximum power for a given V_{OC} and J_{SC} :

$$FF = \frac{V_{mpp} J_{mpp}}{V_{OC} J_{SC}} \quad (2.4)$$

The overall efficiency of the device is determined by the ratio of the incident power P_{in} to the maximum power generated by the device P_{out} :

$$\eta = \frac{P_{out}}{P_{in}} = \frac{V_{OC} J_{SC} FF}{P_{in}} \quad (2.5)$$

2.4.1 Series and Shunt Resistance

In practice, the relationship between current and voltage in a solar cell is heavily influenced by the dissipation of power through parasitic resistances and leakage current. The series resistance R_S of a cell opposes the flow of photocurrent through the device to the external circuit and is generally associated with the resistance of the transport materials and contacts. Shunt resistance R_{SH} describes the resistance to current loss through alternative pathways. These effects can be represented in an equivalent circuit diagram by a series resistor and a parallel resistor respectively (Figure 9). In a perfect device, series resistance would be very low and shunt resistance infinite. Increasing series and decreasing shunt resistance undermine the diodic characteristics of the device and thus affect the shape of the current-voltage response, as illustrated in Figure 10. As series resistance is increased, the gradient of the J-V curve decreases near V_{OC} (in accordance with Ohm's law), potentially limiting the fill-factor of the device. If the series resistance is high enough, short-circuit current can be affected. V_{OC} is unaffected by R_S as no current is flowing through the device. A low shunt resistance causes a reduction in the gradient at which the J-V curve passes through J_{SC} as current is able to bypass the diode. This means that more current can flow at reverse bias, but that photocurrent between J_{SC} and V_{OC} is limited, resulting in a reduced fill-factor. For very low shunt resistances, the amount of charge that can build up in the device under open-circuit conditions is affected and thus V_{OC} can decrease. At short circuit, there is no resistance (other than R_S) to the flow of photocurrent and so no effect of R_{SH} is seen on J_{SC} .

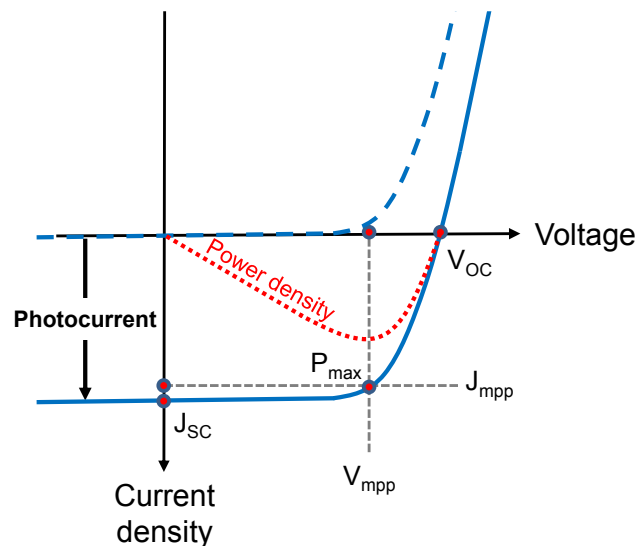


Figure 8 – Illustration of a current density-voltage (J-V) curve in the dark (dashed line) and the light (solid line) to highlight the open circuit voltage V_{OC} , the short circuit current J_{SC} , the maximum power point P_{max} and the current J_{mpp} and voltage V_{mpp} at the maximum power point.

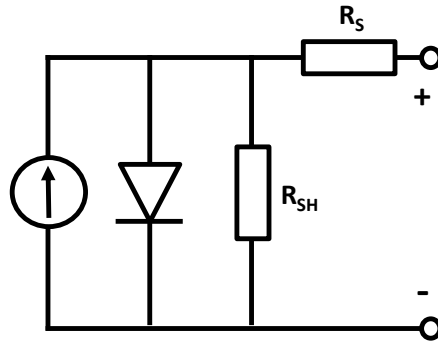


Figure 9 – A simplified equivalent circuit diagram for a solar cell comprising of a current source, a diode, a parallel resistor to illustrate shunt resistance R_{SH} and a series resistor R_S to illustrate series resistance within the device.

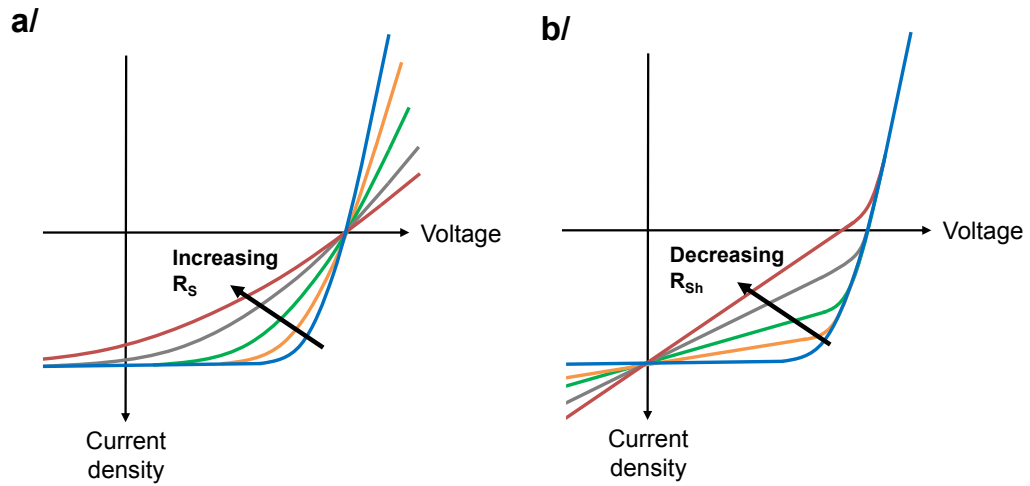


Figure 10 – Illustrations to show the effect of a/ series resistance and b/ shunt resistance on a J-V curve for a photovoltaic device under illumination.

2.5 Project Aims and Motivations

The intention of the preceding discussion has been to provide a small indication of the architectural versatility of nanocrystalline inorganic semiconductors as photovoltaic absorbers. Sb_2S_3 has shown great promise as an extremely thin absorber (ETA) coating for mesoporous TiO_2 , but at the time of commencing this project, understanding of the mechanisms of charge photogeneration was limited and few design rules existed to aid the development of new and increasingly efficient devices. In addition, and indeed perhaps as a result of this, introduction of Sb_2S_3 to alternative hybrid device configurations had not been extensively explored. A key aim of this thesis is to improve understanding of how the interfacial charge separation process proceeds in Sb_2S_3 -sensitised ETA cells and to use the findings to inform the design of novel hybrid devices.

With this objective in mind, transient absorption spectroscopy is used to study interfacial charge separation and recombination in Sb_2S_3 -sensitised solar cells. An attractive feature of using nanocrystalline inorganic semiconductors as photovoltaic absorbers is the ability to modulate photoresponse through quantum size effects. However, changing the absorption properties in this manner also affects the energetic offset between electron donor and acceptor sites and thus the driving force for charge transfer. An aim of the present work is to probe the effect of modulating the driving force on the subsequent yield of long-lived interfacial charge separation. To achieve this, a successive ionic layer adsorption and reaction (SILAR) processing route is developed to control the semiconductor absorption onset. Both the electron injection and hole transfer processes are considered in the hope of elucidating the fundamentals of device operation. This work is described in Chapter 4.

Guided by the results of these studies, the potential of Sb_2S_3 for use in alternative hybrid device architectures is investigated, with a focus on the development of novel, facile and versatile processing routes. In order to determine what constitutes a suitable architectural configuration, it is important to understand the role of electron donor/acceptor interface structure in the charge separation process. In order to study this, it is therefore a pre-requisite to possess a means of controlling film morphology. In an ETA cell, in addition to accepting and transporting photogenerated electrons, the mesoporous metal oxide acts as a structural scaffold and ensures a large interface area. In Chapter 5, the metal oxide is removed from the device architecture but mesostructure is retained through the construction of porous Sb_2S_3 photoanodes. An important requirement is to ensure that pore-size and film morphology can be modified in a controlled manner. This is expected to allow the link between interface area and yields of long-lived charge separation to be probed directly through the use of time-resolved absorption spectroscopy. In Chapter 6 photovoltaic devices based on a planar Sb_2S_3 /polymer hybrid bilayer are developed and compared to analogous ETA-type cells via optical and

optoelectronic measurements. This work aims to determine if, and why, a structured interface is required for effective photocurrent generation.

Finally, in Chapter 7, similar techniques to those developed in the course of this work are employed to study photovoltaic assemblies utilising organic lead halide perovskite absorbers. Recently, it has been shown that remarkably high efficiency photovoltaic devices can be fabricated around either a structured or a non-structured interface. At the time of writing, it is unclear as to which device architecture might possess the strongest claim to long-term commercial viability. The work described in Chapter 7 uses transient absorption spectroscopy to compare and contrast the interfacial charge transfer processes in each of the major structural configurations. The intention of these studies is to determine any potential benefits and/or drawbacks of retaining mesoscale morphological control in the context of a highly efficient and versatile organic-inorganic hybrid system.

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3 Experimental

3.1 Materials and Processing

In this work, thin films of Sb_2S_3 have been prepared by either SILAR dip coating (Chapter 4) or by decomposition of an antimony ethylxanthate precursor (in Chapters 4, 5 and 6). The associated experimental methods are described herein.

3.1.1 Mesoporous $\text{TiO}_2/\text{Sb}_2\text{S}_3$ SILAR

Mesoporous TiO_2 films were deposited on glass microscope slides from Ti-nanoxide T37 paste (37 nm particles, Solaronix) by doctor blading and sintering at 450 °C. Resultant films were measured to be ~6 μm in thickness by profilometry. ZrO_2 films of 20-30 nm particles were also ~6 μm thick. Sb_2S_3 nanocrystals were grown on the surface of the resulting TiO_2 and ZrO_2 mesoporous films by successive ionic layer absorption and reaction (SILAR) from 0.02 M SbCl_3 and 0.02 M Na_2S ethanolic solutions. Reactant solutions were filtered prior to sensitisation. Films were washed in EtOH between immersions in reactant solutions. All immersion times were 1 minute. A single immersion in each reactant solution constitutes one deposition ‘cycle’. Annealing was conducted on a hot plate in a nitrogen glove box. *spiro-OMeTAD* (2,2',7,7'-tetrakis-(N,N-di-p- methoxyphenyl-amine)-9,9'-spirobifluorene, Merck) was deposited by spin coating from a 0.17 M chlorobenzene solution at 2000 rpm for 1 minute. The solution was allowed to rest on the surface of the film for 1 minute prior to spin coating.

3.1.2 $\text{Sb}(\text{EX})_3$ Synthesis and Characterisation

Antimony triethyldithiocarbonate ($\text{Sb}(\text{EX})_3$) was synthesised by the reaction of stoichiometric amounts of antimony (III) chloride (Sigma, no further purification) and potassium ethylxanthate (Sigma, no further purification) in toluene. The reaction mixture was stirred at 70 °C for 1 hour under a mild nitrogen overpressure, developing a bright yellow/green colour in the process. The resulting solution was filtered and evaporated in a rotary evaporator to a viscous oil. The antimony xanthate product was recrystallised from warm chlorobenzene, washed with diethyl ether and dried in a vacuum desiccator to yield yellow crystals (^1H NMR (D_2O): δ 4.66 (3H, q) 1.48 (2H, t)). Thermal

gravimetric analysis confirms that $\text{Sb}(\text{EX})_3$ decomposition occurs between ~ 100 and ~ 150 °C, with the final residual mass of 37 % very close to that expected of Sb_2S_3 (35 %).

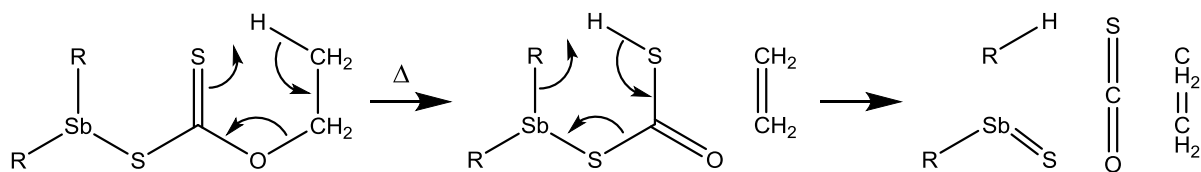


Figure 11 – Proposed mechanism for the thermal decomposition of antimony triethyldithiocarbonate via a Chugaev-type rearrangement, where R represents the ethyldithiocarbonate (xanthate) ligand.¹

3.1.3 Sb_2S_3 -Sensitised Metal Oxides by $\text{Sb}(\text{EX})_3$ Decomposition

For spectroscopic studies (Chapters 4 and 6), mesoporous films of TiO_2 were prepared by spin coating a TiO_2 paste (Dyesol, 18NRT) onto a glass substrate and sintering in air at 450 °C for 1 hour. The mesoporous films were treated with titanium tetrachloride by immersion in a 20 mM solution of titanium (IV) chloride tetrahydrofuran (Aldrich) in water at 70 °C for 30 minutes. Films were subsequently rinsed in water and sintered at 450 °C for a further 30 minutes. A 400 mg mL⁻¹ solution of antimony triethyldithiocarbonate in chlorobenzene was spin-coated onto the mesoporous film and annealed in a nitrogen glovebox at 300 °C to yield the Sb_2S_3 sensitiser. Poly(3-hexylthiophene) (P3HT, Merck) was spin-coated from a 12.5 mg mL⁻¹ chlorobenzene solution at 2000 rpm for 1 minute.

For photovoltaic devices in Chapter 6, the mesoporous films were deposited on a transparent conducting oxide substrate (indium tin oxide) coated with a 20 nm thick dense TiO_2 hole blocking layer, prepared by spin coating a 7:5.5:100 by volume solution of titanium isopropoxide, ethanol amine and 2-methoxyethanol at 6000 rpm for 30 seconds, followed by annealing in atmospheric conditions for 30 minutes at 450 °C. Following spin-coating of P3HT, a 100 nm thick silver contact was deposited by thermal evaporation.

3.1.4 Mesoporous Sb_2S_3

$\text{Sb}(\text{EX})_3$ precursor pastes were prepared by adding a 3:1 molar ratio of hexylamine to a stirred 40 mg mL⁻¹ chlorobenzene solution of antimony triethyldithiocarbonate. Doctor-blading onto cleaned glass (for transient absorption, X-ray diffraction and UV-Vis absorption studies), fluorine-doped tin oxide (FTO, Ossila) substrates (for scanning electron microscopy and X-ray photoelectron

spectroscopy) or indium-doped tin oxide (device fabrication) formed an orange $\text{Sb}(\text{EX})_3$ precursor film. Films were annealed for 30 minutes on a hot plate in a nitrogen glove box to yield porous crystalline Sb_2S_3 films.

Photovoltaic devices include a thin, dense TiO_2 layer in between the ITO substrate and the Sb_2S_3 layer, which was deposited by spin coating a 7:5.5:100 by volume solution of titanium isopropoxide, ethanol amine and 2-methoxyethanol at 6000 rpm for 30 seconds, followed by annealing in atmospheric conditions for 30 minutes at 450 °C. CdS layers (20 nm) were deposited from a 100 mg mL⁻¹ chlorobenzene solution of a pyridine adduct of cadmium ethylxanthate by spin coating at 6000 rpm for 30 seconds, followed by annealing at 160 °C for 30 minutes in a nitrogen glove box.

Poly(3-hexylthiophene) (P3HT, Merck) was spin-coated from a 25 mg mL⁻¹ chlorobenzene solution at 2500 rpm for 1 minute. Poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT:PSS, Ossila) containing 1% Zonyl (du Pont) by volume was spin coated before 100 nm thick Ag contacts were vacuum deposited as the top electrode to give devices with an active area of 0.045 cm².

3.1.5 Sb_2S_3 /P3HT Bilayers

A solution of $\text{Sb}(\text{EX})_3$ in dry chlorobenzene (400 mg mL⁻¹ unless stated otherwise) was spin-coated in air onto the substrate to form a thin yellow film. These precursor layers were annealed (typically at 300 °C) in a nitrogen glove box to yield dark brown thin films of crystalline Sb_2S_3 . Poly(3-hexylthiophene) (Plextronics) was spin-coated in air from chlorobenzene solution (typically 25 mg mL⁻¹) and annealed at 100 °C for 20 minutes to form the bilayer assembly. Where relevant, Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT, Sigma) was spin-coated from a 15 mg mL⁻¹ chlorobenzene solution.

Functioning devices were prepared on indium-tin oxide coated glass (Ossila). A thin TiO_2 electron blocking layer was deposited by spin coating a 7:5.5:100 by volume solution of titanium isopropoxide, ethanol amine and 2-methoxyethanol at 6000 rpm for 30 seconds, followed by annealing in atmospheric conditions for 30 minutes at 450 °C. CdS window layers were prepared by spin coating a 100 mg mL⁻¹ chlorobenzene solution of $\text{Cd}(\text{S}_2\text{COEt})_2(\text{C}_5\text{H}_4\text{N})_2$ (cadmium diethylxanthate with solubilising pyridine adducts) at 6000 rpm for 30 seconds, followed by annealing on a hot plate in a nitrogen glovebox at 160 °C for 30 minutes. The cadmium xanthate precursor was fabricated by Dr. Thierry Lutz and Andrew MacLachlan at Imperial College London according to the method reported by Larionov *et al.*² Sb_2S_3 and P3HT layers were deposited as described above. A

20 nm MoO_x hole blocking layer and a 100 nm Ag top contact were thermally evaporated on top of the assembly to complete the device and define the active area (0.045 cm²).

3.1.6 MAPbI₃ Perovskites

Lead methylammonium trihalide (MAPbI₃) perovskite-based films for transient absorption spectroscopy were prepared by Cameron Jellett from the group of Brian O'Regan at Imperial College London according to literature methods.³ Optical density of the resulting films was controlled by variation in metal oxide layer thickness (for the mesoporous films) and concentration of the MAPbI₃ solution. Bilayer devices were also prepared by Cameron Jellett and mp-TiO₂ devices were prepared by Dr. Yong Hui Lee in Prof. Mohammed Nazeeruddin's group at EPFL Switzerland.

3.2 Physical and Optical Characterisation

3.2.1 UV-Visible Absorption and Emission Spectroscopy

Steady-state absorption spectra were obtained using a Perkin Elmer Lambda 25 UV-vis spectrometer (absorbance measurements). Transmission and reflectance spectra (to calculate % absorption) were measured on a Perkin-Elmer Lambda 750 UV-vis-n-IR absorption spectrometer fitted with an integrating sphere. Photoluminescence emission spectra were measured at room temperature using a Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter.

3.2.2 Raman Spectroscopy

Raman spectroscopy was performed using a Renishaw inVia Raman microscope in a backscattering configuration with a 514 nm Ar laser excitation.

3.2.3 X-ray Diffraction

X-ray diffraction was conducted with a PANalytical X'Pert Pro MRD diffractometer using Ni filtered Cu K-alpha radiation at 40 kV and 40 mA.

3.2.4 Photoelectron Spectroscopy

Photoelectron spectroscopy was performed at beamline I411 at the synchrotron facility MAX-IV (Lund, Sweden).⁴ A photon energy of 758 eV was used and the photoelectrons were detected with a Scienta R4000 analyser. Data in Chapter 4 were collected by Dr. Erik Johansson and Prof. Håkan Rensmo from Uppsala Universitet in Sweden. Here, the pristine TiO₂ spectrum was energy calibrated by setting the Fermi level (the edge of the occupied states) to 0 eV binding energy and spectra for the Sb₂S₃-sensitised TiO₂ films were energy calibrated by aligning the Ti 3p core level peaks to the same binding energy (38 eV) as that of the pristine TiO₂ film. Measurements in Chapter 6 were performed in collaboration with Rebecka Lindblad and Prof. Håkan Rensmo from Uppsala Universitet in Sweden. Here, the binding energies of the XPS spectra were referenced versus the Fermi level at zero binding energy, which was defined by setting the Sn 3d_{5/2} peak (from the FTO conducting substrate) to 487 eV. The spectra are intensity calibrated using the Sb 3d_{5/2} peak

3.2.5 Scanning Electron Microscopy

In Chapter 4, scanning electron microscopy was performed using a Carl Zeiss Ultra Plus Field Emission SEM. Elsewhere, the In Lens detector of a LEO 1525 Field Emission Scanning Electron Microscope operating at 5 kV was used. Samples were sputter coated with a ~17 nm layer of chromium prior the measurement to improve conductivity.

3.2.6 Atomic Force Microscopy

Atomic force micrographs were obtained in air at 25 °C Agilent 5500 AFM/SPM microscope operating in tapping mode (Agilent Technologies), using commercial ‘Super Sharp Silicon’ AFM probes (Windsor Scientific). Images were processed with the Nanotec WSxM Develop programme.⁵ Measurements were collected in collaboration with Dr. Azadeh Bahrami and Dr. Tim Albrecht in the Department of Chemistry at Imperial College London.

3.3 Transient Absorption Spectroscopy

Transient absorption spectroscopy is a pump-probe technique that can be used to monitor the existence of short-lived electronic species. To achieve this, a pulsed laser pump is used to photoexcite a sample and the absorbance of the resulting photogenerated species is monitored with a probe light. Specifically, the difference in absorbance (ΔOD) at the probe wavelength before and after the laser excitation is measured and is thus only representative of changes in the film induced by the pump pulse. The intensity of absorbance of a given species depends upon the concentration of the amount of absorbing species and its extinction coefficient, ε , according to the Beer-Lambert law:

$$OD = \varepsilon c l \quad (3.1)$$

where c is concentration and l is optical path-length. ΔOD can be either positive or negative (i.e. either more or less probe light is absorbed following photoexcitation respectively) with a positive ΔOD corresponding to absorption of light by a photogenerated species, with a negative signal, or photobleach, typically coming as a result of the associated depopulation of the ground state. The regions of the spectrum in which the positive and negative signals occur can overlap to yield a superposition of signals, but bleaching is invariably restricted to the region in which the ground state material absorbs. In addition to the presence and possible overlap of positive and negative signals, a transient absorption spectrum is also an amalgamation of the signals associated with any number of different excited states present at a given time. As such, careful control measurements are required to resolve specific individual contributions.

Once a transient absorption signal has been assigned to a particular species, the evolution and decay of that species can be investigated by changing the delay time between the pulsed laser excitation and the measurement of ΔOD at a given wavelength. This can either be achieved electrically with an oscilloscope and a continuous probe beam, or through the use of a pulsed probe beam with a delay line. The former technique, which is used in the work described in this thesis, typically limits time resolution to the order of hundreds of nanoseconds to seconds, whilst the latter allows for sub-picosecond to nanosecond measurements. In the context of studying solar cells, where charge separation is achieved by the interfacial separation of charges, both of these experimental setups have their merits. Ultrafast measurements are useful for directly monitoring the interfacial electron transfer reactions, whereas the slower technique allows for the long-lived products of interfacial charge separation to be probed, as well as their dynamics of recombination.

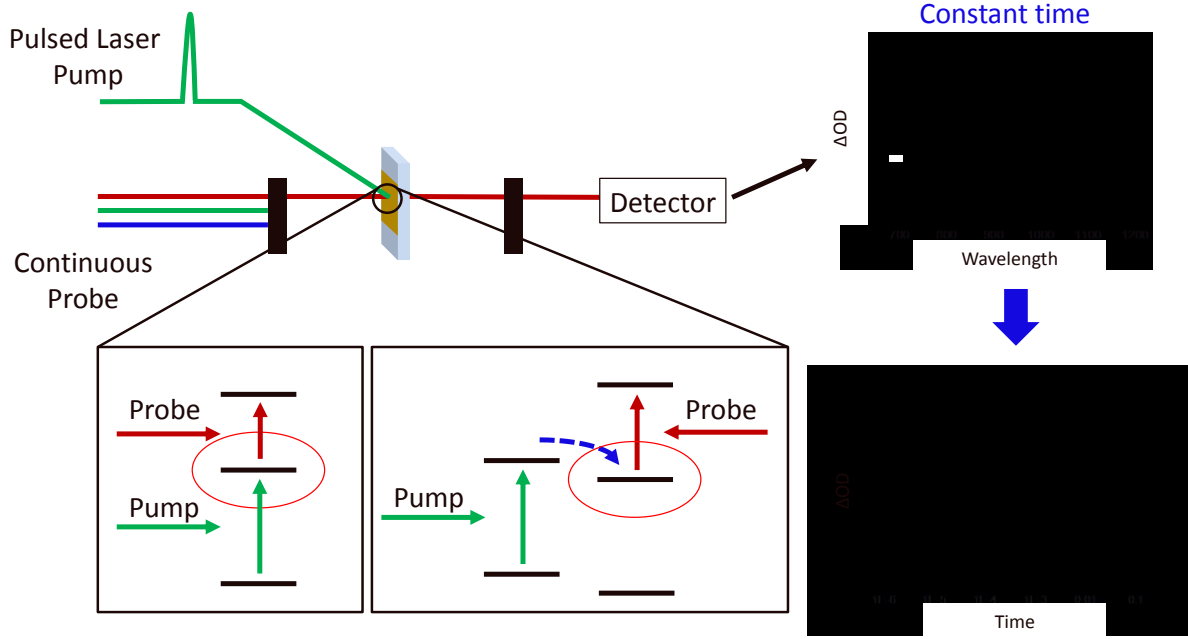


Figure 12 – Schematic to illustrate the transient absorption setup used in the present work.

For pump-probe micro to millisecond transient absorption spectroscopy, films were excited by a dye laser (Photon Technology International GL-301, sub-nanosecond pulse width) pumped by a pulsed nitrogen laser (Photon Technology International GL-3300). A quartz halogen lamp (Bentham IL1) was passed through a monochromator and used to probe changes in the absorption characteristics of the film as a function of time after the laser excitation. The probe light was detected using home-built silicon (≤ 1000 nm) or $\text{In}_x\text{Ga}_{1-x}\text{As}$ (> 1000 nm) photodiodes and an oscilloscope. Unless otherwise stated, films were kept under flowing N_2 during the measurements. Figure 12 shows the basic experimental transient absorption setup and illustrates a transient absorption spectrum (for a given time) and a time-resolved decay (at a given wavelength, λ).

3.4 Device Characterisation

3.4.1 Current-Voltage and IPCE Measurements

Current-voltage characteristics of complete cells were measured using a Keithley 2400 series source meter, in the dark and under illumination from a 150 W Xenon lamp (ScienceTech SS150W solar simulator) with IR filter (Water Filter) and AM1.5 filter (ScienceTech). Light intensities were calibrated to 100 mW cm^{-2} using an independently calibrated silicon photodiode. Illumination for IPCE measurements was provided by a quartz halogen lamp (Bentham IL1) filtered through a monochromator.

3.4.2 Transient Photovoltage Measurements

Transient photovoltage (TPV) measurements were performed by holding a device at open-circuit with a high impedance oscilloscope (Tektronix TDS 3032B) under varying levels of background illumination and using a 522 nm Nd:YAG laser (1Hz, Photonic Solutions Compact Minilite) to optically excite the sample and generate a small number of additional charges. A transient photovoltage is thus induced, which given decays back to equilibrium as the extra charges recombine. The voltage decay is monitored as a function of time using the oscilloscope and can be related to the rate of carrier recombination under these conditions. By ensuring that changes in photovoltage induced by laser excitation are kept low with respect to the V_{OC} created by the background illumination, the resulting TPV decays take the form of a first order process and can thus be fitted by a single exponential. Background light illumination was provided by a white-LED array, whose power was calibrated by matching the resulting current-voltage response of the device in question to that recorded at 1 sun on a calibrated solar simulator. TPV measurements were performed in collaboration with Florent Deledalle and Prof. James Durrant at Imperial College London.

3.5 References

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4 Electron and Hole Transfer at Metal Oxide/Sb₂S₃/Hole Transporter Heterojunctions

Antimony sulfide has demonstrated significant potential as an absorber material in solid-state semiconductor-sensitised solar cells (SSSCs). Here, a transient absorption spectroscopy study of the TiO₂/Sb₂S₃/spiro-OMeTAD heterojunctions is presented to elucidate the key factors influencing charge photogeneration. Efficient device performance requires that photoresponse extends into the near-infrared, yet it is found that the efficiency of charge separation at the TiO₂/Sb₂S₃ interface decreases significantly as increasingly red- absorbing Sb₂S₃ nanocrystals are photoexcited. The efficiency of hole transfer to spiro-OMeTAD appears much less sensitive to shifts in the Sb₂S₃ absorption edge and hole transfer to spiro-OMeTAD is even seen to occur on ZrO₂ substrates, where electron injection is blocked. These observations point to the importance of the hole transfer reaction not simply as a means of regenerating the sensitiser, but rather as an integral part of the charge separation process in Sb₂S₃ SSSCs. Similar behaviour is displayed when spiro-OMeTAD is replaced with the conducting polymer P3HT. However, in this case a high relative yield of charge separation can be achieved on insulating substrates (with respect to TiO₂). The present findings should help inform strategies aimed at further increasing the efficiency of nanocrystal sensitised solar cells.

4.1 Introduction

Nanocrystalline inorganic sensitisers have emerged as attractive alternatives to the molecular dyes traditionally used to light sensitise mesoporous metal oxides in solid state dye-sensitised solar-cell (DSSC) -type devices. It is hoped that by judicious material choice and optimisation of cell design, properties such as tuneable absorption profiles and high extinction coefficients can be exploited to develop high efficiency solid state semiconductor-sensitised solar cells (SSSCs). Sb_2S_3 -based systems have shown particular promise, with a power conversion efficiency of 7.5 % reported for the $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{PCPDTBT}$ system.¹⁻³ Impressive results have also been achieved with alternative solid state hole transport materials (HTMs), including CuSCN ,⁴⁻⁸ *spiro*-OMeTAD,⁹ and P3HT^{2,10,11} as well as liquid electrolytes.^{12,13}

The function of a typical sensitised-electron acceptor solar cell is based upon photoinduced charge transfer at the TiO_2 /nanocrystal sensitiser/HTM heterojunctions. Figure 13a shows the main processes occurring in such systems. Optical excitation of the photoactive layer results in the formation of electrons and holes in the Sb_2S_3 nanocrystals (Process 1 in Figure 13a). In a functioning device, the photogenerated electrons and holes are transferred to the TiO_2 and organic HTM components respectively (Processes 2 and 3 in Figure 13a). In a typical interpretation of these reactions, injection of the photoexcited electron from the sensitiser to the metal oxide is thought to occur very rapidly (ps timescales), whilst hole transfer acts as a subsequent ‘regeneration’ process that restores the ground state of the sensitiser.¹⁴ The design of efficient SSSC devices crucially depends on the achievement of a high yield of both electron and hole transfer, as well as minimisation of charge recombination losses (Processes 4-7 in Figure 13a). However, control and optimisation of these charge transfer reactions require a fundamental understanding of the key parameters influencing the rates and yields of these processes. Whilst numerous studies have addressed the factors influencing charge transfer in dye-sensitised metal oxide films,¹⁴⁻¹⁶ relatively few have probed nanocrystal-sensitised heterojunctions. This is particularly true of Sb_2S_3 -based systems, although work has been presented focussing on the application of Impedance Spectroscopy (IS) to fully functioning $\text{TiO}_2/\text{Sb}_2\text{S}_3$ devices,^{7,17} as well as the use of chemically resolved electrical measurements.^{17,18} In this chapter, transient absorption spectroscopy (TAS) is used to probe directly the photoinduced charge transfer processes in $\text{TiO}_2/\text{Sb}_2\text{S}_3$ /*spiro*-OMeTAD films. The wide bandgap of *spiro*-OMeTAD (Figure 13b) makes it a particularly suitable HTM for this study, as it allows photoexcitation to be selectively induced in the coloured Sb_2S_3 layer.

The reader is advised that subsequent to the publication of the work presented in this chapter,¹⁹ Dennler and co-workers have conducted an extensive study of the mechanisms of charge

photogeneration and recombination in Sb_2S_3 -sensitised TiO_2 solar cells through the use of transient microwave photoconductivity and steady-state photocurrent grating spectroscopy,²⁰ whilst Christians and Kamat have used ultrafast transient absorption spectroscopy to directly monitor the hole transfer reaction.^{21,22} Reference will be made to the key observations and conclusions of these works in the context of experimental results.

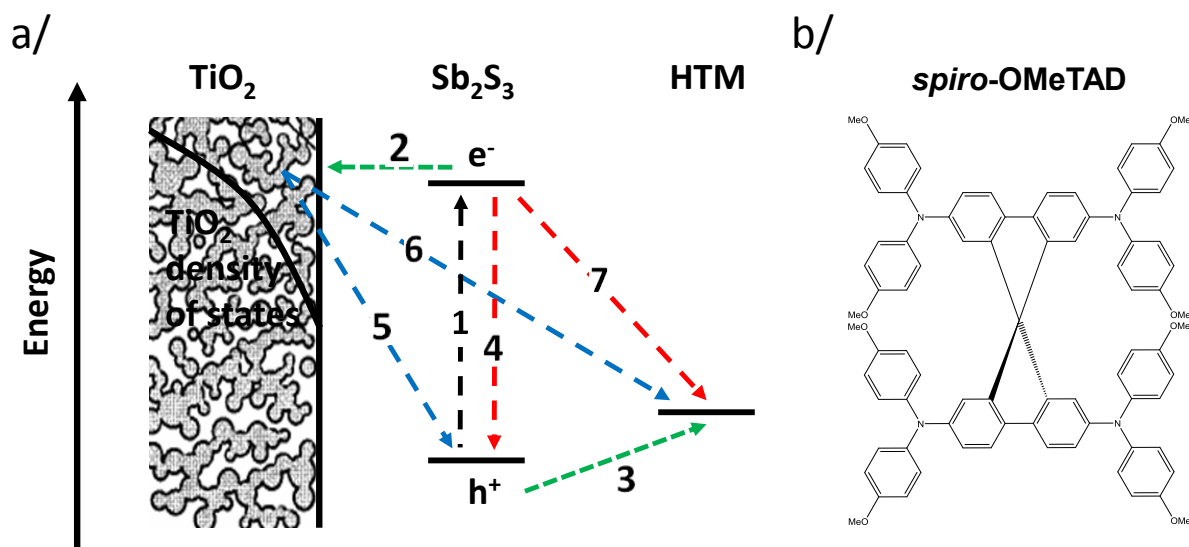


Figure 13 – a/ Simplified schematic to show the various charge separation (green arrows) and recombination (red and blue arrows) processes in a functioning $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{HTM}$ assembly. Absorption of light induces photoexcitation of an electron in Sb_2S_3 (Process 1). Charge separation occurs through transfer of the photoexcited electron to TiO_2 (Process 2) and extraction of the corresponding hole to the *spiro-OMeTAD* hole transporting material (Process 3). Separated charges are then transported through these respective media to contacts. Competing with the charge separation process is the relaxation of the photoexcited state (Process 4) as well as interfacial recombination of electrons in TiO_2 with either holes in the Sb_2S_3 layer (Process 5) or the HTM (Process 6). A possible additional pathway concerns recombination of electrons in the sensitizer and holes in the HTM (Process 7). b/ Chemical structure of *spiro-OMeTAD*.

4.2 Film Preparation and Characterisation

Successive ionic layer adsorption and reaction (SILAR) deposition of Sb_2S_3 was achieved by alternate immersions of the mesoporous metal oxide films in ethanolic solutions of either antimony chloride or sodium sulfide (0.02 M, sources of Sb^{3+} and S^{2-} ions respectively). The constituent ions are able to adsorb to the surface of the TiO_2 substrate and react to form Sb_2S_3 . In between immersions, films were washed thoroughly in ethanol to remove non-adsorbed ions. A single immersion in each of the reactant solutions constitutes one ‘cycle’ of deposition. After SILAR deposition, the sensitised metal oxide films were annealed at 300 °C for 30 minutes in a nitrogen glovebox. Figure 14a and b show the UV-Visible absorption spectra and Raman spectra respectively of a pristine TiO_2 film (black) and the 5 SILAR cycle-sensitised film before (grey) and after (pink) annealing. The annealing process causes the appearance of sharp peaks in the Raman spectrum at ~ 240 , ~ 280 and $\sim 310 \text{ cm}^{-2}$, which are characteristic of crystalline stibnite.^{23,24} This observation, coupled with a red shift in absorption onset due to the reduced bandgap of crystalline Sb_2S_3 (1.73 eV) relative to the amorphous phase (2.24 eV),²⁵ suggest that the as-deposited films are in the amorphous phase, but crystallise when annealed. This is consistent with reports in the literature for Sb_2S_3 deposits on both TiO_2 ⁴ and ZnO .²⁶ Scanning electron micrographs of the pristine TiO_2 film (Figure 15a) and the TiO_2 /annealed Sb_2S_3 film (Figure 15b) indicate that the sensitizer coats clusters of TiO_2 particles as a thin layer, whilst still retaining an overall porous mesostructure. Similar observations have been reported for chemical bath deposited $\text{TiO}_2/\text{Sb}_2\text{S}_3$ films.^{4,9}

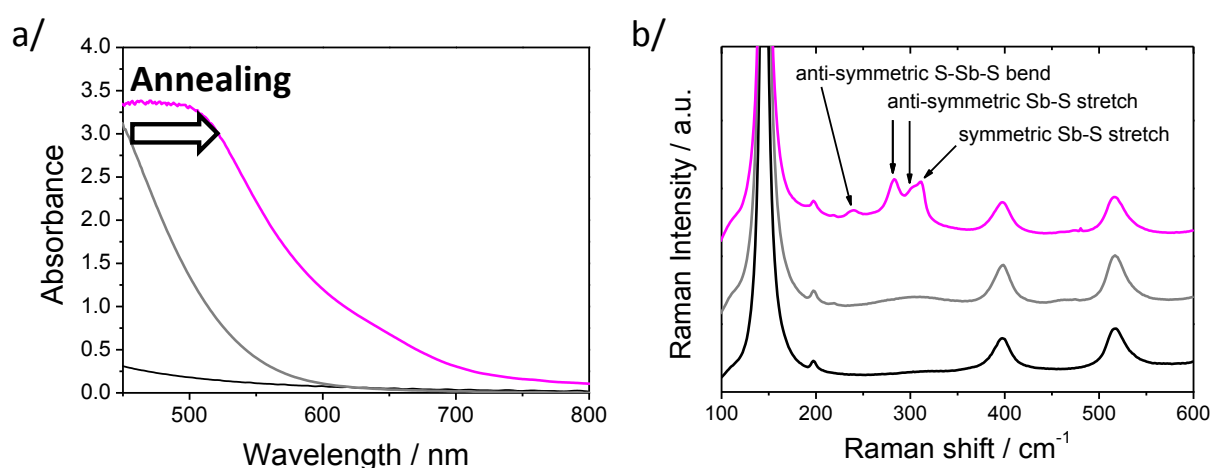


Figure 14 – a/ Absorption spectra and b/ Raman spectra of pristine TiO_2 (black) and $\text{TiO}_2/\text{Sb}_2\text{S}_3$ after 5 SILAR cycles before (grey) and after (pink) annealing at 300 °C in N_2 . Raman spectra were collected with a 514 nm laser excitation.

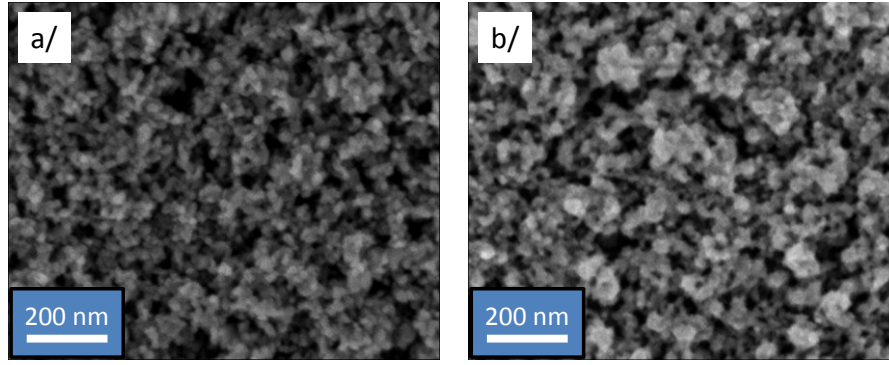


Figure 15 – Scanning electron micrographs of a/ a pristine mesoporous TiO₂ film and b/ a TiO₂/Sb₂S₃ film prepared by 5 SILAR deposition cycles followed by annealing at 300 °C in N₂.

Figure 16a shows UV-Visible absorption spectra of the Sb₂S₃ sensitised TiO₂ films following different numbers of SILAR cycles (main figure) as well as selected illustrative photographs (inset). The Sb₂S₃ deposit consists of a broad and inhomogeneous distribution of crystallite sizes, as highlighted by the shape of the absorption spectra. As the films are highly scattering, Tauc plots^{27,28} (Figure 16b) have been used to estimate the absorption onset according to the relationship:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

where α is the extinction coefficient, $h\nu$ is the photon energy in eV, A is a constant and E_g is the bandgap of the semiconductor and $n=2, 2/3, 1/2$ or $1/3$ for direct allowed, direct forbidden, indirect allowed or indirect forbidden optical transitions, respectively. Therefore, plotting $(\alpha h\nu)^n$ vs. $(h\nu)$ should yield a linear plot with the bandgap equal to the point of intersection with the x-axis. For scattering films, this can be achieved by extrapolating the linear component of the plot. As found by Versavel and Haber,²⁵ the best linear fit for the samples considered here is obtained when $n=2$, which suggests a direct allowed transition between the valence and conduction bands. Using this method, Figure 16c plots the absorption onset of TiO₂/Sb₂S₃ films prepared by SILAR sensitisation against the number of deposition cycles. As the number of cycles is increased, the absorption onset is seen to red-shift towards the bulk value (~ 1.7 - 1.8 eV). This is characteristic of the SILAR process and is typically attributed to the presence of increasingly large nanocrystals and the associated reduction of quantum confinement effects.²⁹⁻³³

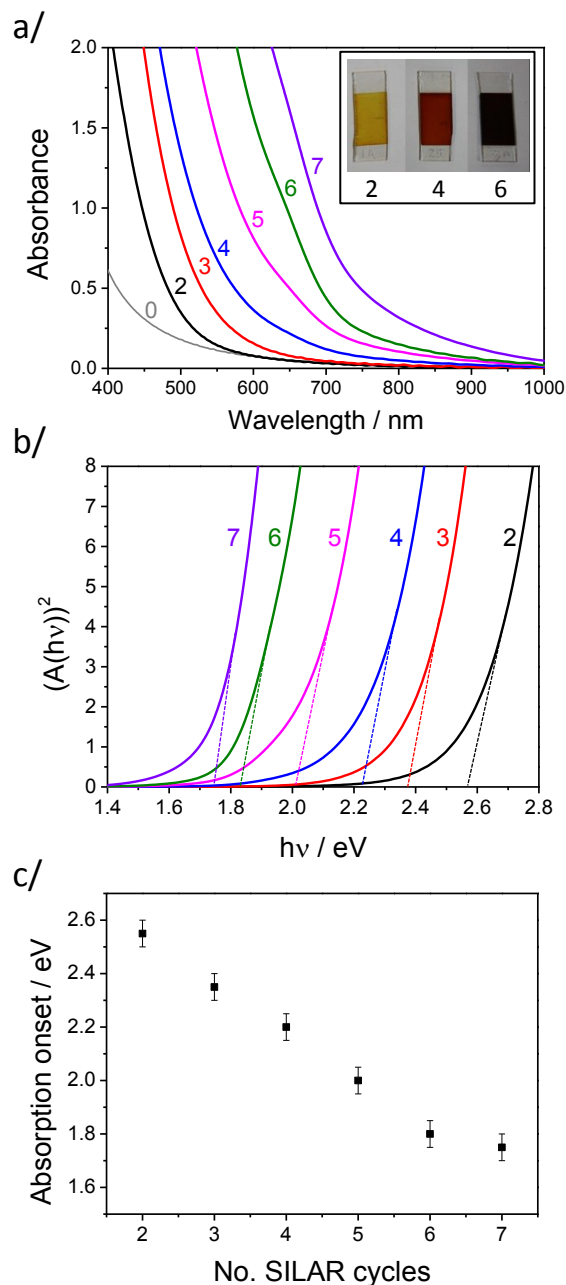


Figure 16 – a/ Absorption spectra of TiO₂/Sb₂S₃ films prepared by SILAR sensitisation and subsequent thermal annealing as a function of the number of deposition cycles, for a pristine TiO₂ film (grey) and following sensitisation with 2 (black), 3 (red), 4 (blue), 5 (pink), 6 (green) and 7 (purple) SILAR cycles. b/ Tauc plots to estimate the absorption onsets of the films presented in (a) assuming a direct allowed optical transition. c/ Absorption onset as determined by Tauc analysis vs. number of SILAR cycles.

Photoelectron spectroscopy (PES) provides further insight into the nature of the observed changes in the energetics of Sb₂S₃ as the number of SILAR cycles is varied. With this technique UV or X-ray radiation is used to photoionize the sample under ultra-high vacuum and the kinetic energy distribution of the photoelectrons emitted is measured, which can subsequently be related to the

density of occupied states in the surface region of the sample. In this manner, it is possible to map the density of valence molecular orbital levels for the given sample. Figure 17 shows the valence band spectra of a mesoporous TiO_2 film before (grey) and after sensitisation with Sb_2S_3 by 3 SILAR cycles (red) and 7 SILAR cycles (purple) and annealing at 300 °C in nitrogen. The pristine TiO_2 spectrum was energy calibrated by setting the Fermi level (the edge of the occupied states) to 0 eV binding energy.³⁴ The TiO_2 valence band edge is then defined by extrapolating the linear part of the valence band to the baseline (dashed line in Figure 17), which gives a binding energy of ~3.2 eV. This is approximately equal to the bandgap of anatase TiO_2 ³⁵ and suggests that the Fermi level of TiO_2 is located very close to the conduction band edge, as reported in literature.³⁶ The density of TiO_2 inter-bandgap states can be seen in the binding energy region between 3.2 and 2 eV, as well as of Ti^{3+} surface states, which account for the peak at ~1.4 eV.³⁶ Spectra for the Sb_2S_3 -sensitised TiO_2 films were energy calibrated by aligning the Ti 3p core level peaks to the same binding energy (38 eV) as that of the pristine TiO_2 film. As such, the TiO_2 valence band edge is expected to appear at the same energy for both the pristine and the sensitised films and the extra states seen within the bandgap of TiO_2 for the sensitised films represent the Sb_2S_3 valence band.

As for the pristine TiO_2 sample, the valence band edge Sb_2S_3 can be estimated by extrapolating the linear region to values of 1.35 eV and 1.20 eV below the TiO_2 Fermi level for the 3 and 7 cycle films, respectively. This corresponds to an increase in valence band energy (moving closer to vacuum) as more SILAR cycles are performed, which is consistent with the red-shifted absorption spectra described above and provides further evidence for the presence of increasingly large nanocrystals and reduced quantum confinement. It is noted that the gradient of the linear region of the Sb_2S_3 spectrum is considerably less steep than that of the pristine TiO_2 film. This suggests a less well defined valence band edge and thus supports the assertion that the Sb_2S_3 deposit is made up of a distribution of nanocrystal sizes. Finally, it is interesting to note that a shift in valence band potential of 150 meV between the 3 SILAR cycle and 7 SILAR cycle Sb_2S_3 deposits is relatively small compared to the associated 600 meV change in optical bandgap (from Figure 16). This shows that quantum confinement have a greater effect on the conduction band energy than that of the valence band, which is in agreement with reports in the literature for other nanocrystalline metal sulfides and indicates that the effective mass of the photogenerated electron in Sb_2S_3 is lower than that of the hole.³⁷

In the following section the effect of changing the absorption onset of the Sb_2S_3 sensitizer on the yield of long-lived interfacial charge separation at $\text{TiO}_2/\text{Sb}_2\text{S}_3$ heterojunctions is explored through the use of transient absorption spectroscopy.

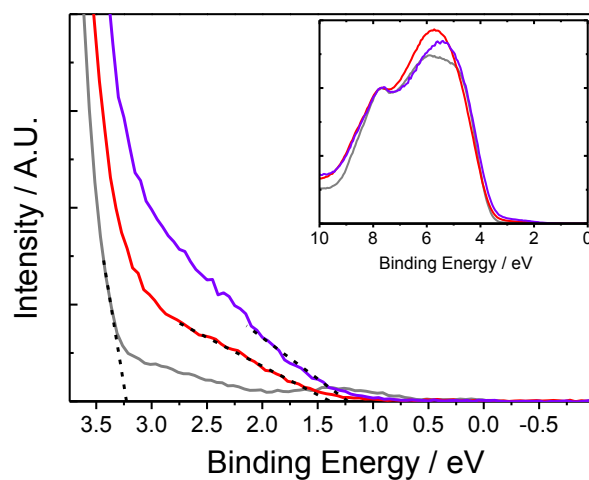


Figure 17 – Valence band spectra of mesoporous TiO₂ films before (grey) and after sensitisation with Sb₂S₃ by 3 SILAR cycles (red) and 7 SILAR cycles (purple) as obtained with ultraviolet photoelectron spectroscopy. The pristine TiO₂ sample was energy calibrated by setting the Fermi level (the edge of the occupied states) to a binding energy of 0 eV. Spectra for the Sb₂S₃-sensitised TiO₂ films were energy calibrated by matching the Ti 3p core level peak to that of the pristine TiO₂ film. Data shown in this figure were collected at the MAX Lab synchrotron facility in Lund, Sweden by Dr. Erik Johansson and Prof. Håkan Rensmo from Uppsala Universitet.

4.3 Transient Absorption Spectroscopy

In an SSSC the potential to optimise the absorption profile of the sensitiser through manipulation of quantum confinement effects is an attractive feature, yet variation of the bandgap also means that the alignment of energy levels at the metal oxide/sensitiser/HTM heterojunctions will change. Typically, a bathochromic shift in absorption corresponds to a decrease in conduction band energy and an increase in that of the valence band. This results in reduced driving force for electron and hole transfer respectively. It has been shown that for a number of SSSC-type systems this can be sufficient to slow electron injection (Process 2 in Figure 13a), which can inhibit charge separation and therefore device performance.³⁸⁻⁴¹ This effect is likely to become increasingly relevant as further efforts are made to extend SSSC photoresponse into the near infrared. In the previous section, it has been shown that the absorption onset (and therefore the lowest energy bandgap) of an Sb_2S_3 deposit on mesoporous TiO_2 can be readily modulated using the successive ionic layer absorption and reaction (SILAR) growth process by varying the number of coating cycles employed. This is expected to modulate the alignment of energy levels at the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ heterojunction and thus potentially influence interfacial charge transfer.

4.3.1 Electron Injection at the Metal Oxide/ Sb_2S_3 Interface

Initially, the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface is isolated by excluding the HTM from the film architecture. For this configuration, photoexcited electrons in the Sb_2S_3 layer should be injected into the TiO_2 whilst corresponding holes remain localised within the nanocrystal sensitiser. As a control, an analogous mesoporous $\text{ZrO}_2/\text{Sb}_2\text{S}_3$ system is also considered. The conduction band of ZrO_2 lies ~ 500 meV above that of TiO_2 and thus energetically prohibits electron transfer from the sensitiser.^{29,42} Figure 18 shows the transient absorption spectra of a typical SILAR-deposited Sb_2S_3 layer on mesoporous TiO_2 (black) and ZrO_2 (red) substrates, recorded 1 μs (filled squares) and 10 μs (hollow triangles) after photoexcitation at 510 nm. A broad positive absorption band centred at ~ 800 nm is seen for the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ films. Conversely, very little signal is observed for the $\text{ZrO}_2/\text{Sb}_2\text{S}_3$ sample, suggesting that majority of photogenerated charges not separated at the metal oxide/sensitiser interface recombine on sub-microsecond timescales. As such, the transient absorption band seen on TiO_2 substrates is associated with the products of interfacial charge separation. Similar features have been reported for other TiO_2 /metal sulfide composites and attributed to the photo-oxidised sensitiser species generated as electrons are injected into the metal oxide.⁴³⁻⁴⁵ It is not expected that the injected electrons themselves will contribute significantly to the amplitude of transient absorption at 800 nm, as they

have been shown to possess a relatively low extinction coefficient, with a broad and featureless absorption profile slowly increasing in intensity into the IR.⁴⁶

The intensity of absorption is directly proportional to the concentration of absorbing species (which in this case is believed to be holes in the Sb_2S_3 layer) and therefore, can be used as a measure of the relative yield of charge separation across the interface. Additionally, the rate at which this transient absorption band decays describes the lifetime of the separated charges and the dynamics of interfacial recombination. In the following sections, the effect of varying both the Sb_2S_3 annealing temperature and the energetics at the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface on the yield of interfacial charge separation are probed in this manner.

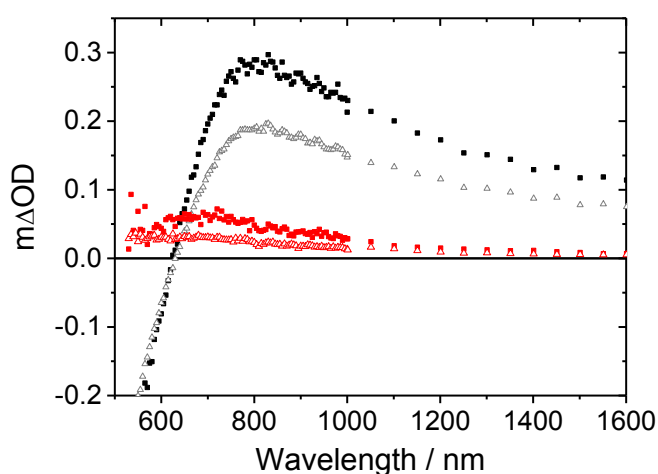


Figure 18 – Transient absorption spectra of $\text{TiO}_2/\text{Sb}_2\text{S}_3$ (black, 3 SILAR cycles) and $\text{ZrO}_2/4$ SILAR cycles- Sb_2S_3 (red, 3 SILAR cycles) recorded 1 μs (filled squares) and 10 μs (hollow triangles) after photoexcitation at 510 nm (pump intensity = 40 $\mu\text{J cm}^{-2}$). Data shown for samples with similar steady state absorption profiles following thermal annealing at 300 $^\circ\text{C}$ and scaled to account for small differences in the number of photons absorbed at the pump wavelength.

4.3.1.1 Electron Injection - Effect of Annealing Temperature

In Section 4.2, it has been shown that the SILAR deposition process yields an amorphous Sb_2S_3 film in which thermal annealing can induce crystallisation. Figure 19a shows the effect of varying the temperature at which this annealing process is conducted on the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ absorption spectra (5 SILAR cycles). Annealing at temperatures $\leq \sim 100^\circ\text{C}$ is found to have little effect on the absorption spectra of the as-deposited Sb_2S_3 films, whereas annealing at both 200°C and 300°C causes the red-shift associated with crystallisation to materialise. This effect is more dramatic for the higher temperature sample. At 150°C , there appears to be some increased absorption at longer wavelengths, although the actual onset is not noticeably different.

Figure 19b illustrates the effect of annealing temperature on the interfacial charge recombination in $\text{TiO}_2/\text{Sb}_2\text{S}_3$ systems. The data presented therein follow the reaction between the photogenerated electrons and holes in the TiO_2 and Sb_2S_3 respectively and were obtained by monitoring the decay of the photoinduced transient absorption feature at 800nm. Given that ΔOD is directly proportional to the concentration of absorbing species (photo-oxidised Sb_2S_3 in this case), the amplitude of the transient signal can be used to probe the relative yield of interfacial charge separation at a given time. On this basis, it is apparent that either no or low temperature annealing ($\leq 100^\circ\text{C}$ – black, red and blue traces) makes no discernable difference to the yield of long-lived charges generated, whilst annealing at 150°C (grey trace), 200°C (pink) and 300°C (green trace) leads to increasingly large degrees of charge separation ($m\Delta\text{OD}$ increases from 0.10 to 0.15 to 0.30 at $1\ \mu\text{s}$ respectively). It is noted that annealing at even higher temperatures, even in a nitrogen glovebox, was found to cause the Sb_2S_3 films to become increasingly transparent, probably due to the formation of antimony oxide.⁴ Improved charge separation may result from an enhanced efficiency of electron transfer from Sb_2S_3 to TiO_2 as the Sb_2S_3 becomes crystalline. Itzhaik *et al.* have reported that extensive electron trapping occurs in amorphous Sb_2S_3 , but that it does not take place following annealing-induced crystallisation.⁴ Such trapping might be expected to compete with electron injection into the TiO_2 and thus limit the yield of interfacial separation. Moreover, these observations are consistent with the work of Liu *et al.*, who show an increase in Sb_2S_3 crystallinity as annealing temperature is raised to 300°C and a concurrent improvement in efficiency for $\text{ZnO}/\text{Sb}_2\text{S}_3/\text{P3HT}$ devices.²⁶ The slight shifts in absorption spectra of the films annealed at 150°C and 200°C may indicate that partial crystallisation is achieved, which results in an improved but still sub-optimal yield of charge generation. On this basis, all other samples considered in this chapter are annealed at 300°C .

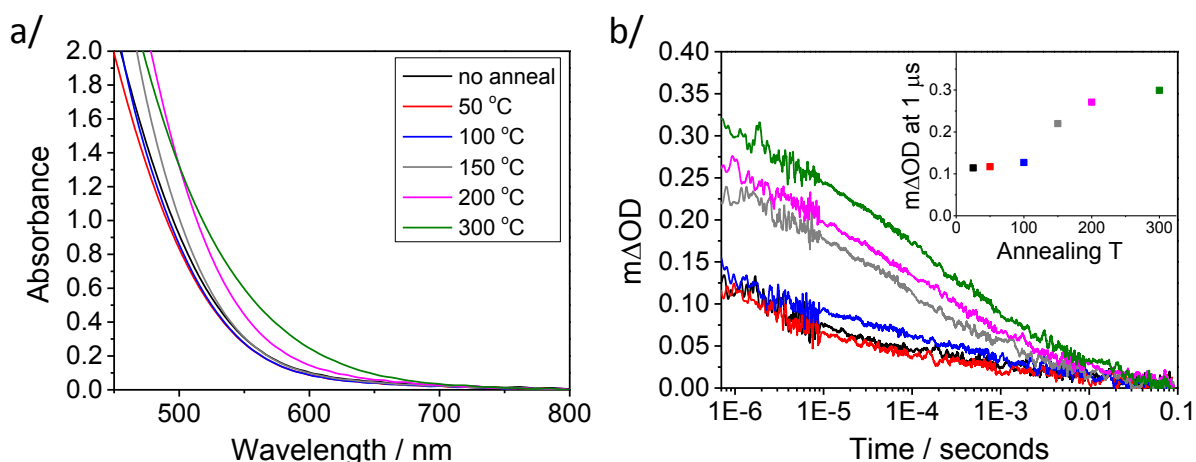


Figure 19 – a/ Absorption spectra and b/ Transient absorption decay kinetics of Sb_2S_3 -localised holes (probed at 800 nm) for metal oxide/ Sb_2S_3 films (5 SILAR cycles) as a function of Sb_2S_3 annealing temperature - no annealing (black), annealing at 50 °C (red), 100 °C (blue), 150 °C (grey), 200 °C (pink) and 300 °C (green). All films were annealed for 30 minutes in N_2 . Inset of (b/) shows the average mΔOD value between 0.9 and 1.1 μs for each temperature. TAS traces have been scaled to account for small differences in number of photons absorbed at the excitation wavelength (500 nm, energy density = $38.5 \mu\text{J cm}^{-2}$).

4.3.1.2 Electron Injection – Effect of Cycle Variation

For a photovoltaic device, red-shifting the absorption onset of the light harvesting material means that a broader range of incident light can be absorbed and thus potentially a higher photocurrent achieved. However, for a given material, the associated change in energy levels might also be expected to affect the dynamics of interfacial charge transfer. For the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ system considered in this chapter, it has been shown that the absorption onset can be controlled through variation of the number of SILAR deposition cycles performed. In Figure 20a, the decay in transient absorption at 800 nm for metal oxide/ Sb_2S_3 films is shown as a function of SILAR deposition cycles. As described previously, the Sb_2S_3 deposit is likely to consist of a distribution of different sized nanocrystals, therefore so as to probe the effect of a reduced Sb_2S_3 bandgap more directly, the laser excitation wavelength λ_{pump} is also varied in concurrence with the red-shifting absorption onset. λ_{pump} was selected so as to ensure similar ground state absorbance for the different samples of ~ 0.5 . The amplitude of the transient absorption signal at 1 μs decreases noticeably with increasing SILAR cycles (and as λ_{pump} red-shifts between 450 nm (black trace) and 650 nm (pink trace)), which indicates that the yield of long-lived charge separation across the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface decreases as increasingly red-absorbing Sb_2S_3 nanocrystallites are excited. A similar trend is observed when exciting a 6 SILAR cycle Sb_2S_3 deposit on TiO_2 at different excitation wavelengths (see Figure 21), whereby the yield of long-lived charge separation at the $\text{TiO}_2 / \text{Sb}_2\text{S}_3$ interface is decreased as the excitation wavelength is red-shifted

(purple, orange and grey traces – samples have been scaled for the number of pump photons absorbed). This discounts the possibility that increasing film thickness is inhibiting charge transfer. For comparison, a 2 cycle $\text{Sb}_2\text{S}_3/\text{TiO}_2$ film is also shown following excitation at 450 nm (black trace). It is important to note that this method (relative to that applied in Figure 20) does not afford the possibility of selectively probing only the most blue-absorbing Sb_2S_3 nanocrystals, which could explain the difference in yield of photogenerated holes for a 2 cycle and a 6 cycle film excited at 450 nm.

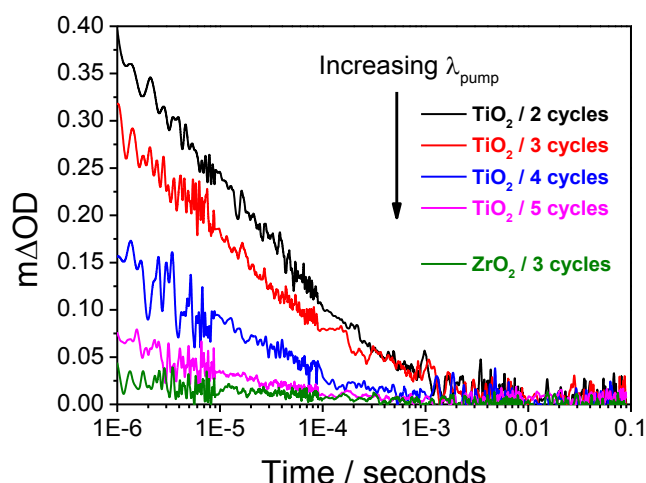


Figure 20 - Transient absorption decay kinetics of Sb_2S_3 -localised holes in metal oxide/ Sb_2S_3 /films probed at 800 nm. λ_{pump} is varied to probe increasingly red-absorbing nanocrystals whilst ensuring similar ground state absorbance (2 SILAR cycles (black trace)- 450 nm excitation, 3 cycles (red) – 510 nm, 4 cycles (blue) – 570 nm, 5 cycles (pink) – 650 nm)). Values of ΔOD are scaled to the number of photons absorbed at λ_{pump} . Laser excitation energy density = $26 \mu\text{J cm}^{-2}$ at 450 nm.

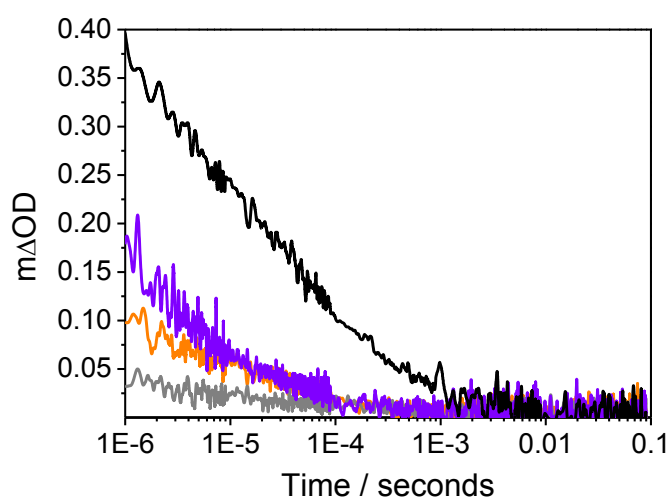


Figure 21 - Transient decay kinetics of Sb_2S_3 -localised holes in Sb_2S_3 /metal oxide films probed at 800 nm. Values of ΔOD are scaled to the number of photons absorbed at λ_{pump} . Laser excitation energy density = $26 \mu\text{J cm}^{-2}$ at 450 nm. Sb_2S_3 layers are grown by SILAR on TiO_2 (2 cycles, $\lambda_{\text{pump}} = 450 \text{ nm}$ (black), 6 cycles $\lambda_{\text{pump}} = 450 \text{ nm}$ (purple), 510 nm (orange), 650 nm (grey)).

A diminished yield of long-lived charge separation as the Sb_2S_3 absorption red-shifts is consistent with a reduction in driving force for interfacial electron transfer (Figure 22). In a number of SSSC systems, the reduction in excited state energy associated with decreasing degrees of quantum confinement has been shown to directly retard electron injection from the nanocrystal to TiO_2 .³⁸⁻⁴¹ Of particular note, Guijarro *et al.* have used transient grating spectroscopy to observe a reduction in the rate of electron injection from SILAR grown CdSe with an increase in the number of deposition cycles performed.³² A drop in the rate of injection is expected to increase kinetic competition between charge separation and relaxation of the excited state in the sensitiser (Process 2 versus Process 4 in Figure 13a), thus reducing the total yield of charge separation across the heterojunction.⁴² It is noted that the differences in long-lived charge separation yield in the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ assembly could also be due to variations in the rate of interfacial charge recombination (Process 5 in Figure 13a). Whilst this possibility cannot be ruled out unequivocally, the similarity in half time of decay ($t_{50\%} \approx 10 \mu\text{s}$) from the maxima of each trace (at $1 \mu\text{s}$) leads to the belief that this explanation is less likely. A further contributory factor could be that spatial separation of electron donor and acceptor sites increases as more SILAR cycles are performed.

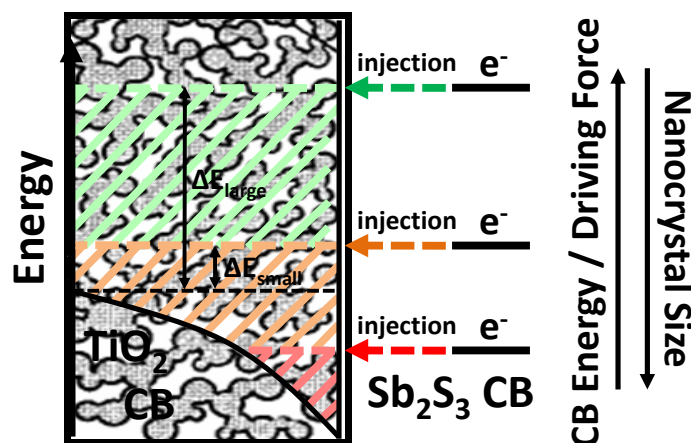


Figure 22 – Schematic to show the variation in driving force for electron injection (ΔE) as the Sb_2S_3 conduction band energy is varied.

Reducing the yield of charge separation at the metal oxide/sensitiser interface may be expected to inhibit the performance of complete devices by reducing internal conversion efficiency, notably at longer wavelengths. However, IPCE spectra of $\text{TiO}_2/\text{Sb}_2\text{S}_3$ -based devices reported in the literature do not seem to suffer such limitations.^{4,9} In the hope of understanding this apparent contradiction, the solid-state hole conductor *spiro*-OMeTAD is added to the system and the hole transfer process (Process 3 in Figure 13a) is probed.

4.3.2 Hole Transfer from Sb₂S₃ to *spiro*-OMeTAD

Attention is now turned to the hole-transfer reaction in the TiO₂/Sb₂S₃/*spiro*-OMeTAD assembly. Figure 23 shows a typical transient absorption spectrum of this system, 10 μs after laser excitation at 500 nm (black squares). The shape of the spectrum bears a remarkable similarity to the absorption spectrum of a solution of *spiro*-OMeTAD that has been chemically oxidised with N(PhBr)₃SbCl₆ (also shown - blue line). As such, the broad transient absorption band in the near-IR region of the transient spectrum is attributed to the oxidised *spiro*-OMeTAD species generated by the ‘regeneration’ reaction (Process 3 in Figure 13a), as has been reported elsewhere,^{29,45} and the intensity can be used as an indication to the yield of hole transfer. Furthermore, an estimated extinction coefficient of 22800 M⁻¹ cm⁻¹ has been reported at 1600 nm, which through the Beer-Lambert law allows quantitative determination of the number of absorbing species and therefore of the ratio of photogenerated charges per photon absorbed.⁴⁵

$$\Delta OD = \varepsilon \cdot c \cdot l = \varepsilon \cdot \frac{\text{mols}}{\text{volume}} \cdot l = \varepsilon \cdot \frac{\text{mols}}{\text{area}}$$

$$\frac{n}{\text{area}} = \frac{N_A \cdot \Delta OD}{\varepsilon}$$

$$\begin{aligned} \% \text{ yield} &= \frac{n \text{ (/unit area)}}{\text{no. photons absorbed (/unit area)}} \\ &= \frac{n}{\left(\frac{\lambda_{\text{pump}} \text{ energy density}}{h\nu} \cdot \text{absorbance at } \lambda_{\text{pump}} \right)} \end{aligned}$$

where ε = extinction coefficient (M⁻¹cm⁻¹), c = concentration (mols dm⁻³), n/area = number of absorbing species per unit area.

This ratio thus describes the overall efficiency of charge separation across the metal oxide/Sb₂S₃/HTM heterojunctions at a given time. It is noted that electrons injected into the TiO₂ matrix are also expected to absorb at 1600 nm and could contribute to the observed transient absorption signal, although their extinction coefficient is thought to be much lower than that of the oxidised HTM and so only a small degree of error is induced.^{46,47} Figure 24 shows the effect of red-shifting the absorption onset of Sb₂S₃ through variation of the number of deposition cycles on the yield of hole transfer. As in the previous section, the excitation wavelength is concurrently red-shifted. It is clear from these data that when excitation wavelength (and absorption onset) red-shift, the yield of charge separation is seen to drop from ~83 % for the 2 cycle sample, to ~69 %, 60 % and

41 % for 3, 4 and 5 cycles respectively. This trend loosely reflects that seen in Figure 20, indicating a degree of coupling between the injection and regeneration reactions. This effect is likely to be due to increased kinetic competition between antimony sulfide-localised recombination and electron injection with increasing nanocrystal size, such that the number of holes available to be transferred to the HTM also decreases and overall charge separation efficiency decreases. However, it is pertinent to note that for a 5-cycle film, 41 % represents surprisingly extensive hole transfer, given the poor charge separation seen at the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface in this case. Additionally, hole transfer appears to occur when using ZrO_2 substrates, as evidenced by the shape of the transient absorption spectrum of a $\text{ZrO}_2/\text{Sb}_2\text{S}_3/\text{spiro-OMeTAD}$ film, recorded 1 μs after photoexcitation (Figure 24b, red trace). For comparison, data is also shown in this figure for a $\text{ZrO}_2/\text{Sb}_2\text{S}_3$ film with no *spiro-OMeTAD* (blue trace), as well as the absorption spectrum of a solution of *spiro-OMeTAD* that has been chemically oxidised with $\text{N}(\text{PhBr})_3\text{SbCl}_6$. These observations indicate that photoinduced hole transfer and not only electron injection could initiate device operation, and that this process can also successfully compete with the direct recombination of photogenerated charges within the sensitiser layer (Process 4 in Figure 13a).

The rate of decay of the transient signal at 1600 nm is much greater on ZrO_2 substrates (Figure 24a, inset - green trace) than on TiO_2 . On ZrO_2 , where electron injection from the Sb_2S_3 to the metal oxide is prohibited, recombination is likely to occur between electrons localised within the Sb_2S_3 and holes transferred to the HTM (Process 7 in Figure 13a). This process appears to be faster than the equivalent reaction of electrons in TiO_2 (Process 6 in Figure 13a). It is possible that this results from the increased proximity of recombining species when the electron remains in the sensitiser. This effect means that quantitative estimation of the yield of hole transfer on ZrO_2 based films is not possible, as unlike for TiO_2 -based films, no plateau in transient signal is seen. Importantly, although long-lived charge separation across the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ heterojunction becomes inhibited as increasingly large Sb_2S_3 nanocrystals are excited, it appears that the impact of this effect can be partially offset by effective hole transfer from the sensitiser to the HTM.

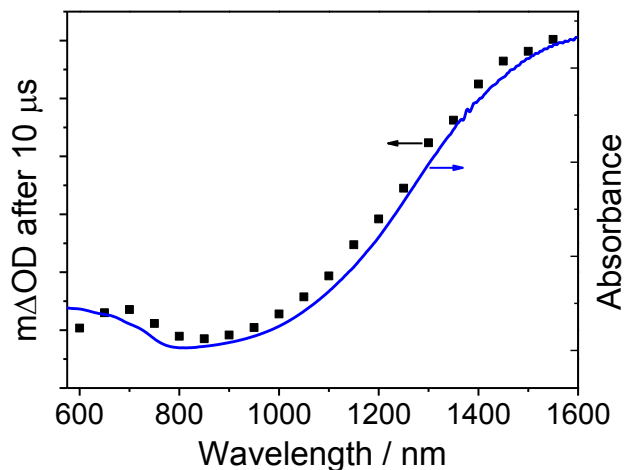


Figure 23 - Transient absorption spectrum of a $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{spiro-OMeTAD}$ film (black squares, 5 SILAR cycles) after photoexcitation at 500 nm (pump intensity = $36 \mu\text{J cm}^{-2}$). Also shown is the absorption spectrum of a solution of chemically oxidised *spiro-OMeTAD* (blue line).

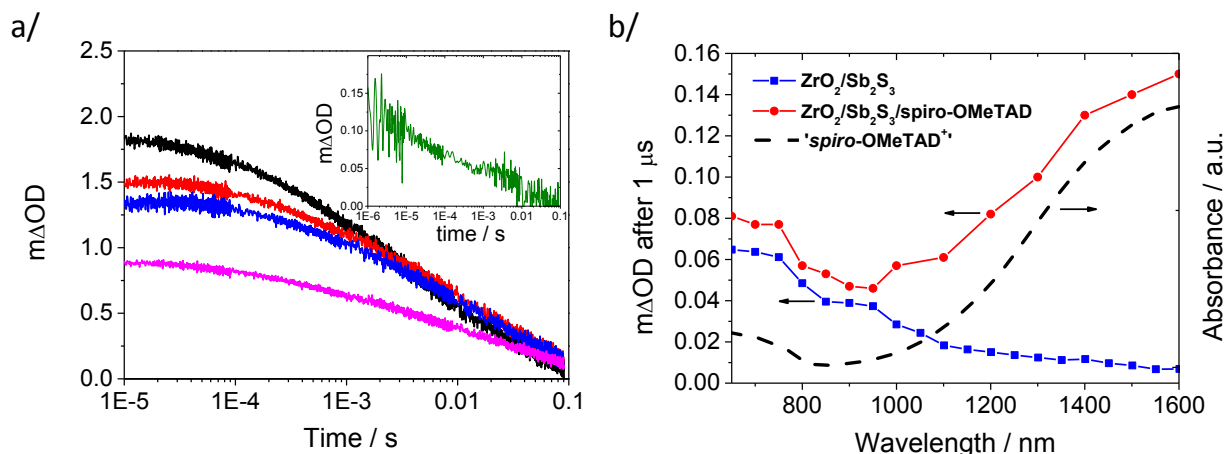


Figure 24 - Transient decay kinetics of spiro-OMeTAD^+ absorption in $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{spiro-OMeTAD}$ (main figure) and $\text{ZrO}_2/\text{Sb}_2\text{S}_3/\text{spiro-OMeTAD}$ (inset) films probed at 1600 nm. In both (a) and (b), λ_{pump} is varied to probe increasingly red-absorbing nanocrystals whilst ensuring similar ground state absorbance (2 SILAR cycles (black trace)- 450 nm excitation, 3 cycles (red) – 510 nm, 4 cycles (blue) – 570 nm, 5 cycles (pink) – 650 nm)). Values of ΔOD are scaled to the number of photons absorbed at λ_{pump} . Laser excitation energy density = $26 \mu\text{J cm}^{-2}$ at 450 nm.

In an SSSC, extending photoresponse into the near infra-red is vital to the achievement of high performance devices. However, for $\text{TiO}_2/\text{Sb}_2\text{S}_3$ -based devices, the observations presented in this work indicate that charge separation at the metal oxide/ Sb_2S_3 interface is increasingly limited as the absorption onset of the Sb_2S_3 sensitiser is red-shifted, which is consistent with work by other groups on analogous TiO_2 /quantum dot systems.³⁸⁻⁴¹ In a device, this would be expected to reduce internal quantum efficiency, especially at longer wavelengths, and thus limit performance. On the other hand, it is found that significant photoinduced hole transfer to *spiro*-OMeTAD can take place, even when charge separation at the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ heterojunction is limited. This may imply that hole transfer is also in kinetic competition with the recombination of charges within the Sb_2S_3 layer and so can itself initiate device operation. Subsequent to the publication of the work presented here, Christians and Kamat have studied the hole transfer process from Sb_2S_3 to CuSCN (an alternative transparent solid-state HTM) with ultrafast transient absorption spectroscopy and report that photogenerated holes in Sb_2S_3 are rapidly localised on sulphur atoms (~40 ps timescales) in the crystal lattice, before subsequently being transferred to a hole acceptor.²¹ It is possible that the trapping of holes in this manner disrupts the recombination process within the bulk of the absorber, thus allowing more time for the hole transfer reaction to occur. In the current configuration, the electron must ultimately be transferred to the metal oxide for the device to; it is possible that the negative charge on the sensitiser nanocrystal added by hole extraction could induce a rise in the energy of the electron excited state and thus encourage electron injection, or that electrons could build up in the sensitiser until electron injection becomes favourable.^{33,48} Given the increasingly poor charge separation at the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface as the excitation wavelength is red-shifted, such effects are expected to be significant contributory factors to the efficient performance of Sb_2S_3 -based devices. Therefore, focus on further optimisation of the hole transfer reaction should help accelerate the development of these already high performance systems.

4.3.3 Hole Transfer from Sb_2S_3 to P3HT

In a recent comparison of conjugated polymers as hole transporting materials for Sb_2S_3 -sensitised TiO_2 solar cells, Seok and co-workers found that the best performing devices were achieved when the HTM contained neighbouring thiophene moieties, such as poly(3-hexylthiophene) (P3HT).² It was suggested that these functional groups are able to chelate to antimony atoms in the Sb_2S_3 crystal lattice, and that this interaction causes an increase in device efficiency. Although the precise reasons for this improvement are unclear, the work presented in this chapter has highlighted the important role that hole transfer plays in the charge generation process. As such, it is not hard to imagine that a direct chemical interaction between hole donor and acceptor might help expedite the hole transfer reaction. On this basis, a similar strategy as was used to interrogate the hole transfer process to *spiro*-OMeTAD is applied to a system using P3HT.

For this study, rather than preparing the Sb_2S_3 sensitiser by SILAR deposition, a single source metal xanthate precursor was spin-coated onto a metal oxide, which was subsequently thermally annealed to yield the crystalline metal sulfide. For a more complete description of this deposition process, the reader is referred to both Chapter 3 and references 49 and 50. P3HT was subsequently introduced by spin-coating to complete the assembly. Figure 25 shows the absorption spectrum of a $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$ film prepared in this manner, as well as that of an equivalent assembly where TiO_2 is replaced by ZrO_2 . It is noted that films resulting from this preparation route display a broad absorption spectrum with an onset at ~ 750 nm, which is similar to that achieved following a high number of SILAR cycles in section 4.2, as well as for typical high-efficiency devices reported in the literature.^{4,9,10}

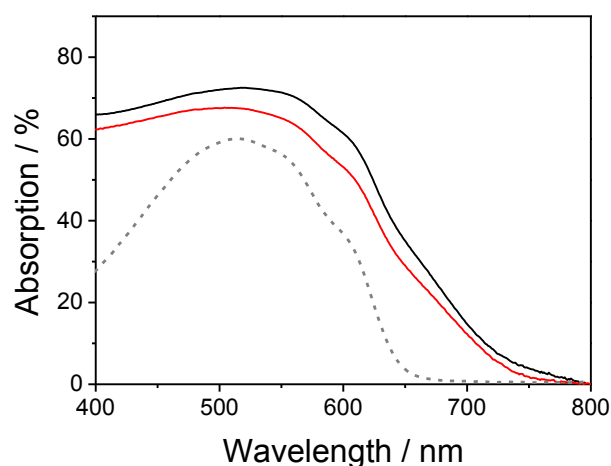


Figure 25 – Absorption spectra of glass/ $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$ (black) and glass/ $\text{ZrO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$ films. Also shown is the absorption spectrum of a pristine glass/ P3HT film (dashed grey).

As before, transient absorption spectroscopy is used to compare samples prepared on TiO_2 , which is expected to be able to accept electrons from Sb_2S_3 , and ZrO_2 , which should act as an insulator. Figure 26a shows the transient absorption spectrum of Sb_2S_3 -sensitised TiO_2 and ZrO_2 films (black and red traces, respectively), with and without the P3HT hole transporter (solid and hollow shapes, respectively) recorded 10 μs after photoexcitation at 700 nm. By exciting at this wavelength, it is ensured that no photons are absorbed by the P3HT, which has an absorption onset of ~ 650 nm. As such, the possibility of electron transfer from P3HT to Sb_2S_3 and/or TiO_2 can be discounted. Firstly, it is interesting that for both TiO_2 and ZrO_2 , very little signal is seen for when the HTM is not present. This indicates that little charge separation is occurring at the $\text{Sb}_2\text{S}_3/\text{metal oxide}$ interface, which for ZrO_2 is consistent with the high energy conduction band and for TiO_2 , with the observations reported above for SILAR Sb_2S_3 -sensitised TiO_2 films excited at increasingly red wavelengths. When the hole conductor is introduced, the transient absorption spectra of both TiO_2 and ZrO_2 -based samples closely

resemble that associated with P3HT hole polarons.^{51,52} This shows that again, hole transfer can occur from Sb_2S_3 despite electron injection being blocked. However, unlike for the samples utilising *spiro*-OMeTAD, where only a very small yield of hole transfer was detected on ZrO_2 substrates, with P3HT the scale of the transient absorption signal on both metal oxides is remarkably similar. This observation suggests that the yield of direct hole transfer from Sb_2S_3 to P3HT is more efficient than the equivalent reaction to *spiro*-OMeTAD. In terms of Figure 13a, this would mean that hole transfer (process 3) is able to kinetically compete more effectively with the recombination of photogenerated charges within the sensitiser (process 4). Whilst it is possible that the presence of P3HT is acting to retard the relaxation of photoexcited electrons within the bulk of the Sb_2S_3 , a more likely explanation is that the transfer of holes from Sb_2S_3 to P3HT is faster than the equivalent reaction to *spiro*-OMeTAD. This appears to be consistent with work by Im *et al.* in which it is proposed that a chemical interaction between the HTM and Sb_2S_3 is key to achieving efficient device performance.² In the hope of better understanding this process, further studies are currently underway using picosecond-resolved transient absorption spectroscopy to directly monitor the dynamics of the hole transfer reaction.

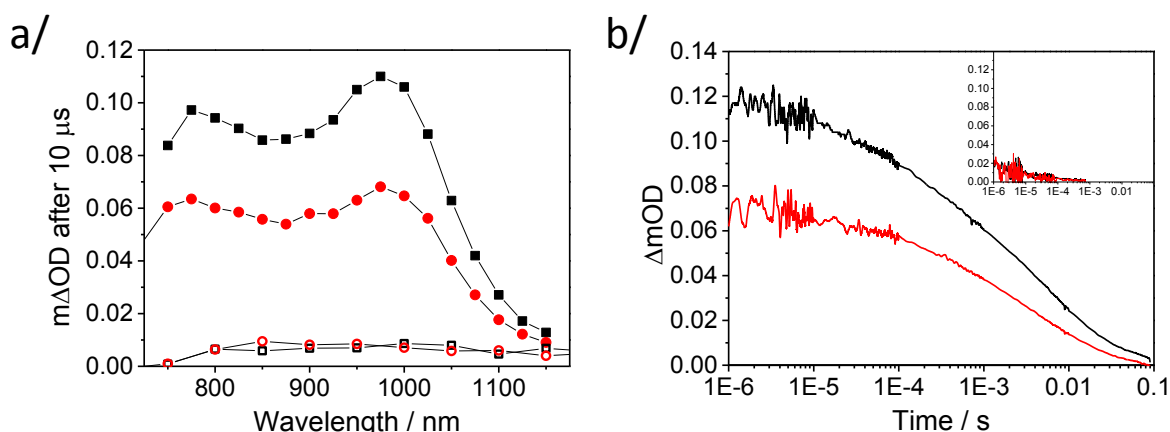


Figure 26 – a/ Transient absorption spectra of metal oxide/ Sb_2S_3 films (hollow shapes) and with metal oxide/ Sb_2S_3 /P3HT films (solid shapes) recorded 10 μs after photoexcitation at 700 nm. Black squares represent TiO_2 -based films and red circles correspond to ZrO_2 equivalents. b/ Time resolved decay of transient absorption peak at 1000 nm – main figure shows samples with P3HT, inset without P3HT. All samples excited with laser energy density = 13 $\mu\text{J cm}^{-2}$ and signals scaled to account for small differences in absorption at the excitation wavelength.

4.4 Conclusions

In conclusion, transient absorption spectroscopy has been used to study charge transfer in $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{spiro-OMeTAD}$ systems. It has been demonstrated that the yield of charge separation at the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface is inhibited as increasingly red-absorbing nanocrystals are excited, which is consistent with a variation in the dynamics of electron transfer as the Sb_2S_3 excited state energy decreases. Despite this, hole transfer to *spiro-OMeTAD* is observed even when electron injection is inhibited by replacing the TiO_2 with an insulator (ZrO_2). This indicates that charge separation within the assembly could be initiated by hole transfer. A similar effect is seen when P3HT is used in place of the *spiro-OMeTAD*, but in this case, even more significant relative yields of hole transfer are achieved as the TiO_2 is replaced with ZrO_2 . On the basis of these observations, it is believed that effective hole transfer is key to efficient performance of $\text{TiO}_2/\text{Sb}_2\text{S}_3$ devices and that strategies designed to enhance this will be integral to further improvements in cell efficiency. Furthermore, the ability to effect interfacial charge separation by hole transfer without the need for extraction of photoexcited electrons introduces the possibility of alternative Sb_2S_3 -based device architectures that do not incorporate a specific electron acceptor material.

Following on from the work discussed in this chapter, we have studied metal oxide/ $\text{Sb}_2\text{Se}_3/\text{spiro-OMeTAD}$ in a similar manner.³³ In this system hole transfer has also been shown to play a key role in the charge generation process, indicating that the conclusions made in this chapter are not unique to the Sb_2S_3 -based system considered. Indeed, more recently, the advent of lead halide perovskite-based solar cells, in which it has also been shown that hole transfer can initiate charge separation,⁵³⁻⁵⁵ has highlighted the great potential of photovoltaic cells that exploit this process.

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5 Low-Temperature Solution Processing of Mesoporous Metal Sulfide Semiconductors as Light-Harvesting Photoanodes

Mesoporous films of highly crystalline Sb_2S_3 are prepared from a doctor bladed precursor paste that is thermally annealed. This facile and versatile processing route allows for control of pore size through variation of annealing temperature. The resulting high surface area allows for efficient charge transfer to a polymeric hole acceptor, with such films forming the basis of a novel hybrid organic-inorganic photovoltaic device. Transient absorption spectroscopy is used to demonstrate charge separation at the inorganic-organic heterojunction, which is found to be dependent on the pore size/interface area. Functioning solar cell devices exhibit photocurrents in excess of 5 mA cm^{-2} , providing evidence for electrical connectivity of the nanocrystals.

5.1 Introduction

Nano- and mesoscale photoactive structures are central to a number of light conversion technologies, including photovoltaics and catalysts for solar hydrogen production.^{1,2} Often, these applications involve the use of a wide band-gap semiconductor such as TiO_2 or ZnO to transport photogenerated charge and impose mesostructure. Whilst these materials are convenient structural scaffolds and efficient charge transport materials, they must be sensitised with a thin layer of a narrow band gap absorber in order to efficiently harvest incident light. Such systems form the basis of dye-sensitised and semiconductor sensitised solar cells (DSSC and SSSC respectively), in which photogenerated electrons in the sensitiser are transferred to and subsequently transported through a porous metal oxide.³⁻⁵ The associated holes are transferred to a liquid electrolyte or a solid hole transport material (HTM). A disadvantage of this configuration is the energetic cost inherent to the transfer of photoexcited electrons and holes from the sensitiser, which limits open circuit voltage. Furthermore, metal oxide films must be thick enough for sufficient light absorption by the thin sensitiser layer. Increasing film thickness raises the probability of charge recombination and can restrict uniform penetration of a solid-state HTM. Such issues can potentially be addressed by employing a single material that combines the electrical, optical and structural functions of the sensitised metal oxide as a light-harvesting photoanode, where charge separation is instigated by hole transfer to an HTM and photogenerated electrons are transported through the absorber material. Metal sulfides and selenides are promising candidates to fulfil this multifaceted role, with large extinction coefficients and red-shifted absorption onsets reported for a wide range of materials, as well as high electrical conductivities. However, a key requirement is the ability to control the morphology of the absorbing material to maximise the yield of charge separation at the absorber/HTM interface whilst maintaining electrical conductivity. In this chapter, a strategy is presented for the low-temperature, solution-based preparation of photosensitive, mesoporous metal chalcogenide films from a printable metal xanthate-based paste. The size of the absorber crystals, and thus the size of the pores in the film can be controlled by variation of the temperature at which the precursor layer is annealed. To consider the potential of these films for use in hybrid organic-inorganic solar cells, the pores are filled with an organic polymer and transient absorption spectroscopy is used to study charge separation via hole transfer at the inorganic-organic heterojunction. The electrical connectivity of the Sb_2S_3 crystals is explored through the fabrication of prototype photovoltaic devices.

The use of metal xanthates and similar complexes as thermally decomposable precursors to metal sulfides is well established,^{6,7} as described in Chapter 2. In the context of photovoltaics, this process has been used in the preparation of nanostructured metal sulfide/polymer blends for use as inorganic-organic hybrid solar cell active layers,⁸⁻¹² as well as to photosensitise mesoporous TiO_2 for SSSC-type

heterojunctions.¹³ Here, a general approach to the preparation of mesoporous Sb₂S₃ films from a printable metal xanthate precursor paste is described. In the study of Sb₂S₃-sensitised solar cells presented in Chapter 4, it has been shown that charge separation in such systems can be instigated by hole transfer to an organic hole conductor,¹⁴ whilst it has been long established that Sb₂S₃ is an n-type semiconductor with the potential to conduct photogenerated electrons.¹⁵⁻¹⁷ As such, Sb₂S₃ is a very promising candidate to undertake the dual role of light absorption and charge transport required of a light-harvesting photoanode.

5.2 Film Preparation

To form mesoporous films of Sb₂S₃, a precursor paste was prepared by adding hexylamine to a stirred chlorobenzene solution of antimony triethyldithiocarbonate precursor (antimony ethyl xanthate, Sb(EX)₃, Figure 27) at a 3:1 molar ratio. Alkylamines have previously been reported to promote decomposition of metal xanthates, potentially through nucleophilic attack of the (thio) carbonyl centre (Figure 28).¹⁸ In the present work, addition of the amine causes the pale yellow xanthate solution to become dark brown/orange and viscous, indicating at least partial decomposition of the precursor (Figure 27). The paste is doctor bladed to form an orange precursor layer on a glass or conducting glass substrate, and subsequently thermally annealed in a nitrogen glove box for 30 minutes, becoming grey and highly optically scattering in the process. Figure 29a shows absorption spectra of a glass slide coated with the precursor layer before (grey trace) and after (black trace) thermal annealing at 120 °C. For the annealed film, the absorption onset at ~740 nm is consistent with the bandgap of crystalline antimony sulfide (1.7 – 1.8 eV).¹⁹ The composition of the annealed film is confirmed by Raman spectroscopy (Figure 29b), where annealing of the precursor causes sharp peaks to appear in the Raman spectrum at ~240, ~280 and ~310 cm⁻¹ (Figure 29b),^{20,21} and X-ray diffraction (Figure 29c), which displays the characteristic peaks of the stibnite mineral (ICDB reference pattern 00-042-1393). It is remarkable to find that highly crystalline Sb₂S₃ can be produced with this method at 120 °C, which is significantly below the reported 250 °C crystallisation temperature of pristine Sb₂S₃.^{15,19,22-24} Previously, sacrificial amine additives have been used to modulate the crystallinity of CdS nanocrystals grown by metal xanthate decomposition in a polymer matrix.²⁵ It may therefore be possible here that the initial decomposition induced by the amine imposes some structural order within the precursor film and that this facilitates the crystallisation process.

Figure 29d is a cross sectional scanning electron micrograph of the Sb₂S₃ layer on a fluorine-doped tin oxide substrate, showing a mesoporous film of Sb₂S₃ of ~400-500 nm in thickness. Additional evidence for the formation of pure Sb₂S₃ is given by core-level X-ray photoelectron spectroscopy (XPS) (Figure 30). Importantly, XPS confirms the presence of nitrogen in the precursor layer but not

after thermal annealing. This indicates that the amine does not remain bound to the antimony sulfide but rather acts as a processing additive. Moreover, the narrow core-level antimony 3d and sulphur 2p XPS peaks for the annealed film indicate complete conversion of the precursor to Sb_2S_3 and the absence of Sb_2O_3 , which would be expected to cause additional, shifted Sb 3d peaks to appear. A small amount of carbon and oxygen are still present after annealing (as evidenced by the respective 1s peaks), but this is to be expected on the surface of samples prepared outside of ultrahigh vacuum. The chlorine peak seen in the non-annealed film is likely to be associated with the solvent (chlorobenzene) and also disappears with annealing.

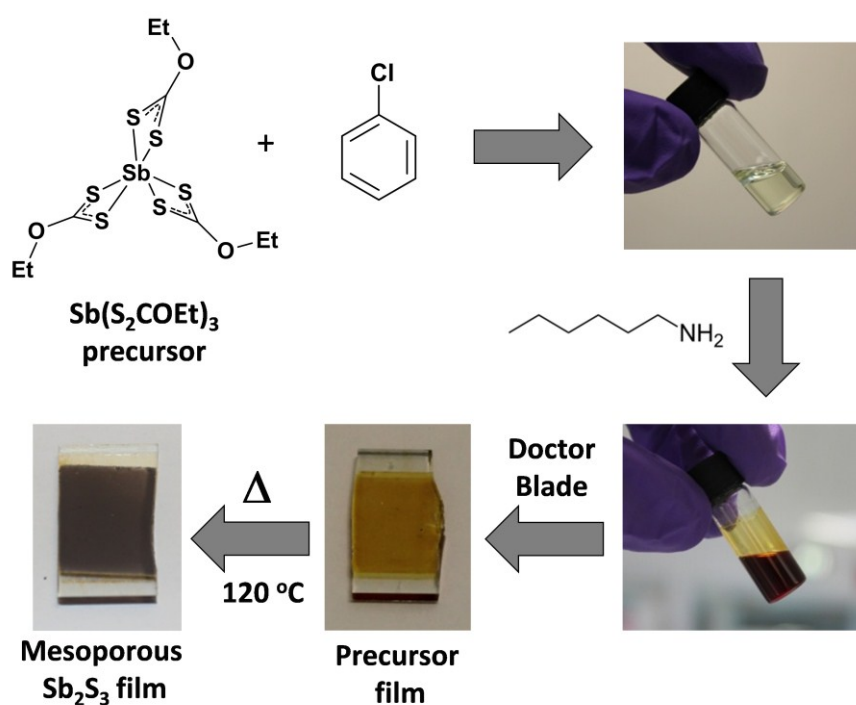


Figure 27 - Schematic to show the processing of antimony ethylxanthate into mesoporous films of Sb_2S_3 .

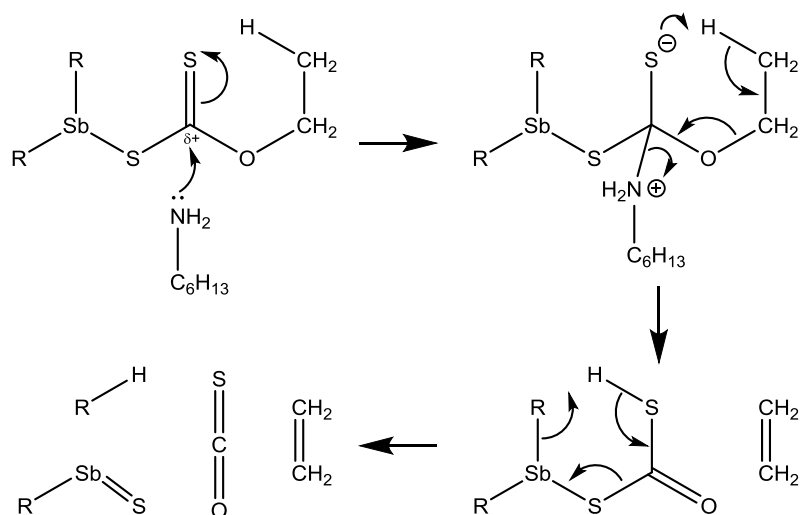


Figure 28 – Possible mechanism for amine-activated decomposition of antimony triethyldithiocarbonate, where R represents an ethyl xanthate ligand.¹⁸

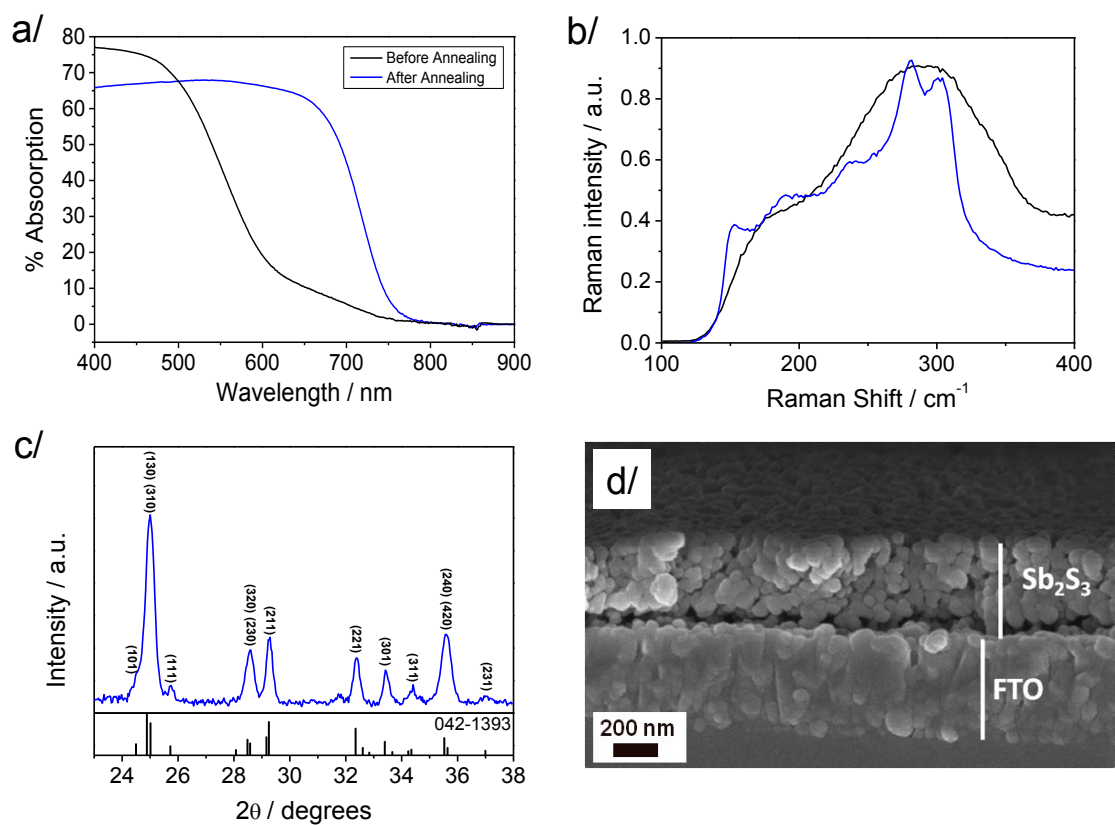


Figure 29 - a/ Absorption spectra and b/ Raman spectra of $\text{Sb}(\text{EX})_3$ film as deposited (grey curve) and after (blue curve) annealing at 120 °C in a nitrogen glovebox, c/ X-ray diffraction pattern of a Sb_2S_3 film following annealing at 120 °C in a nitrogen glovebox, d/ Scanning electron micrograph showing the cross sectional profile of the Sb_2S_3 deposit (annealed 160 °C).

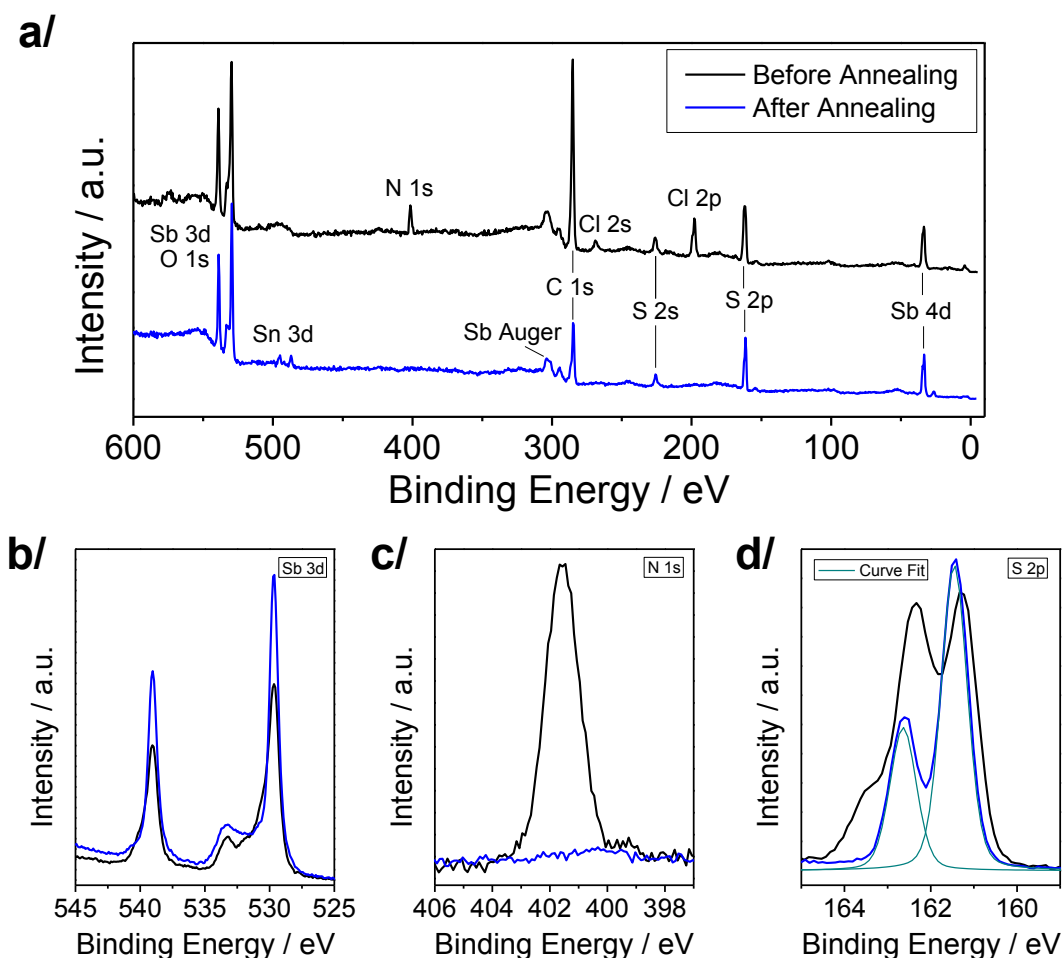


Figure 30 – XPS overview measurements before (black) and after (blue) thermal annealing at 160°C using a 758 eV photon energy: a/ overview spectra showing elemental core-levels in the samples. Also visible is the Sn 3d level from the conducting glass substrate. Nitrogen and chlorine disappear upon annealing together with most of the carbon, b/ Sb 3d core level doublet (peaks at 539 and 530 eV). Also visible is the O 1s core level peak at 533 eV, c/ N 1s core-level and d/ S 2p core level doublet with fit to show deconvolution to two individual but slightly overlapping peaks.

5.2.1 Control of Pore Size

It is now demonstrate that the size of the Sb_2S_3 crystals and the porosity of the resulting films can be controlled through the temperature at which the $\text{Sb}(\text{EX})_3$ precursor layer is annealed. Figure 31a and b show the absorption spectra and XRD patterns of films prepared by annealing $\text{Sb}(\text{EX})_3$ precursor layers at a range of annealing temperatures between 120 °C and 300 °C. From these data, it is clear that crystalline Sb_2S_3 is formed in all cases. Figure 31c shows the variation in full-width half-maximum (FWHM) of the (211) peak from the Sb_2S_3 X-ray diffraction pattern with annealing temperature. The FWHM values obtained are shown in Figure 31d as well as average crystallite sizes calculated using the Scherrer formula. Peak sharpness is seen to increase at higher annealing

temperatures, which indicates an increase in average crystallite size. In similar fashion, top-down scanning electron micrographs reveal a dramatic increase in particle size with increased annealing temperature (Figure 32). At the lowest temperature, a relatively homogenous film of sub-100 nm crystals is observed, whereas at 160 °C, there is a mixture of the smaller crystals with platelets ~200 nm in size. As annealing temperature is increased further, the number of the smaller crystals decreases, leading to a greater average crystallite size and the formation of larger pores.

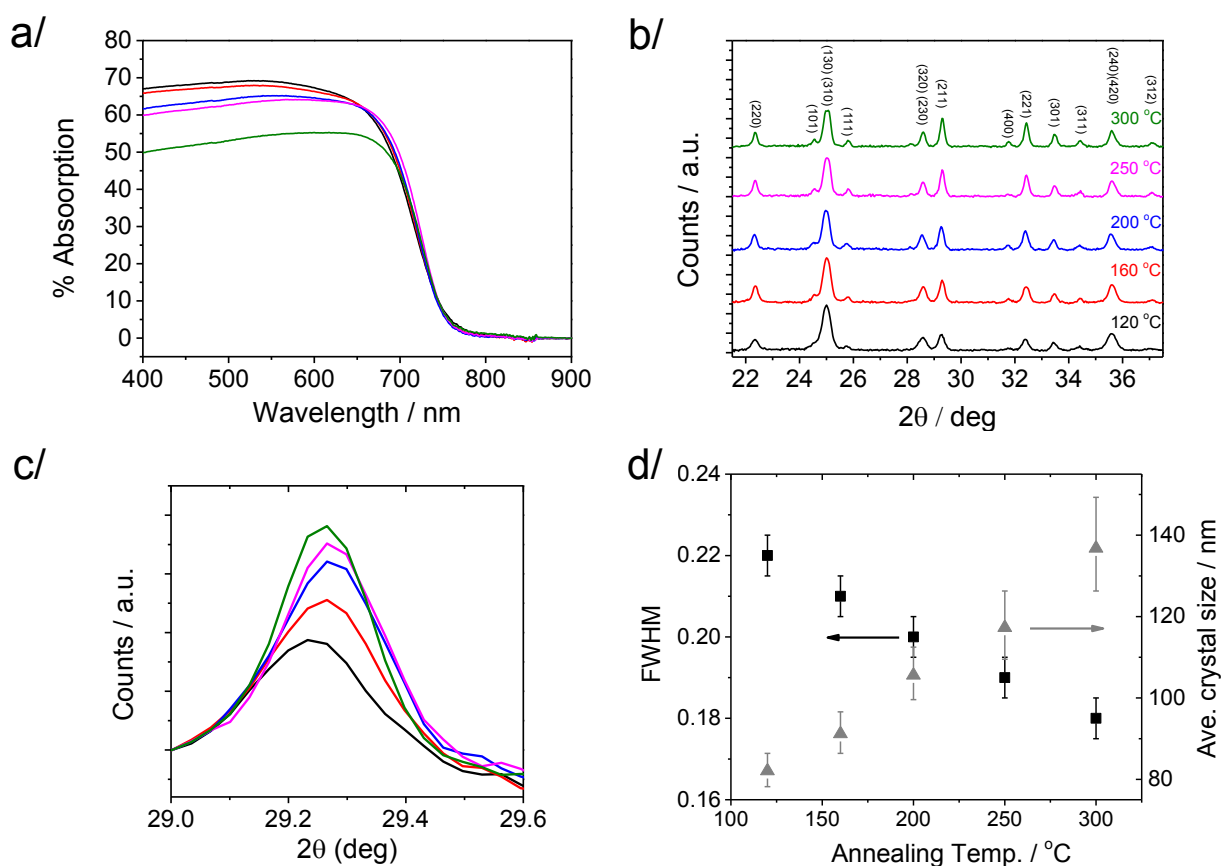


Figure 31 – a/ Absorption spectra and b/ X-ray diffraction patterns of mesoporous Sb_2S_3 films prepared by thermal annealing of the $\text{Sb}(\text{EX})_3/\text{HXA}$ precursor layer at 120 °C (black), 160 °C (red), 200 °C (blue), 250 °C (pink) and 300 °C (green). c/ Increased resolution Sb_2S_3 (211) X-ray diffraction peak to show the variation in peak sharpness with annealing temperature. d/ Full-width half-max (FWHM) of the Sb_2S_3 (211) peak and corresponding average crystallite size in this plane as calculated by the Scherrer equation.

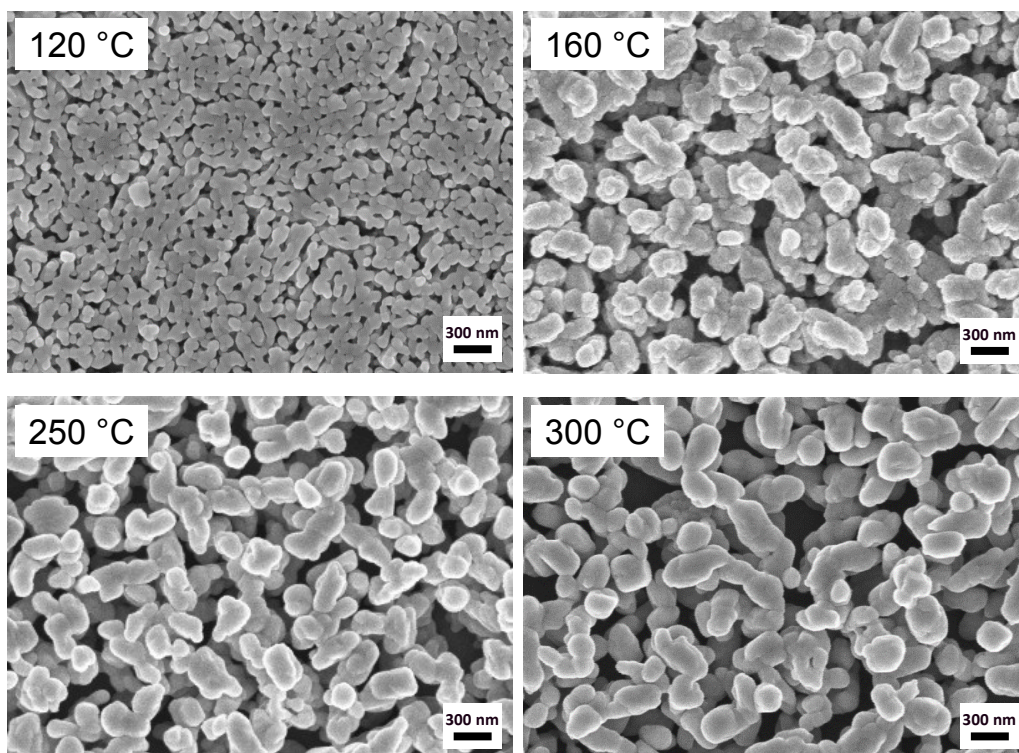


Figure 32 - Top-down scanning electron micrographs of an FTO/Sb₂S₃ film prepared by thermal annealing of the Sb(EX)₃/HXA precursor layer at 120 °C, 160 °C, 250 °C and 300 °C.

5.3 Transient Absorption Spectroscopy

The porous nature of the Sb₂S₃ films described in Section 5.2 provides a large surface area and therefore the potential for efficient interfacial charge separation in the presence of a suitable acceptor material. In order to assess this, poly(3-hexylthiophene) (P3HT) is spin-coated into the pores of the annealed Sb₂S₃ films and microsecond-millisecond transient absorption spectroscopy is used to probe charge separation across the Sb₂S₃/P3HT heterojunction. As the absorption profiles of Sb₂S₃ and P3HT strongly overlap between ~500 and ~640 nm (Figure 33a), the composite layer is excited at 650 nm. In this manner, the contribution of the inorganic component is primarily probed, rather than potential charge transfer from P3HT to Sb₂S₃. Figure 33b shows the transient absorption spectrum of a typical Sb₂S₃/P3HT composite 1 μs after pulsed photoexcitation. The shape of the absorption spectrum closely resembles that reported for P3HT hole polarons (P3HT⁺).⁸ As optical excitation of a pristine Sb₂S₃ or P3HT film yields negligible signal within the time resolution of the system, it is concluded that hole transfer is occurring from Sb₂S₃ to P3HT. Figure 33c shows the intensity of the P3HT⁺ polaron band at 980 nm as a function of time for different Sb₂S₃ annealing temperatures, where all signals have been scaled to account for small differences in the number of photons absorbed at the excitation wavelength. The signals decrease over the measured timescales indicating that the

hole transfer process occurs on shorter timescales than that of the measurement, and instead the dynamics of recombination of electrons and holes across the P3HT/Sb₂S₃ interface are monitored. In all cases, long-lived interfacial charge separation is observed, with decay half-times from the maximum value extending into the millisecond regime. Moreover, the transient absorption intensity at 1 μ s drops as the Sb₂S₃ annealing temperature is raised. This implies a reduction in the yield of interfacial charge separation per photon absorbed as interface area decreases (as seen in the scanning electron micrographs in Figure 32), and thus highlights the crucial importance of a means to control system morphology for efficient charge photogeneration in the composite assembly.

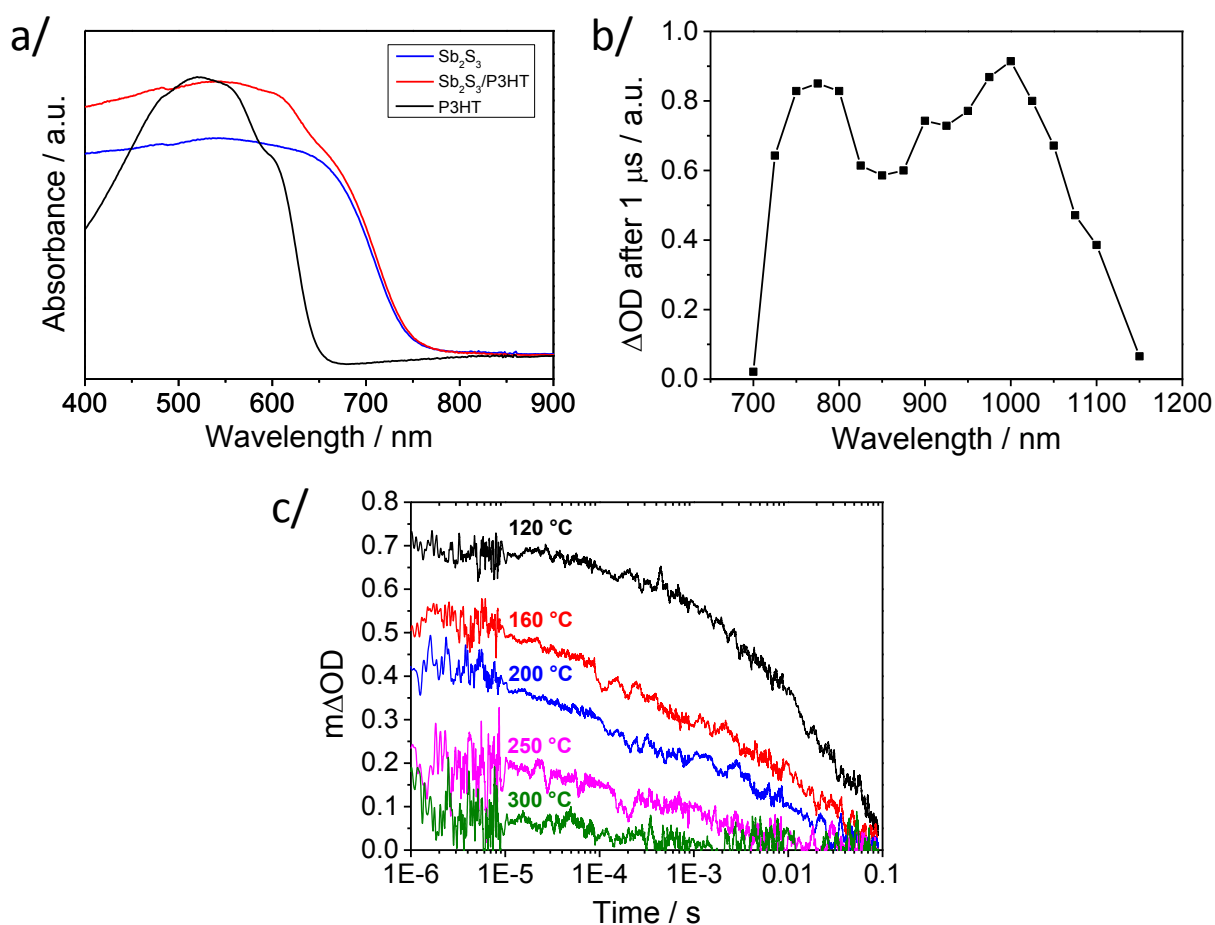


Figure 33 – a/ Steady state absorption spectra of a mesoporous Sb₂S₃ film (annealed 160 °C, blue trace), a pristine P3HT film (black trace) and the Sb₂S₃/P3HT composite (red trace). **b/** Transient absorption spectrum of a mesoporous Sb₂S₃/P3HT composite film, recorded 1 μ s after laser photoexcitation at 650 nm. The precursor layer was annealed at 120 °C and the laser energy density = 8.0 μ J cm⁻². **c/** Decay in transient absorption of the P3HT hole polaron at 980 nm for Sb₂S₃/P3HT films as a function of annealing temperature. Laser excitation at 650 nm (8.7 μ J cm⁻²). Signals are scaled to account for small differences in the number of photons absorbed at 650 nm.

5.4 Photovoltaic Devices

It has been shown in Section 5.3 that long-lived separation of photogenerated charges in the Sb_2S_3 layer can be achieved via hole transfer to P3HT. This highlights the potential for the use these mesoporous photoanodes in light conversion technologies. However, in order for the Sb_2S_3 structures to assume both the optical and electrical roles of a sensitised wide-band gap metal oxide film, it is also necessary that they conduct electrons. To investigate this, photovoltaic devices have been fabricated using an architecture borrowed from the blended inorganic-organic hybrid system (glass/ITO/ TiO_2 (dense)/CdS/ Sb_2S_3 /P3HT/PEDOT:PSS/Ag).^{9,11} In these cells, photogenerated electrons and holes are collected at the ITO and Ag electrodes respectively. Full details of the device fabrication procedure are given in Chapter 3. Figure 34a shows the current-voltage trace for a typical device under 1 sun illumination with an overall power conversion efficiency (PCE) of 0.94 % (black solid trace). Importantly, whilst the overall efficiency is relatively low, a short circuit current of 4.6 mA cm^{-2} is achieved, showing that the Sb_2S_3 layer is indeed able to conduct photogenerated charge. Figure 34b shows a typical IPCE spectrum, with the generation of photocurrent beyond 700 nm highlighting the contribution of photoinduced hole transfer from Sb_2S_3 to P3HT. The IPCE also indicates that current generation as a result of the transfer of photoexcited electrons from P3HT to Sb_2S_3 is much less efficient than hole transfer from Sb_2S_3 to P3HT, as a spectral depression is observed in the region in which the polymer absorbs ($\sim 500\text{-}640 \text{ nm}$). This is consistent with reports in the literature of $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$ systems,²⁶ although it is unclear as to whether electron transfer is just relatively inefficient or entirely prohibited. It is expected that the parasitic light filtering effect induced by the polymer could be addressed by the use of either transparent or near-infrared-absorbing hole transporters, whilst further tuning of system morphology and an improved understanding of the interfacial electron transfer process might encourage improved photocurrent contribution. Control devices fabricated without the Sb_2S_3 layer (namely in the glass/ITO/ TiO_2 (dense)/CdS/P3HT/PEDOT:PSS/Ag configuration) displayed very low efficiencies (red line, Figure 34a), thus confirming the contribution to current generation from light absorbed by the Sb_2S_3 .

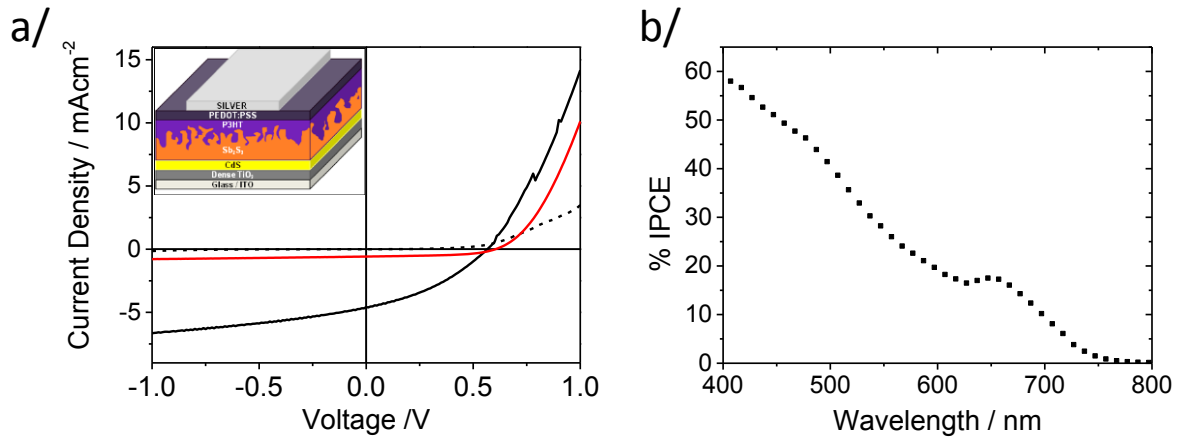


Figure 34 – a/ Main figure shows current-voltage response of an ITO/TiO₂/CdS/Sb₂S₃/P3HT/PEDOT:PSS/Ag photovoltaic device in the dark (black dashed line) and under 1 sun illumination (black solid line). The Sb(EX)₃ precursor layer was annealed at 160 °C. Also shown is a control device without the Sb₂S₃ layer (ITO/TiO₂/CdS/ P3HT/PEDOT:PSS/Ag - red solid line). Inset shows an illustration of device architecture. b/ Incident photon-to-current efficiency of an ITO/TiO₂/CdS/Sb₂S₃/P3HT/PEDOT:PSS/Ag device.

	$J_{SC} / \text{mA cm}^{-2}$	V_{OC} / V	FF	PCE / %
With Sb₂S₃	4.58	0.57	0.36	0.94
Without Sb₂S₃	0.58	0.60	0.53	0.11

Table 2 - J-V parameters of best ITO/TiO₂/CdS/Sb₂S₃/P3HT/PEDOT:PSS/Ag device (from Figure 34) and a control device without the mesoporous Sb₂S₃ layer.

It is expected that significant improvements in device performance will be achieved by tailoring the device architecture specifically to the present system, for example through optimisation of charge-selective interlayers and contacts. At present, a very high series resistance appears to be severely limiting performance, as indicated by the shallow slope of the light JV curve in Figure 34a as it passes through V_{OC} and from the weak sensitivity of dark current to voltage at forward bias. These observations are consistent with atomic force microscopy (AFM) measurements (an example of which is shown in Figure 35), which reveal the surfaces of the devices to be very rough prior to evaporation of the Ag top electrode. This is likely to result in significant contacting problems thus contributing to the high series resistances. It is probable that this problem is at least partly a product of the great difficulty experienced in wetting the surface of the P3HT coated film with PEDOT:PSS, despite the presence of the Zonyl surfactant. Perhaps for the same reason, significant batch-to-batch (and indeed device-to-device) variation was encountered, which severely limited the fabrication of consistent series of devices for iterative study of factors such as the effect of Sb(EX)₃ annealing temperature. It is suggested that future strategies aimed at improving performance of these devices will focus on

‘smoothing’ the surface of the assembly before the top contact is deposited, perhaps through the introduction of a selective conductor that can penetrate the pores of the film and still yield a flat top surface. However, the device work described here acts as an important proof of concept that the Sb_2S_3 crystals are electrically conductive.

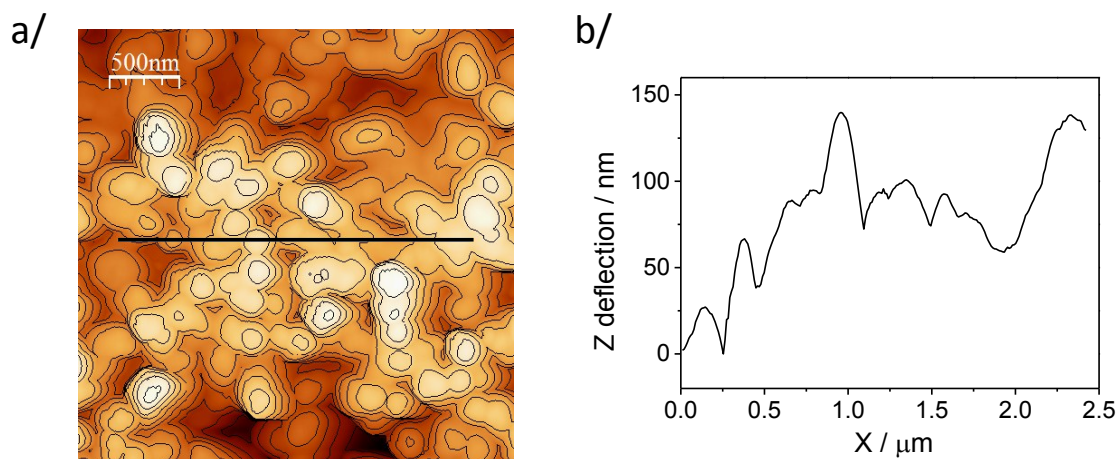


Figure 35 – a/ Tapping-mode atomic force microscopy (AFM) surface topography plot with contour lines of a glass/ Sb_2S_3 /P3HT/PEDOT:PSS film. b/ Surface profile along the black line passing through the centre of (a/). Data collected in collaboration with Azadeh Bahrami and Dr. Tim Albrecht at Imperial College London.

5.5 Conclusions

For Sb_2S_3 , interfacial charge separation can be effected by hole transfer, without the requirement for extraction of photogenerated electrons.¹⁴ Given that Sb_2S_3 can also conduct electrons, this draws into question the need for a mesoporous metal oxide electron acceptor, as used in the ETA-type architecture. An alternative strategy to the preparation of Sb_2S_3 -based hybrid photovoltaics is to condense the multifaceted electrical, optical and structural roles of a sensitised mesoporous metal oxide into a single component.

In this chapter, a strategy has been introduced for the low-temperature, solution-based preparation of photosensitive, mesoporous metal chalcogenide films from a printable metal xanthate-based paste. The size of the absorber crystals, and thus the size of the pores in the film can be controlled by variation of the temperature at which the precursor layer is annealed. Resultant films are highly photosensitive, with absorption extending into the near-infrared. The potential of these films for use in hybrid organic-inorganic solar cells has been considered by filling the pores with an organic polymer. Transient absorption spectroscopy reveals that charge separation does take place via hole transfer at this inorganic-organic heterojunction. It is determined that the yield of interfacial charge separation is highly sensitive to interface area, which highlights the importance of a means to control film morphology. Photovoltaic devices demonstrate short circuit currents of almost 5 mA cm^{-2} , indicating that the Sb_2S_3 crystals are electrically connected. The work described in this chapter shows that Sb_2S_3 is not limited to use as a simple absorber material for ETA cells, but that it can also be used to transport photogenerated charge carriers. This significantly expands the library of potential hybrid device architectures into which it can be incorporated.

Whilst this method has been applied to the decomposition of antimony xanthates, it is expected to be equally applicable to other metal xanthate precursors, providing a general platform for the growth of coloured, electrically connected mesoporous films of inorganic semiconductors.

5.6 References

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6 Hybrid Sb₂S₃/Polymer Thin-Film Photovoltaics by Solution-Processing of Single-Source Precursors

In the previous chapters, it has been shown that electron injection from Sb₂S₃ to a metal oxide is not a pre-requisite for the interfacial separation of photogenerated charges via hole transfer. In this chapter, mesostructuring is eliminated from the device architecture and solar cells based on a flat Sb₂S₃/hole transport material (HTM) interface are considered. To facilitate the preparation of these devices, a novel method for the deposition of thin films of Sb₂S₃ is developed, whereby a single-source metal xanthate precursor is spin-coated and thermally decomposed to yield the crystalline metal sulfide. An iterative and systematic study of the effects of a range of processing parameters on device performance is described, which reveals optimal conditions for the preparation of efficient devices. As a result of this work, a short circuit photocurrent of 11.5 mA cm⁻² and a power conversion efficiency of 3.28 % is achieved under 1 sun illumination, with the latter figure rising to almost 4 % at 0.1 sun.

Subsequently, preliminary investigations of the mechanisms of device function are conducted, as bilayer devices are compared with Sb₂S₃ SSSC-type cells that are prepared in an analogous manner. It is found that although these two classes of device are structurally very different, overall performance is similar. This highlights the impressive performance of the thin-film assembly, but also draws into question the importance of meso-scale morphological control. To compare and contrast the way in which the two systems function, transient absorption spectroscopy is employed to study the interfacial charge transfer processes at the Sb₂S₃/polymer heterojunction. Whilst for the mesoporous configuration, hole transfer can occur from Sb₂S₃ to P3HT even when the semiconducting TiO₂ electrode is replaced with an otherwise analogous insulator (ZrO₂), there is no evidence to suggest that interfacial charge separation is able to take place in the flat Sb₂S₃/P3HT bilayer film, despite the high short-circuit currents achieved in the full devices. This observation suggests fundamental differences in the operational mechanisms of charge separation in the two systems. Transient optoelectronic measurements are used to help understand the origins of these effects.

6.1 Introduction

As a solar cell absorber, Sb_2S_3 has been the subject of considerable study in the semiconductor sensitised solar cell (SSSC) architecture, where it is used to coat a wide bandgap, mesoporous metal oxide, such as TiO_2 .¹⁻¹⁰ The pores of the sensitised electrode are filled with a hole transport material (HTM) that extracts holes from the sensitiser and transports them to a counter electrode, thus completing the circuit. A traditional understanding of the operational mechanism of such devices involves the instigation of charge separation by a rapid electron transfer reaction from the sensitiser to the metal oxide. Subsequently, the sensitiser ground state is 'regenerated' by hole transfer to the HTM.

In Chapters 4 and 5, it has been demonstrated that photoinduced hole transfer can take place from Sb_2S_3 to a suitable acceptor, even when electron injection is prohibited. This observation suggests that rather than simply acting as a 'regeneration' process, hole transfer can itself effect the separation of photogenerated electrons and holes in Sb_2S_3 . As Sb_2S_3 is an electron conducting n-type semiconductor,¹¹ this draws into question the need for a specific electron acceptor. These factors have informed and motivated the development of alternative hybrid device architectures where Sb_2S_3 is not only used as a light harvesting material, but is also required to conduct photogenerated electrons. As well as the mesoporous Sb_2S_3 photoanode approach described in Chapter 5,¹² a bulk heterojunction-type Sb_2S_3 /P3HT system has also been developed, whereby an antimony xanthate precursor was blended with the polymer and thermally decomposed to yield a conducting network of Sb_2S_3 in an organic hole transporter matrix.¹³ This strategy resulted in the preparation of photovoltaic devices delivering 1.3 % power conversion efficiency. One question that arose from the study of these systems was whether the structured nature of the Sb_2S_3 /P3HT interface is fundamental to device performance, or whether similar results could be achieved at a flat interface. So as to further explore this question, this chapter removes the mesoporous TiO_2 layer from the device architecture considered in Chapter 4 and explores a two-component Sb_2S_3 /hole acceptor active layer in the simplest possible configuration - a flat bilayer.

In the early 1990s, Savadogo and co-workers explored the use of Sb_2S_3 as an absorber in more traditional, all-inorganic thin film solar cells. However, much of this work required the n-type metal sulfide to be paired with a highly crystalline p-type material, such as single crystals of doped silicon¹⁴ or germanium¹⁵ (achieving power conversion efficiencies of 1.03 % and 2.4 %, respectively). One interesting exception was when a thick (2.2 μm) Sb_2S_3 layer was sandwiched between a conducting glass substrate and a gold top contact to form a Schottky barrier solar cell with a PCE of 0.4 %.¹⁶ It is noted that in these works, improvements in device performance were achieved when the Sb_2S_3 was doped with tungsten oxide,^{17,18} which the authors attribute to the elimination of surface trap states

from the Sb_2S_3 bandgap.¹⁶ Subsequently, Messina *et al.* considered the use of solution processed lead sulfide in place of single crystal p-type materials, with devices reaching almost 1 %.^{19,20} More recently, Boix *et al.*²¹ and Darga *et al.*²² have coupled Sb_2S_3 with P3HT in a bilayer configuration for use as a model system to compare with mesoporous SSSC devices, although efficiencies have not exceeded 1.43 %. In all of these examples, as for the most efficient SSSC devices,^{8,10} preparation of Sb_2S_3 photovoltaic absorber layers has exclusively been achieved by chemical bath deposition (CBD), where a substrate is immersed in a reacting solution containing an antimony source (e.g. SbCl_3 , $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2$) and a sulphur source ($\text{Na}_2\text{S}_2\text{O}_3$), often for several hours, thus allowing amorphous Sb_2S_3 to form on the surface.^{23,24} Subsequent thermal annealing yields the crystalline product. A notable alternative preparation route is described by Bello and co-workers, who have thermally evaporated 100 nm thick layers of Sb_2S_3 on rough ZnO substrates and added P3HT to achieve a maximum PCE of 2.4 %.^{25,26} Alternative deposition methods such as spray pyrolysis,^{27,28} SILAR²⁹ and atomic layer deposition,³⁰ have generally yielded less efficient devices than their CBD-prepared counterparts.

Currently, and particularly in light of the recent advent of lead perovskite-based solid state solar cells, for which a number of different device architectures have delivered high power conversion efficiencies,³¹⁻³³ two key issues in the field of solution-processed hybrid photovoltaics are: 1/ furthering understanding of the influence of physical interface structure on device performance and 2/ the development of facile and scalable processing routes to achieve the fabrication of photovoltaic thin films. In this chapter, a novel route is presented for the preparation of thin films of crystalline Sb_2S_3 through the one-step decomposition of a single-source precursor. These films can be coupled with a conducting polymer to form a flat bilayer and the basis of a hybrid thin-film photovoltaic device. Following a number of iterative optimisation studies, described herein, a maximum power conversion efficiency (PCE) exceeding 3.25 % under 1 sun illumination is achieved with a short circuit-current of 11.5 mA cm^{-2} . PCE rises to almost 4 % at 0.1 sun.

In order to demonstrate the versatility of this facile and flexible deposition approach, ETA-type solar cells have also been prepared, where Sb_2S_3 is used to photosensitise a mesoporous TiO_2 electrode. It is found that although these devices are structurally very different to the bilayer cells, overall performance is remarkably similar. This observation, which contrasts with previous comparisons of the performance of mesostructured and flat Sb_2S_3 solar cells,^{21,22,26} not only highlights the impressive efficiency of the thin-film assembly, but also draws into question the importance of meso-scale morphological control in the design of hybrid photovoltaics. To compare and contrast the ways in which the two systems function, transient absorption spectroscopy and transient photovoltage measurements are used to study the interfacial charge separation and recombination processes at the Sb_2S_3 /polymer heterojunction.

6.2 Sb₂S₃ Thin-Film Processing and Characterisation

In the present work, a novel process for the preparation of Sb₂S₃ thin films is introduced, which is based upon the thermal decomposition of an antimony triethyldithiocarbonate precursor (antimony ethyl xanthate, Sb(EX)₃, Figure 36a). Sb(EX)₃ was synthesised by the reaction of antimony chloride and potassium ethyl xanthate, as described in Chapter 3. Thermal gravimetric analysis (TGA) of the Sb(EX)₃ compound (Figure 36b) shows the decomposition process occurring between ~100 °C and 150 °C, with the final residual mass (37 %) close to that expected of Sb₂S₃ (35 %). Figure 36c illustrates the method for preparation of Sb₂S₃ thin films, where a solution of Sb(EX)₃ is prepared in anhydrous chlorobenzene and spin coated onto a substrate, with a subsequent thermal annealing step causing the precursor to decompose to the metal sulfide. The mechanism of xanthate decomposition is described in greater detail in the Experimental Section (Chapter 3).

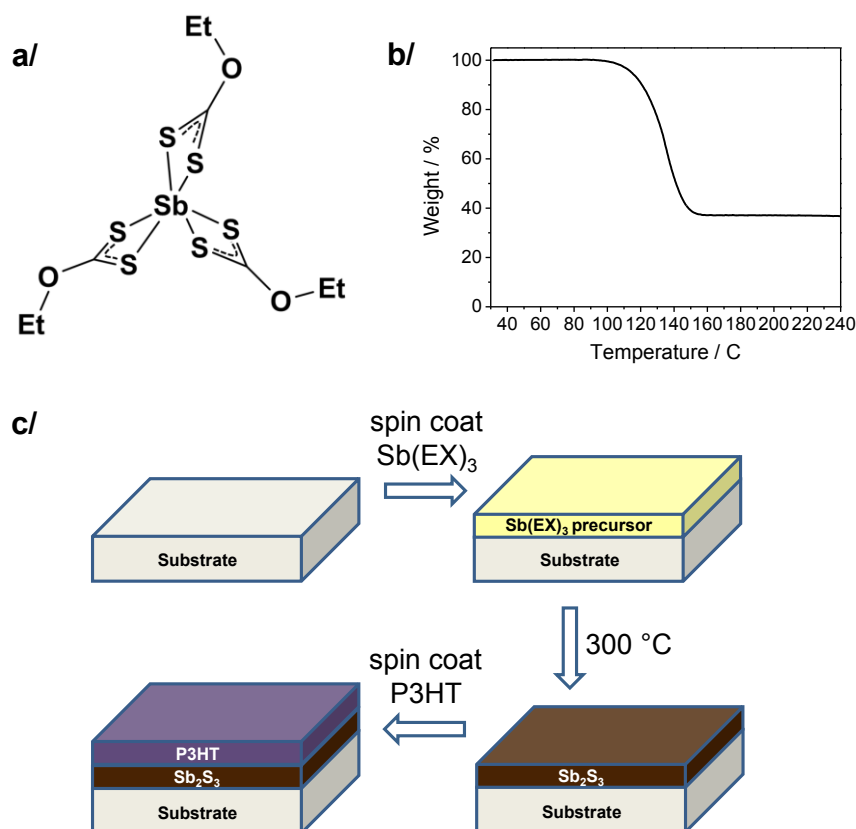


Figure 36 – a/ Chemical structure of the antimony triethyldithiocarbonate (Sb(EX)₃) precursor. b/ Thermal gravimetric analysis of Sb(EX)₃. c/ Illustration to show the preparation of Sb₂S₃ thin-films by spin coating and thermal annealing of the Sb(EX)₃ precursor.

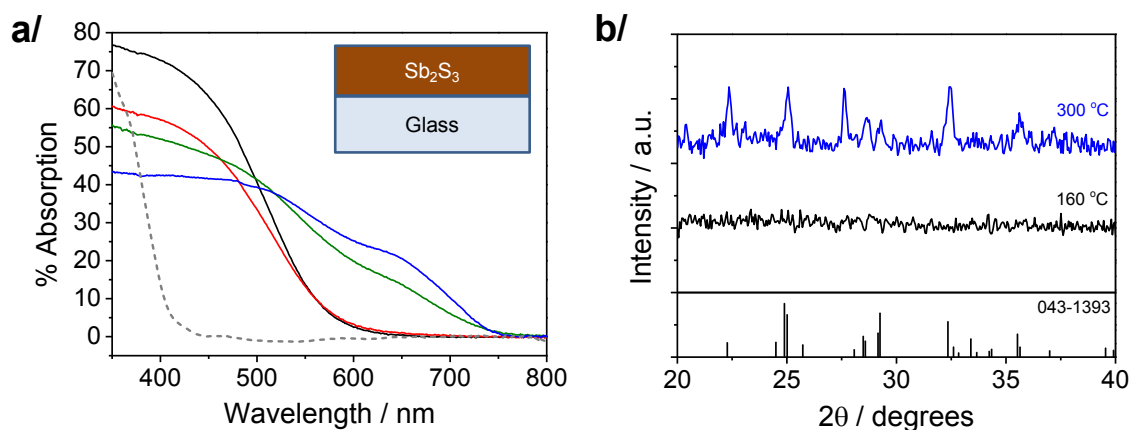


Figure 37 - a/ Absorption spectra and b/ X-ray diffraction patterns of glass/Sb₂S₃ films, prepared by annealing an Sb(EX)₃ precursor layer at 160 °C (black), 200 °C (red), 250 °C (green) and 300 °C (blue). a/ also shows the pristine glass/Sb(EX)₃ substrate (grey dashed line). Sb(EX)₃ layers spun at 6000 rpm from 400 mg mL⁻¹ chlorobenzene solution.

Figure 37a shows the absorption spectra of Sb(EX)₃ films spin-coated on a glass substrate from chlorobenzene solution before (grey dashed line) and after thermal annealing for 30 minutes in N₂ at 160 °C, 200 °C, 250 °C and 300 °C (black, red, green, blue solid lines, respectively). Within this range, three distinct spectral profiles are observed: the as-deposited precursor film is almost transparent, displaying little absorption in the visible range; annealing at 160 °C and 200 °C causes the metal xanthate to decompose to the metal sulfide and the film becomes orange in colour with an absorption onset at ~600 nm, whilst higher temperatures cause the films to become dark brown and further red-shift the absorption onset to ~740 nm. The values of 600 nm and 740 nm are consistent with the bandgaps of amorphous and crystalline antimony sulfide, respectively, indicating a simple and effective means of controlling of the structural phase of the metal sulfide. X-ray diffraction measurements confirm that crystalline Sb₂S₃ is formed when the precursor layer is annealed at 300 °C, as shown in Figure 37b where the measured peaks (blue line) overlap precisely with those of a stibnite reference (ICDB 00-042-1393). The absence of diffraction peaks for the film annealed at 160 °C further suggests that the amorphous phase is formed in this case. These observations are consistent with the 250 °C Sb₂S₃ crystallisation temperature widely reported in the literature.³⁴ It is noted that if the precursor layer is heated to above ~150 °C in ambient conditions for any prolonged period of time, rather than assuming the dark brown colour characteristic of the metal sulfide, the films become white indicating oxidation to the wide band gap Sb₂O₃.¹

The reproducible preparation of good quality Sb₂S₃ layers on glass substrates proved to be extremely challenging, with a key variable appearing to be the way in which the substrate surface is treated prior to spin-coating. When attempting to spin-coat the precursor layer, it was found that the Sb(EX)₃ solution would not wet a clean glass substrate, forming a high contact-angle droplet in the middle of

the surface. ‘Dynamic’ spin-coating, whereby the precursor solution was deposited directly onto the already spinning substrate, yielded very mild improvement, but after thermal annealing, only a very sparse coating of Sb_2S_3 remained. A photograph of a film prepared in this manner is shown in Figure 38a. To combat these issues, a number of surface treatments were trialled, with oxygen plasma treatment of the substrate directly prior to spin coating yielding a certain degree of success. This technique was used in the preparation of the films presented in Figure 37a and a photograph of the resulting Sb_2S_3 deposit is shown in Figure 38b. Although reasonable Sb_2S_3 surface coverage was achieved in this manner, films remained visibly inconsistent and highly optically scattering as seen by the white/grey appearance of some regions of the film (see Figure 38b).

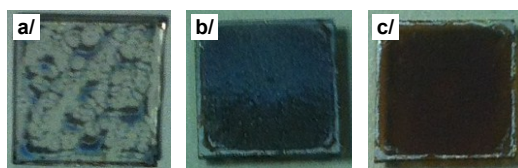


Figure 38 – Photographs to illustrate the surface coverage and film quality of Sb_2S_3 layers on a/ pristine glass, b/ glass cleaned with oxygen plasma treatment and c/ glass coated with a 20 nm CdS layer.

Previously, Messina *et al.* have reported that Sb_2S_3 films prepared by chemical bath deposition adhere more strongly to glass substrates when coated with a thin CdS layer.²⁴ Here, it is found that introduction of a thin cadmium sulfide interlayer (~ 20 nm - also by spin coating and thermally annealing a metal xanthate precursor ($\text{Cd}(\text{S}_2\text{COEt})_2(\text{C}_5\text{H}_4\text{N})_2$)) prior to spin coating of $\text{Sb}(\text{EX})_3$ resulted in dramatic and consistently reproducible improvements in film quality. When deposited on a CdS underlayer, the Sb_2S_3 appeared much smoother, more specularly reflective and less scattering (Figure 38c). Scanning electron microscopy (SEM) clearly shows the difference in Sb_2S_3 surface coverage for films deposited on oxygen plasma treated fluorine-doped tin oxide (FTO) (Figure 39a and b) and FTO/CdS substrates (Figure 39c and d). In the former case, very poor surface coverage is observed, whereas considerably more consistent and continuous Sb_2S_3 films are achieved on CdS. In Figure 39c, the CdS layer is too thin to be clearly resolved. When $\text{Sb}(\text{EX})_3$ was deposited on CdS, the crystalline Sb_2S_3 phase was found to form at annealing temperatures $\geq \sim 180$ °C, as shown in the UV and XRD spectra in Figure 40, as opposed to ~ 250 °C without a CdS underlayer. This may indicate that the CdS layer is acting as a source of nucleation sites for the growth of the Sb_2S_3 crystals, as well as allowing for favourable surface interactions with the precursor solution. CdS has been used as a n-type hole blocking layer in various polymer-inorganic hybrid photovoltaics,³⁵ including those based on Sb_2S_3 ,¹³ as well as numerous thin-film technologies.^{19,20,24,36,37} As such, its presence here between the photoactive layer and the electron collecting contact may also be expected to affect the electrical performance of the device. The influence of the CdS layer, beyond that as a seed layer for Sb_2S_3 growth, is considered later in this chapter.

As the temperature is further increased beyond the threshold at which crystallisation occurs, the films become increasingly absorbent in the region between ~ 500 nm and 750 nm (Figure 40a). This is not accompanied by any noticeable sharpening of the X-ray diffraction peaks and is thus unlikely to relate to variation in the size of the crystal domains; however it might be due to an increasing ratio of crystalline to amorphous regions within the film as the temperature is raised. It is expected that the increased absorption in this region will result in improved matching to the solar spectrum, allowing a greater proportion of incident photons to be converted to electrical current in a working device.

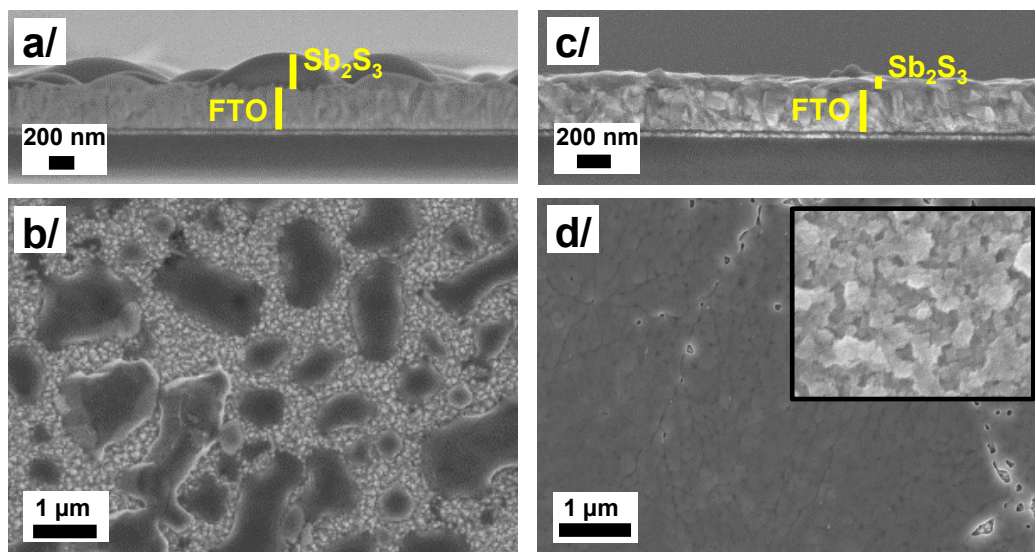


Figure 39 – Scanning electron microscope images of Sb_2S_3 films grown by decomposition of $\text{Sb}(\text{EX})_3$ at 300°C on FTO substrates (a/ and b/ - cross-sectional and top-down respectively) and FTO substrates coated with a thin (~ 20 nm) CdS layer (c/ and d/ - cross-sectional and top-down respectively). Inset to d/ shows a top down SEM image of the pristine CdS layer on FTO at the same scale as the main image. All $\text{Sb}(\text{EX})_3$ layers spun at 2000 rpm from a 400 mg mL^{-1} chlorobenzene solution.

In the previous chapter, it has been shown that separation of photogenerated charges in Sb_2S_3 can be effected at an interface with poly(3-hexylthiophene) (P3HT) via hole transfer. Here, P3HT is used as a p-type transport material and is spin-coated on top of the Sb_2S_3 thin-films to form a hybrid bilayer. Figure 41 shows the absorption spectrum and a scanning electron micrograph of the full CdS/ Sb_2S_3 /P3HT assembly.

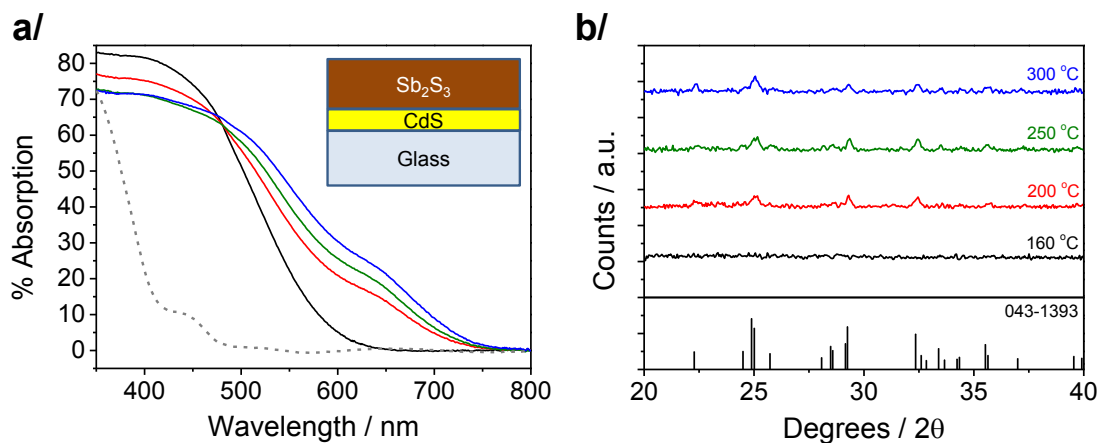


Figure 40 – a/ Absorption spectra and b/ X-ray diffraction patterns of glass/CdS/Sb₂S₃ films, prepared by annealing an Sb(EX)₃ precursor layer at 160 °C (black), 200 °C (red), 250 °C (green) and 300 °C (blue). a/ also shows the pristine glass/CdS/Sb(EX)₃ substrate (grey dashed line). Sb(EX)₃ layers spun at 6000 rpm from 400 mg mL⁻¹ chlorobenzene solution.

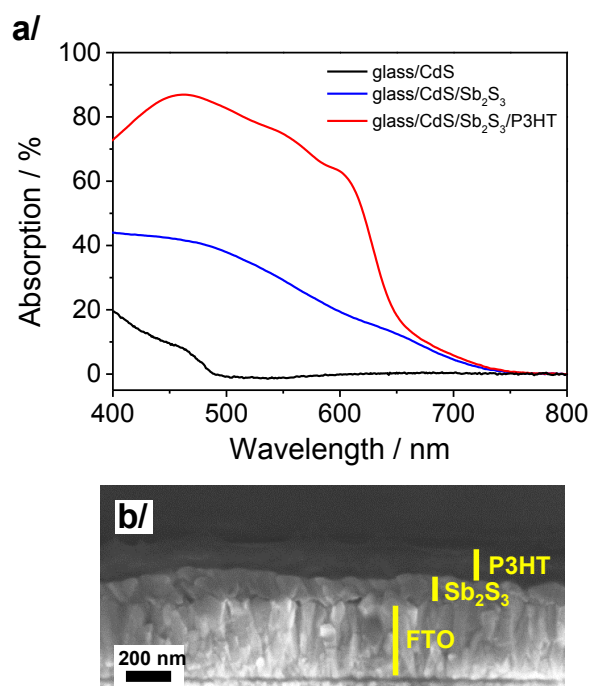


Figure 41 – a/ Absorption spectra of glass/CdS (black), glass/CdS/Sb₂S₃ (blue) and glass/CdS/Sb₂S₃/P3HT (red) and b/ Scanning electron micrograph of an FTO/Sb₂S₃/P3HT film.

6.3 Device Optimisation

In order to assess the potential of Sb_2S_3 as an absorber in a bilayer solar cell configuration, processing parameters and material choices that influence device performance must be identified and optimised to ensure that the system is operating to its maximum capacity. With this in mind, the first part of this chapter focuses on the growth of flat Sb_2S_3 layers by decomposition of a single-source precursor and identifies a number of key variables that can influence device performance. Specifically, the effects of the thickness of the active layer, the HTM and relevant interlayers are considered, as are the conditions under which the precursor is decomposed (such as temperature and local atmospheric environment). In addition to ensuring optimal device performance, the study of such parameters in this simple system allows a number of pertinent questions in the field of Sb_2S_3 -based photovoltaics to be considered, including the importance of Sb_2S_3 crystallinity, the effect of oxidation, the charge conducting properties of Sb_2S_3 , the role of hole transfer and the possibility of generating extra photocurrent with a coloured hole conductor via electron injection.

All devices were prepared on glass substrates coated with a transparent conducting oxide (TCO), which acts as an electron collecting contact. Generally, indium-doped tin oxide (ITO) was used, but samples for scanning electron microscopy were prepared on fluorine-doped tin oxide (FTO) substrates. For devices, a thin, dense TiO_2 layer (~20 nm, as measured by profilometry) was deposited on top of the transparent conducting oxide (TCO) as a hole blocking layer, to avoid potential shunt pathways developing between the HTM and the electron collecting contact. Preliminary studies indicated that variation in the thickness of this TiO_2 layer had little influence on cell performance. As such, all TiO_2 layers were deposited by spin-coating a titanium isopropoxide solution at 6000 rpm and sintering in air at 450 °C for 1 hour, as described in Chapter 3. The presence of a thin cadmium sulfide layer (~20 nm) was found to improve wetting of the $\text{Sb}(\text{EX})_3$ precursor layer and allows for the formation of consistent and continuous Sb_2S_3 layers (see Section 6.2). CdS was deposited on top of the dense TiO_2 layer by spin coating and thermal decomposition of a cadmium xanthate precursor - see Chapter 3). The effect of CdS layer thickness is discussed in Section 6.3.5. Poly-3-hexylthiophene (P3HT) was used as a hole transport material and spin-coated from chlorobenzene solution. MoO_3 (20 nm) and Ag (100 nm) were thermally evaporated on top of the P3HT layer as an electron blocking layer and hole collecting contact, respectively.

6.3.1 Sb₂S₃ Crystallisation

In Section 6.2, it has been shown that either amorphous or crystalline Sb₂S₃ can be formed by decomposition of antimony ethylxanthate, with the resulting phase defined by the temperature at which the precursor layer is annealed. The performance of each of these phases as absorber layers in a Sb₂S₃/P3HT bilayer device is considered.

Figure 42a and b compare the absorption spectra and XRD patterns respectively of glass/CdS/Sb₂S₃ films annealed at 160 °C (amorphous, black) and 300 °C (crystalline, blue). Also shown in Figure 42a is the absorption spectrum of a pristine glass/CdS film (grey). The crystalline Sb₂S₃ film displays a broad absorption profile with an onset at 740 nm consistent with the expected bandgap of ~1.8 eV, whilst the amorphous phase absorbs wavelengths $\geq$ ~650 nm. It is thus expected that a greater amount of photocurrent can be realised with the crystalline phase as more incident photons are absorbed, whilst the amorphous phase should yield a higher voltage. Figure 42c, which shows the current density-voltage response of an ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag device both in the dark (dashed lines) and under 100 mW cm⁻² AM 1.5 illumination (solid lines), and Table 3, which details the associated device parameters under illumination, reveal this to indeed be the case.

Firstly, it is noted that a short circuit current of 7.7 mA cm⁻² and a conversion efficiency of 1.45 % for a non-optimised hybrid bilayer device using crystalline Sb₂S₃ was both remarkable and encouraging. Despite the higher voltage achieved in the device utilising an amorphous Sb₂S₃ absorber layer, overall performance with the crystalline absorber is significantly better as a result of a dramatically increased short-circuit current. The IPCE spectra of the two devices, as shown in Figure 42d, reflect the increased absorption range of the crystalline film, with light harvesting extending to ~750 nm. However, there appears to be little photocurrent contribution stemming from the P3HT. For the crystalline films, there even appears to be a depression in IPCE that coincides with the absorption spectrum of the P3HT hole transport material. This suggests that light absorbed by the P3HT is not efficiently converted to charges and that the polymer acts as a parasitic light filter in this system. This issue is considered in greater depth in Section 6.3.4. In addition to the increased amount of light absorbed by the crystalline film, it is expected that electrical conductivity will change between the amorphous and crystalline phases. Specifically, it has been shown that the resistivity of the crystalline phase is two orders of magnitude less than that of the amorphous phase,¹⁷ which is highly likely to contribute to the improved performance of devices incorporating Sb₂S₃ in the former state.

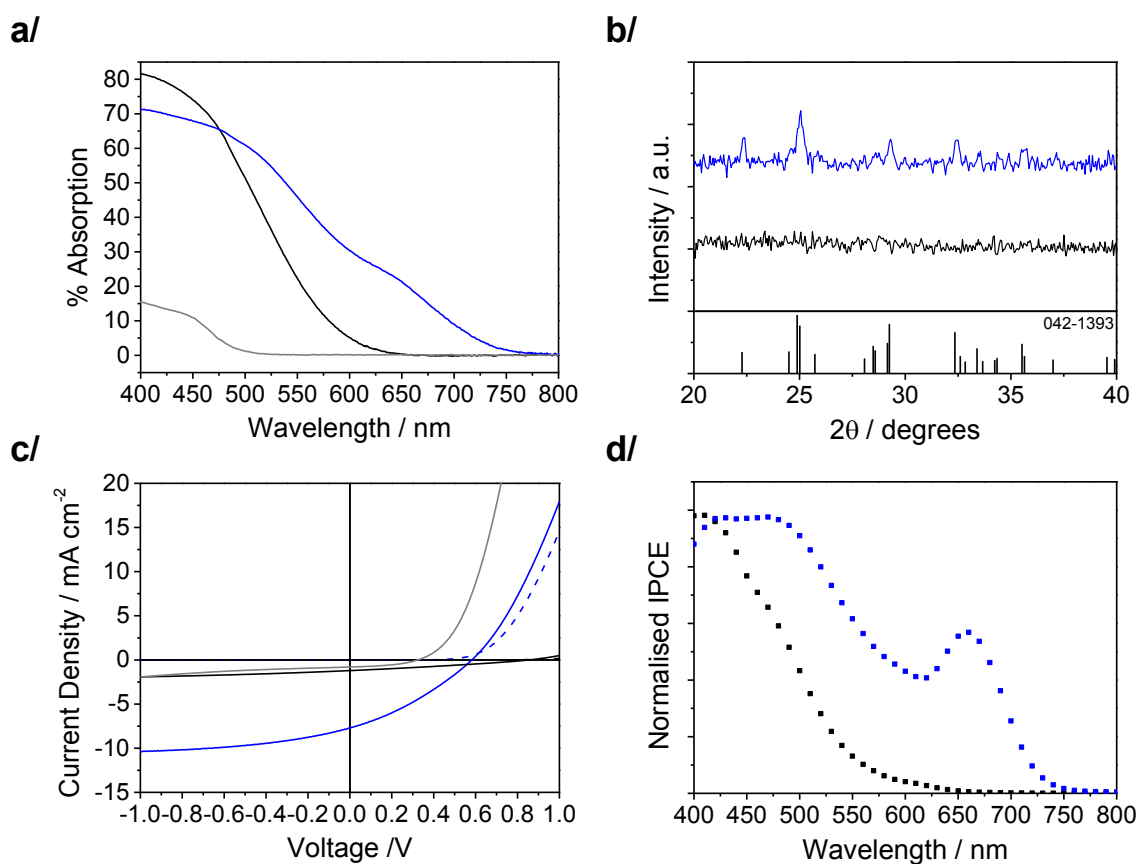


Figure 42 – Comparison of $\text{Sb}(\text{EX})_3$ films annealed at 160 °C (black, amorphous) and 300 °C (blue, crystalline). a/ glass/CdS film (grey) and absorption spectra of glass/CdS/ Sb_2S_3 films, b/ X-ray diffraction patterns of glass/CdS/ Sb_2S_3 films, c/ current density-voltage response in the dark (dashed lines) and under 100 mW cm^{-2} AM 1.5 illumination (solid lines) and d/ incident-photon-to-current conversion efficiency of typical ITO/ TiO_2 /CdS/ Sb_2S_3 /P3HT/ MoO_3 /Ag photovoltaic devices. All $\text{Sb}(\text{EX})_3$ layers spun at 6000 rpm from a 400 mg mL^{-1} chlorobenzene solution.

	$J_{\text{SC}} / \text{mA cm}^{-2}$	V_{OC} / V	FF	PCE / %
No Sb_2S_3	0.80	0.32	0.42	0.11
Amorphous Sb_2S_3	1.21	0.85	0.29	0.30
Crystalline Sb_2S_3	7.71	0.58	0.32	1.45

Table 3 - J-V parameters of ITO/ TiO_2 /CdS/ Sb_2S_3 /P3HT/ MoO_3 /Ag devices in Figure 42c for amorphous and crystalline Sb_2S_3 .

6.3.2 Light Soaking Effects

In the course of measuring the $\text{Sb}_2\text{S}_3/\text{P3HT}$ bilayer devices, it was found that performance would improve with extended exposure to light. In order to understand the origins of this effect, the variation in power conversion efficiency is monitored as a function of time under inert and atmospheric conditions. These results are summarised in Figure 43a and b, where each data point represents an average of at least 4 separate device pixels on the same substrate. When measured from new in a sealed nitrogen environment (Figure 43a, Sector i/), a small and steady improvement in device performance is observed during the first hour, which subsequently plateaus. After dark storage overnight, the device reverts to its original starting efficiency. Subsequent light soaking in nitrogen yields a similar rate of and magnitude of improvement (Sector ii/). This effect was consistently seen across different batches of devices and shows that there is a reversible component to the performance improvement, which being observed in an inert atmosphere is unlikely to be associated with any chemical change. Rather, it may be due to the light driven population of inter-band trap states in the dense TiO_2 blocking layer, which can be expected to increase the conductivity of this layer and reduce series resistance in the device.³⁸ Comparison of current-voltage responses under 100 mW cm^{-2} illumination (solid line) before and after light-soaking in nitrogen (Figure 44) show that the gradient at which the curve passes through V_{OC} increases after extended exposure to light, which is consistent with a reduction in series resistance, leading to improved fill-factors and short-circuit currents. The amount of current flowing through the device in forward bias in the dark also increases, further supporting the proposed explanation.

Figure 43b considers the effect of light soaking in atmospheric air. In this case, device performance is seen to increase much more dramatically over a similar time period (Sector i/). What is more, after overnight storage in dark, inert conditions, the performance does not regress to its starting value (0 minutes, Sector ii/), suggesting that a permanent change has taken place. As this does not occur in nitrogen, it is likely to be due to a reaction taking place between a component or components in the film and the surrounding atmospheric environment. One possible explanation is that the P3HT is doped by partial oxidation in the presence of light and oxygen,^{39,40} which can be expected to increase the conductivity of the polymer layer,^{41,42} thus further reducing series resistance (Figure 44). It is noted that this improvement requires the sample to be illuminated; it does not occur in the dark.

The above observations are confirmed in Figure 43c, where a device is measured as a function of light soaking time in nitrogen (Sector i/), stored overnight and re-measured under nitrogen (Sector ii/), then immediately opened to air (Sector iii/). As soon as the device is exposed to air, the efficiency increases significantly and continues to do so over the course of an hour before stabilising. It is interesting to note that Nezu *et al.* have reported similar phenomena for mesoporous

TiO₂/Sb₂S₃/CuSCN ETA-type photovoltaic cells,⁴ even though a different hole conductor is used. The authors of this work suggest that photo-catalysed oxygen doping of the HTM may explain the improved device performance, but also that oxygen could penetrate through to the inorganic surface and react to form an antimony oxide passivating layer that inhibits interfacial recombination. The effect of oxidation at the Sb₂S₃ surface is considered in Section 6.3.6.

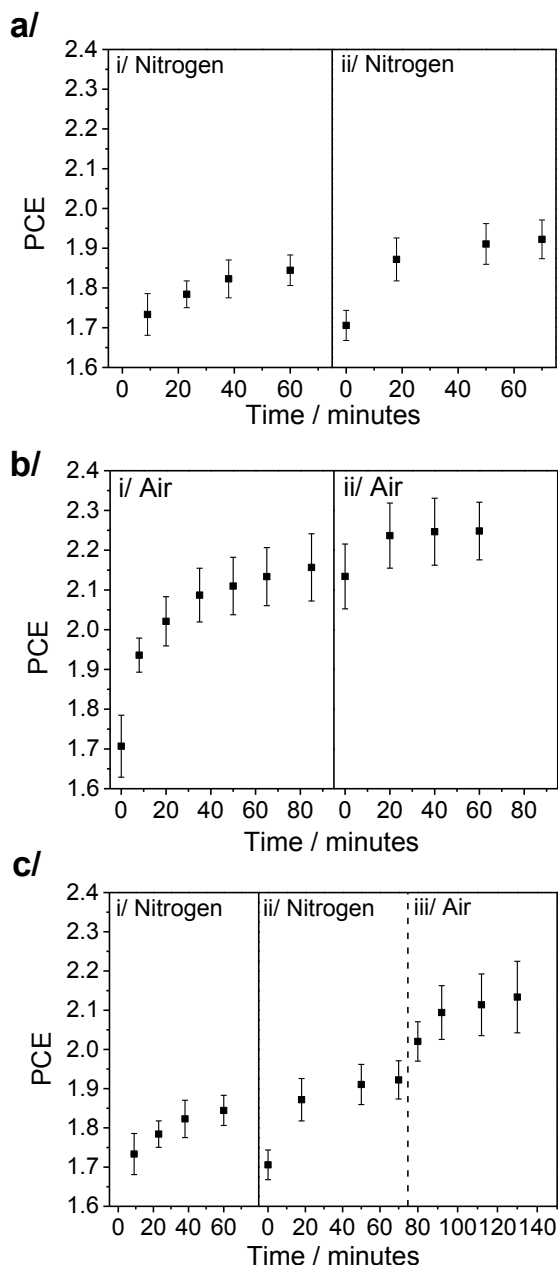


Figure 43 – The evolution in power conversion efficiency (PCE) of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices under continued 100 mW cm⁻² AM 1.5 illumination in different atmospheric environments. Each of a/ b/ and c/ monitor one individual device but which have all been prepared under identical conditions. In a/ the device is measured under N₂ (Sector i), stored overnight in the dark in N₂, and re-measured in N₂ (Sector ii), b/ is measured in air (Sector i), stored overnight in the dark in N₂, and re-measured in air (Sector ii), c/ is measured in N₂ (Sector i), stored overnight in the dark in N₂, re-measured in N₂ (Sector ii), then directly opened to air and continually measured (Sector iii). All Sb(EX)₃ layers were spin coated at 2000 rpm from a 400 mg mL⁻¹ chlorobenzene solution and annealed at 300 °C.

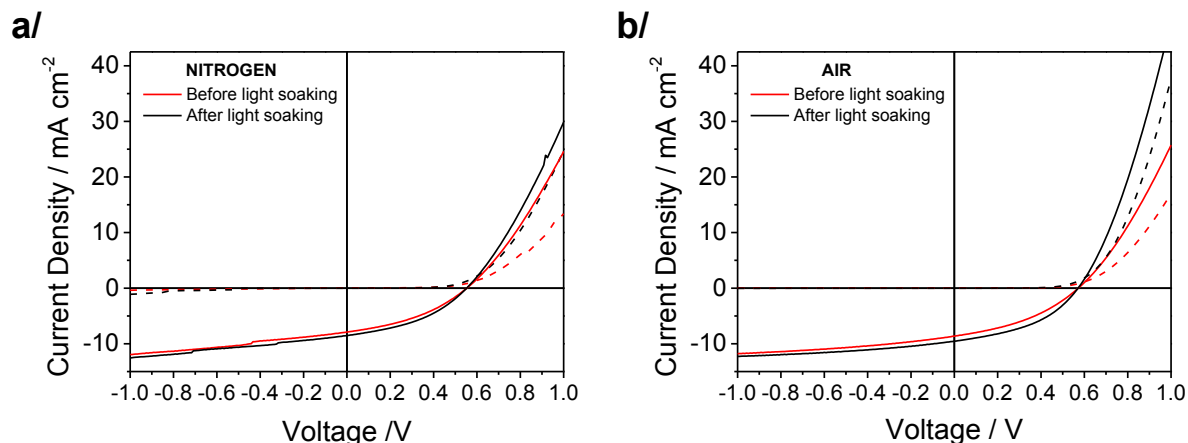


Figure 44 – Current density-voltage response in the dark (dashed lines) and under 100 mW cm^{-2} AM 1.5 illumination (solid lines) of typical ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices before (red) and after (black) light soaking at 100 mW cm^{-2} for 90 minutes in a/ nitrogen and b/ air. Sb(EX)₃ layers were spin coated at 2000 rpm from a 400 mg mL^{-1} chlorobenzene solution and annealed at 300°C .

		$J_{\text{SC}} / \text{mA cm}^{-2}$	V_{OC} / V	FF	PCE / %
N_2	New	7.90	0.55	0.38	1.66
	After light soaking	7.71	0.58	0.40	1.90
Air	New	8.65	0.57	0.38	1.87
	After light soaking	9.53	0.57	0.43	2.30

Table 4 – J-V parameters of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices in Figure 44 for different light soaking conditions.

6.3.3 Optimising Sb₂S₃ Thickness

For a given solar cell material configuration, the amount of light absorbed (and therefore the maximum photocurrent that can be generated) is defined by the thickness of the photoactive layer. The relationship between path length and the amount of light absorbed at a given wavelength depends on the extinction coefficient of the relevant material, but fundamentally as the film becomes thicker, more photons are absorbed and more charge can potentially be extracted. However, for extraction to proceed efficiently, photogenerated charges must be removed from the active layer before they are able to recombine. The distance that can be travelled before recombination occurs is defined by the mobility and the lifetime of the charge, which are closely related to the dielectric constant of the material and the electric field strength. In materials with a low dielectric constant such as organic polymers, photogenerated electrons and holes remain tightly bound to one another through coulombic attraction and can only travel a short distance before recombining. As the dielectric constant of the material increases, the exciton binding energy is reduced and can more readily be thermally overcome, leading to greater diffusion lengths. When considering a flat donor/acceptor interface, increasing the thickness of the active layer also increases the mean separation from the point of light absorption to the interface; ultimately, the absorbing layer can become so thick that no photogenerated charges are able to reach an interface, but recombine within the bulk of the material and are wasted. Given the contrasting requirements of needing to absorb as much light as possible whilst still ensuring efficient extraction, establishing an optimal Sb₂S₃ layer thickness is key to ensuring efficient device performance.

One way in which the thickness of the Sb₂S₃ layer can be controlled is by varying the speed at which the Sb(EX)₃ precursor layer is spin-coated. Slower spin speeds correspond to thicker precursor layers, which in turn decompose to thicker Sb₂S₃ layers. Figure 45 shows the absorption spectra of glass/CdS/Sb₂S₃ films as a function of precursor spin-speed, following annealing at 300 °C in N₂. Also shown is the absorption profile of a pristine glass/CdS film. Scanning electron micrographs of films prepared under the same conditions are presented in Figure 46 and associated approximate Sb₂S₃ layer thicknesses in Table 5. Figure 45 reveals that there is little difference in the absorption of films coated at 8000-4000 rpm suggesting fairly consistent thickness across this range, but a significant increase in light harvesting ability is achieved when coating the precursor at 2000 rpm. At 1000 rpm, the shape of the absorption spectrum changes, but the overall amount of light absorbed decreases. Figure 46 shows that the integrity of the Sb₂S₃/substrate interface is compromised for films deposited at 1000 rpm, with large cavities appearing between the Sb₂S₃ layer and the FTO/CdS substrate. This might be a result of the inability of the gases released during precursor decomposition to escape the thicker films sufficiently quickly and so becoming trapped within. Such a disruption of the interface between Sb₂S₃ and the substrate is expected to significantly limit the performance of devices based on layers deposited under these conditions.

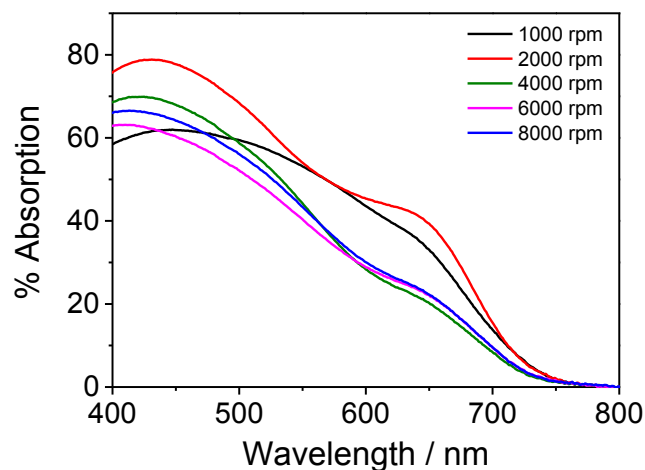


Figure 45 – Absorption spectra of glass/CdS/Sb₂S₃ films as a function of Sb(EX)₃ precursor layer spin-speed, where Sb(EX)₃ has been spin coated at 8000 rpm (blue), 6000 rpm (pink), 4000 rpm (green), 2000 rpm (red) and 1000 (black) and annealed in N₂ at 300 °C for 30 minutes.

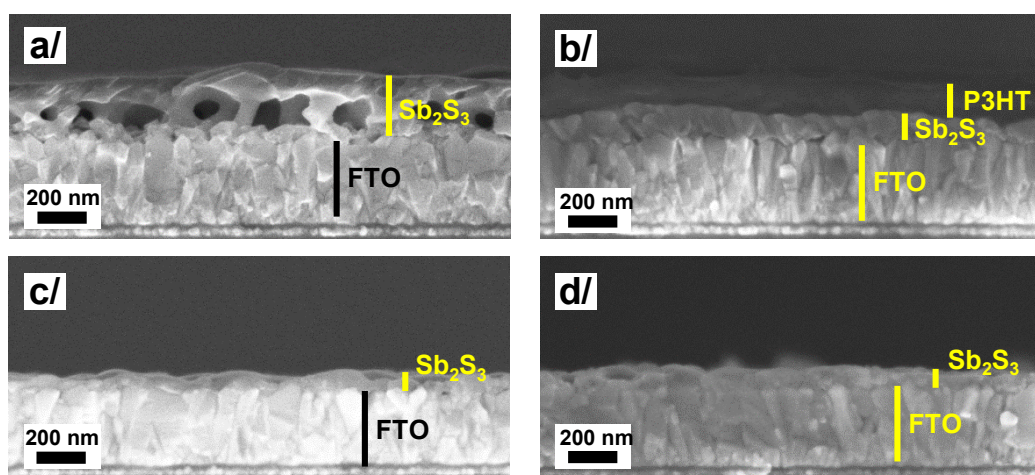


Figure 46 – Scanning electron micrographs of FTO/CdS/Sb₂S₃ layers where the Sb(EX)₃ precursor layer has been spin coated from a 400 mg mL⁻¹ chlorobenzene solution at a/ 1000 rpm, b/ 2000 rpm, c/ 6000 rpm and d/8000 rpm and annealed at 300 °C in N₂. b/ has a P3HT layer spin coated on top of the Sb₂S₃ layer at 2500 rpm from a 25 mg mL⁻¹ chlorobenzene solution.

	Sb(EX)₃ spin speed / rpm	Thickness / nm
a	1000	200
b	2000	110
c	6000	50
d	8000	40

Table 5 – Sb₂S₃ layer thickness as a function of Sb(EX)₃ spin speed (400 mg mL⁻¹ solution) as estimated from SEM images in Figure 46.

Figure 47 and Figure 48 show the effect of varying the Sb(EX)₃ precursor spin-speed on the performance of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices. All devices have been light soaked in air at 100 mW cm⁻² for 90 minutes prior to measurement. As the spin-speed decreases from 8000 to 2000 rpm, a sizable increase in short circuit current contributes to improved power conversion efficiency. This is commensurate with the improved light harvesting ability of the thicker films. It is also noted that as the Sb(EX)₃/Sb₂S₃ films become thinner, the probability of pinhole formation is likely to increase, which may further inhibit efficiency. At 1500 and 1000 rpm, performance declines dramatically, which may be due to the disruption of the CdS/Sb₂S₃ interface, as described above. As such, it is unclear as to whether an Sb₂S₃ layer of ~110 nm represents an optimal thickness with respect to cell efficiency. There is a steady but consistent decline in fill-factor as Sb₂S₃ thickness increases, which is consistent with increased series resistance, although this effect is more than offset by the associated enhancement of light-harvesting ability.

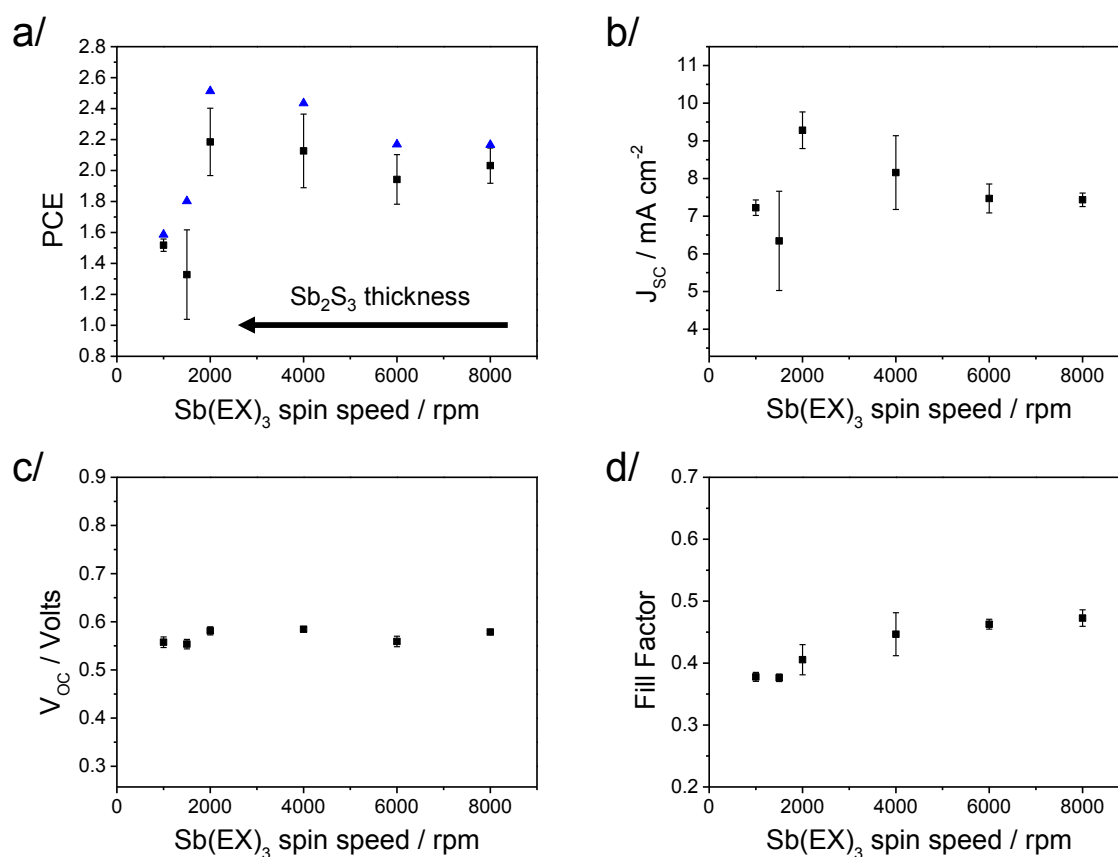


Figure 47 – Effect of Sb_2S_3 layer thickness in $\text{ITO}/\text{TiO}_2/\text{CdS}/\text{Sb}_2\text{S}_3/\text{P3HT}/\text{MoO}_3/\text{Ag}$ devices: Device performance under 100 mW cm^{-2} AM 1.5 illumination as a function of spin-speed of $\text{Sb}(\text{EX})_3$ precursor chlorobenzene solution. Measurements recorded after light soaking in air at 100 mW cm^{-2} for 90 minutes. Black squares represent an average over at least 4 separate devices with error bars representing the standard deviation and blue triangles correspond to maximum achieved values.

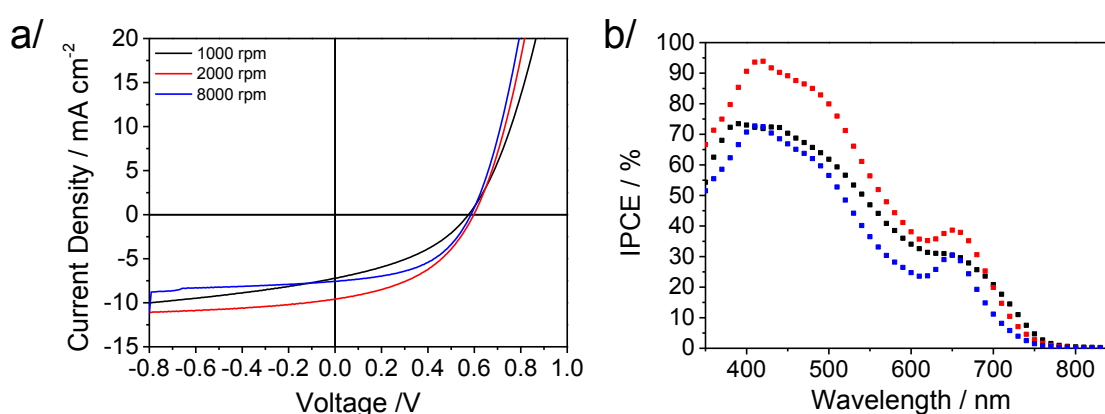


Figure 48 – a/ Current density-voltage responses under 100 mW cm^{-2} AM 1.5 illumination and b/ IPCE spectra of best $\text{ITO}/\text{TiO}_2/\text{CdS}/\text{Sb}_2\text{S}_3/\text{P3HT}/\text{MoO}_3/\text{Ag}$ devices, where the $\text{Sb}(\text{EX})_3$ precursor layer has been spin-coated at 1000 rpm (black), 2000 rpm (red) and 8000 rpm (blue) from a 400 mg mL^{-1} chlorobenzene solution and annealed at 300°C for 30 minutes in N_2 . All measurements were recorded after light soaking of devices in air at 100 mW cm^{-2} for 60 minutes.

Sb(EX)₃ spin-speed / rpm	J_{SC} / mA cm⁻²	V_{OC} / V	FF	PCE / %
1000	7.23	0.57	0.38	1.59
2000	9.57	0.60	0.43	2.49
8000	7.56	0.59	0.49	2.17

Table 6 - J-V parameters of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices in Figure 48a.

The thickness of the Sb(EX)₃ layer can also be modified by varying the concentration of precursor in the spin-coated solution. Figure 49 shows the relationship between the precursor concentration and the absorption spectra of the annealed film. All Sb(EX)₃ layers are spin-coated at 2000 rpm, as per the conclusions of the previous study. It is clear that effective control of Sb₂S₃ thickness is achieved. Scanning electron micrographs in Figure 50 show that the interface between the thickest Sb₂S₃ film and the CdS layer beneath it is cleaner than for those obtained by reducing the spin-speed, although some gaps do still appear. The Sb(EX)₃ chlorobenzene solution reaches saturation at ~600 mg mL⁻¹, which leads to a ~150 nm thick Sb₂S₃ film.

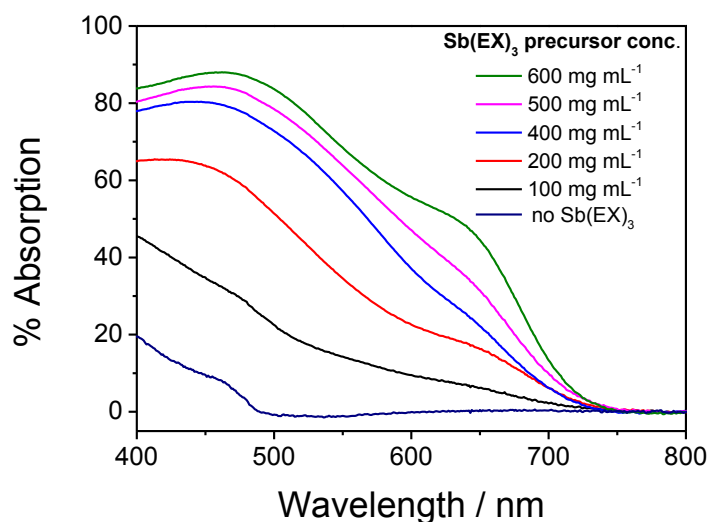


Figure 49 – Absorption spectra of glass/CdS/Sb₂S₃ films as a function of Sb(EX)₃ precursor solution concentration, where Sb(EX)₃ precursor layer has been spin coated from a 600 mg mL⁻¹ (green), 500 mg mL⁻¹ (pink), 400 mg mL⁻¹ (blue), 200 mg mL⁻¹ (red) and 100 mg mL⁻¹ (black) chlorobenzene solution at 2000 rpm. The dark blue line represents the pristine glass/CdS film.

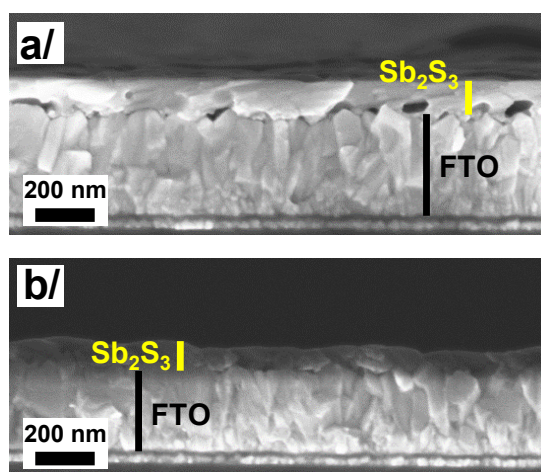


Figure 50 – Scanning electron micrographs of FTO/CdS/Sb₂S₃ layers, where the Sb(EX)₃ precursor layer has been spin coated from a/ 600 mg mL⁻¹ and b/ 400 mg mL⁻¹ chlorobenzene solution at 2000 rpm and annealed at 300 °C in N₂.

	Sb(EX) ₃ concentration / mg mL ⁻¹	Thickness / nm
a	600	150
b	400	100

Table 7 – Sb₂S₃ layer thickness as a function of Sb(EX)₃ precursor concentration, following spin coating at 2000 rpm and annealing at 300 °C under N₂, as estimated from SEM images in Figure 46.

Figure 51 and Figure 52 describe the relationship between Sb(EX)₃ precursor concentration and cell performance under 1 sun AM1.5 illumination. At low precursor concentrations, very little photocurrent or photovoltage is achieved as insufficient light is absorbed. For films deposited from 400 mg mL⁻¹ solution, a maximum efficiency of 2.34 % is achieved with a short-circuit current of 9.61 mA cm⁻². As the films become thicker still, the short circuit current decreases, although the open-circuit voltage remains relatively constant. As such, ~100 nm (from Figure 50) appears to represent optimal absorber layer thickness. In thicker films, although more light is absorbed, it is not all converted into photocurrent. This may indicate that minority carrier diffusion limits current generation at thicknesses in excess of ~100 nm, i.e. charges generated at greater distances than this from the interface recombine within the absorber layer before they can be separated. Sb₂S₃ is reported to be an n-type semiconductor and it is therefore likely that hole diffusion is limiting the maximum achievable photocurrent. These observations are in reasonable agreement with recent work by Darga *et al.*, who have used steady-state photocurrent grating measurements to estimate the limiting hole diffusion length in Sb₂S₃ to ~140 nm (as opposed to ~1 µm for electrons),²² as well as with empirical device work by Liu *et al.* on evaporated Sb₂S₃ films.²⁶

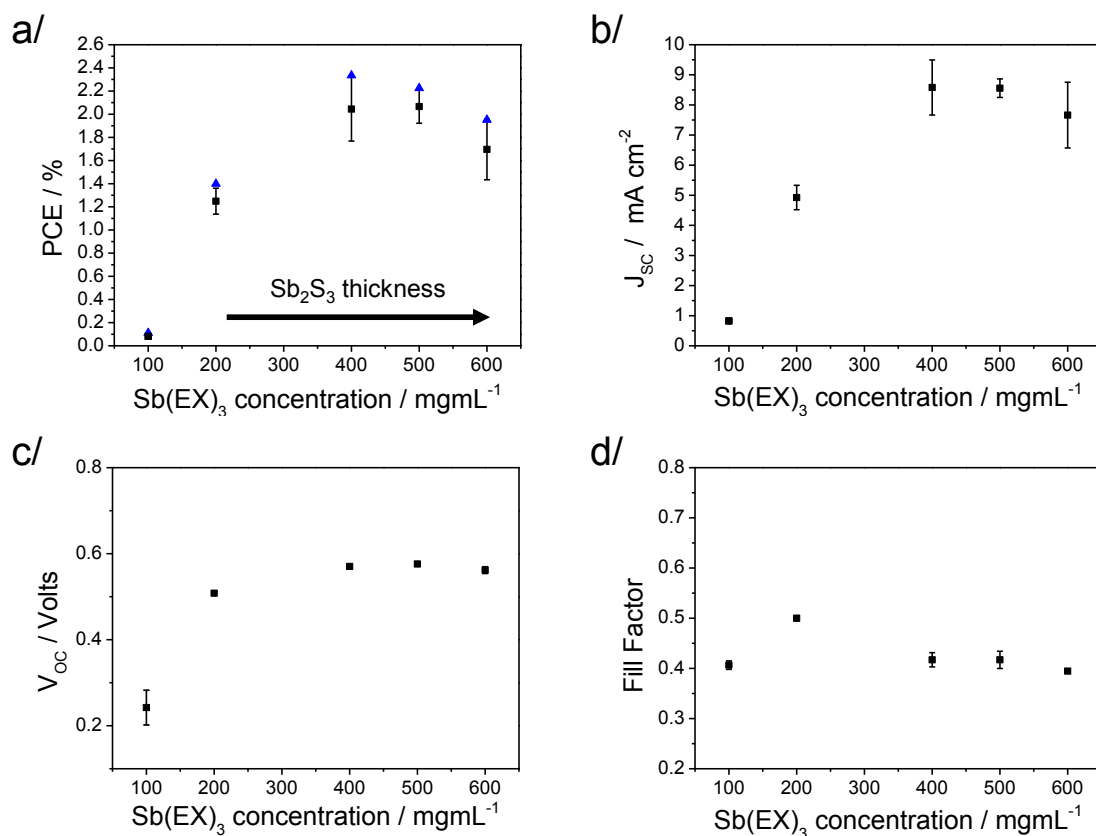


Figure 51 – Effect of Sb_2S_3 layer thickness in $\text{ITO}/\text{TiO}_2/\text{CdS}/\text{Sb}_2\text{S}_3/\text{P3HT}/\text{MoO}_3/\text{Ag}$ devices: Device performance under 100 mW cm^{-2} AM 1.5 illumination as a function of $\text{Sb}(\text{EX})_3$ precursor concentration in chlorobenzene solution. Measurements recorded after light soaking in air at 100 mW cm^{-2} for 90 minutes. Black squares represent an average over at least 4 separate devices with error bars representing the standard deviation and blue triangles corresponding to the most efficient device.

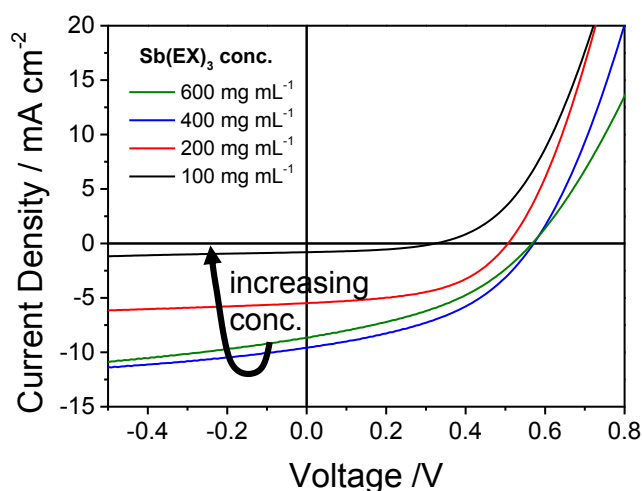


Figure 52 – Current density-voltage responses of best $\text{ITO}/\text{TiO}_2/\text{CdS}/\text{Sb}_2\text{S}_3/\text{P3HT}/\text{MoO}_3/\text{Ag}$ devices under 100 mW cm^{-2} AM 1.5 illumination as a function of Sb_2S_3 layer thickness, where the $\text{Sb}(\text{EX})_3$ precursor layer has been spin-coated from a 100 mg mL^{-1} (black), 200 mg mL^{-1} (red), 400 mg mL^{-1} (blue) and 600 mg mL^{-1} (green) chlorobenzene solution at 2000 rpm and annealed under N_2 at 300°C for 30 minutes. All measurements were recorded after light soaking of devices in air at 100 mW cm^{-2} for 60 minutes.

Sb(EX)₃ concentration / mg mL⁻¹	J_{SC} / mA cm⁻²	V_{OC} / V	FF	PCE / %
600	8.63	0.57	0.40	1.95
400	9.61	0.57	0.43	2.34
200	5.49	0.51	0.50	1.40
100	0.81	0.32	0.42	0.11

Table 8 – J-V parameters of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices in Figure 52.

6.3.4 Polymer Layer Thickness and Photocurrent Contribution

As described above, there seems to be little or no photocurrent contribution from P3HT in the Sb₂S₃/P3HT bilayer device and indeed there is an apparent depression in the IPCE spectrum in the region in which it absorbs. This indicates that P3HT is acting as a parasitic light filter in this system. It is noted that as the architecture described in the present work is a flat bilayer and light first passes through the Sb₂S₃ layer before reaching the P3HT, the filtering effect would only be expected to limit absorption of light by Sb₂S₃ on the second pass, i.e. the light which is not initially absorbed but is reflected off the silver contacts and back through the device. On this basis, the filtering effect is likely to be less dramatic than for a blended bulk heterojunction-type system.¹³ In order to further explore these issues, the effect of changing the thickness of the P3HT layer on the shape of the IPCE spectrum is monitored. It is expected that as the P3HT thickness is reduced, the polymer will absorb less light and the filtering effect will be reduced. Figure 53 compares the IPCE spectra of Sb₂S₃/P3HT bilayer devices (solid lines) where the P3HT has been spin-coated from different concentration solutions, leading to different film thicknesses. With the exception of the P3HT concentration, all cells were prepared under identical conditions. In order to focus primarily on the filtering effect, all IPCE spectra have been normalised to the shoulder at the edge of the P3HT absorption (640 nm). For reference, the absorption spectra of glass/CdS/Sb₂S₃ and glass/CdS/Sb₂S₃/P3HT films have also been included (dashed lines). In the region beyond the Sb₂S₃ absorption edge, all samples show a very similar relative IPCE fraction. However, at shorter wavelengths, the depression in conversion efficiency becomes more pronounced as the P3HT layer becomes thinner, suggesting that the polymer does indeed filter otherwise useful light. This may be due to the short diffusion length of excitons in P3HT (<10 nm),⁴³ restricting interfacial separation of charges, and is also consistent with reports in the literature for both Sb₂S₃ SSSC cells^{6,8} and Sb₂S₃:P3HT hybrid blends.¹³

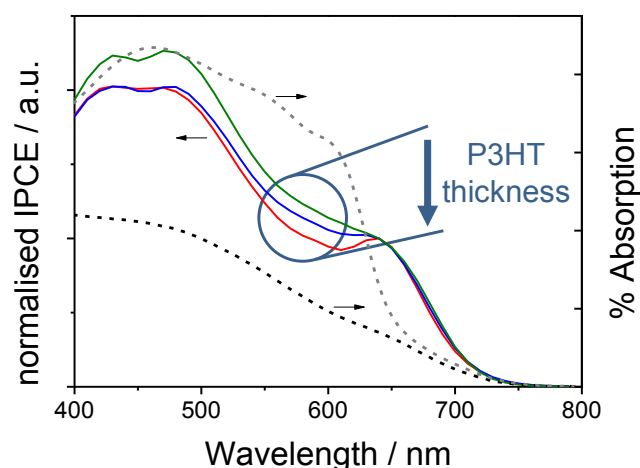


Figure 53 –IPCE spectra of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices for different P3HT thicknesses (solid lines), where the polymer has been deposited from a 15 mg mL⁻¹ solution (red), 10 mg mL⁻¹ (blue) and 5 mg mL⁻¹ (green). IPCE spectra have been normalised to 640 nm to highlight the depression where the P3HT most strongly absorbs. Absorption spectra of glass/CdS/Sb₂S₃ and glass/CdS/Sb₂S₃/P3HT films are also shown (dashed lines).

Despite the apparent reduction in light filtering as the P3HT layer thickness is reduced, the magnitude of the short-circuit current and the overall device performance remains largely constant, except for the thinnest layer considered (that deposited from a 5 mg mL⁻¹ solution) for which J_{SC} is actually found to decrease (Figure 54). The origins of this effect are unclear, but it may be that the integrity of the polymer layer is compromised as the concentration is reduced such that shorting pathways begin to form. This possibility is supported by the measurement of ITO/TiO₂/CdS/Sb₂S₃/MoO₃/Ag devices (those with no P3HT), which are almost entirely shorted as shown by the grey trace in Figure 54. It may also be the case that whatever is causing J_{SC} to decrease for the thinnest film is also incrementally masking the expected improvement in J_{SC} associated with reducing light filtering by the P3HT, meaning that ultimate device performance in the 10-25 mg mL⁻¹ range remains approximately constant.

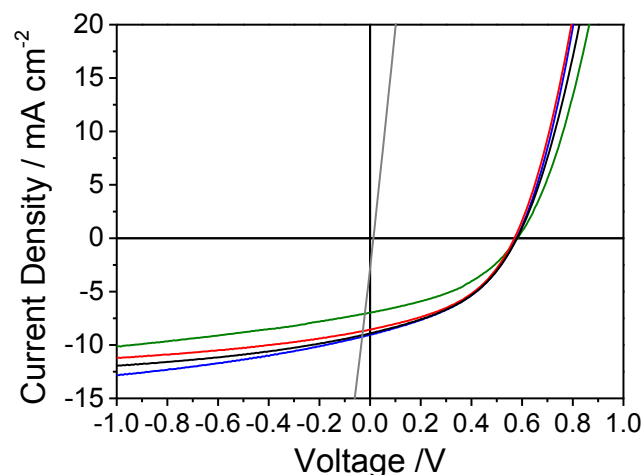


Figure 54 - Current density-voltage responses under 100 mW cm⁻² AM 1.5 illumination of best ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices, where P3HT has been deposited by spin coating of a chlorobenzene solutions of concentration 25 mg mL⁻¹ (black), 15 mg mL⁻¹ (red), 10 mg mL⁻¹ (blue), 5 mg mL⁻¹ (pink) and no P3HT (grey). Sb(EX)₃ layers were deposited at 2000 rpm from a 400 mg mL⁻¹ chlorobenzene solution. Measurements were obtained after light soaking in air, under 100 mW cm⁻² illumination for 60 minutes.

P3HT concentration / mg mL⁻¹	J_{SC} / mA cm⁻²	V_{OC} / V	FF	PCE / %
25	8.93	0.58	0.42	2.16
15	8.57	0.57	0.43	2.11
10	9.02	0.58	0.41	2.15
5	6.99	0.58	0.41	1.66
0	2.82	0.01	0.36	0.01

Table 9 – J-V parameters of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices in Figure 54.

What is not clear from the data presented here, nor from that in the SSSC literature, is whether electron injection from P3HT to Sb₂S₃ is entirely prohibited or is just relatively inefficient. In order to investigate this, the structurally similar polymer PCPDTBT is considered as an alternative to P3HT (Figure 55). Unlike P3HT, PCPDTBT has a narrower bandgap (1.4 eV)⁴⁴ than Sb₂S₃, and as such, any photocurrent contribution should be unambiguous in the IPCE spectrum. J-V curves under illumination for preliminary Sb₂S₃/PCPDTBT devices are shown in Figure 56a alongside an Sb₂S₃/P3HT control. Figure 56b shows the associated IPCE spectra of the two devices as well as the absorption spectra of the two pristine polymers. So as to highlight the difference in shapes of spectral response, IPCE spectra have been normalised to equal integrated short-circuit current equivalents (the

integral of the IPCE spectrum) to account for the different J_{SC} of the two devices. As expected, the IPCE for both systems is depressed in the regions where the respective polymers absorb most strongly, suggesting a filtering effect. However, the fact that photocurrent is generated beyond the absorption edge of Sb_2S_3 (wavelengths $> \sim 750$ nm) for the PCPDTBT device shows that light absorbed by the polymer is being converted to free charges. Unfortunately, the magnitude of current generated is very low despite the polymer absorbing strongly in this region, thus confirming that only a small proportion of light absorbed by the polymer is converted to charge. This is consistent with the interpretation that exciton diffusion limits separation of charges generated in the polymer; only those generated very close to the polymer/ Sb_2S_3 interface ($< \sim 10$ nm for P3HT) can be extracted. For a flat bilayer, this limitation will always be a problem. One means of overcoming it might be to structure the donor/acceptor interface on a suitably small scale to form a bulk heterojunction, although preliminary efforts in this direction have been largely unsuccessful (in terms of increasing the polymer's contribution).¹³ On this basis, a transparent hole conductor, or at least one whose absorption spectrum does not overlap with that of the inorganic absorber, might ultimately be preferable.

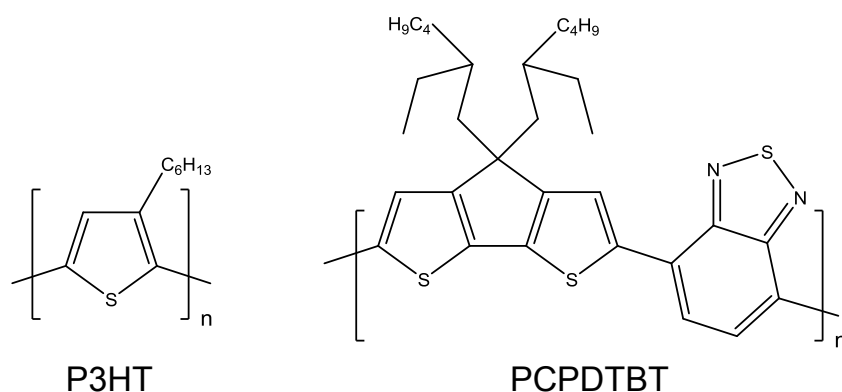


Figure 55 – Chemical structures of P3HT and PCPDTBT.

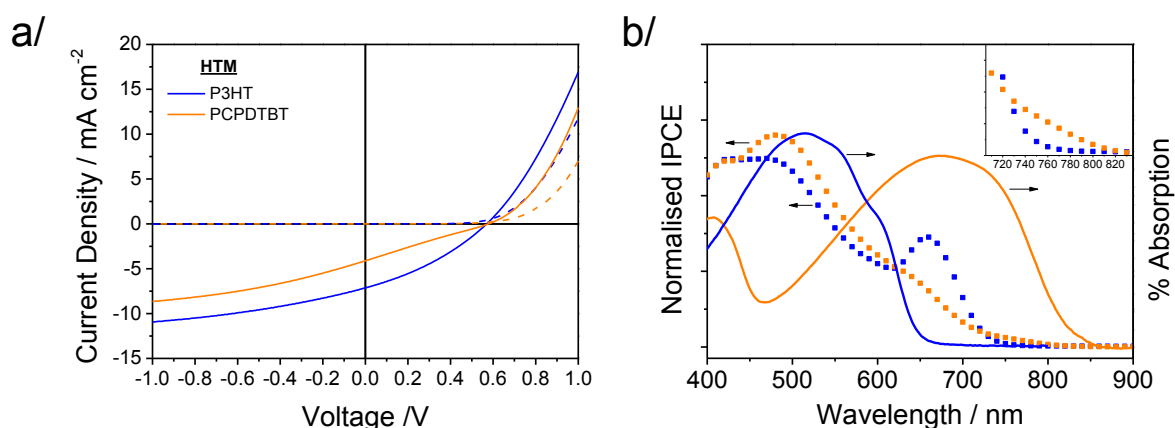


Figure 56 – a/ Current density-voltage responses under 100 mW cm^{-2} AM 1.5 illumination and b/ IPCE spectra of typical ITO/ TiO_2 /CdS/ Sb_2S_3 /HTM/ MoO_3 /Ag devices, where HTM = P3HT (blue) and PCPDTBT (orange). Inset to b/ highlights the photocurrent generated beyond the Sb_2S_3 absorption edge for the PCPDTBT device.

6.3.5 Role of CdS Window Layer

Thin layers of cadmium sulfide have been incorporated into a range of photovoltaic device architectures, perhaps most notably as recombination-blocking n-type window layers in thin-film solar cells.^{19,20,24,36,37} In these cases, CdS is introduced between the n-type side of the p-n junction and the electron collecting contact. The conduction band energy of the CdS is sufficiently low to allow electrons in the photoactive material to cascade through, but the low energy valence band stops minority carriers in the n-type material (holes) reaching the electron collecting contact and recombining. The relatively large bandgap of CdS also means that it does not significantly filter light that would otherwise be absorbed within the photoactive layers and converted to charges, hence its description as a ‘window’ layer. The presence of a CdS ‘seed’ layer has also been shown to dramatically improve the performance of both blended CdS/P3HT³⁵ and Sb₂S₃/P3HT¹³ bulk-heterojunction-type solar cells, although its precise role in these systems remains unclear.

In the present work, deposition of a thin CdS layer on the substrate is found to be crucial to subsequently achieving a consistent surface coverage of Sb₂S₃ (as prepared by thermal decomposition of Sb(EX)₃). However, its presence can also be expected to affect the electrical properties of the resulting devices. Figure 57 and Figure 58 show the effect of varying the thickness of the CdS layer (by modulating the speed at which the cadmium xanthate precursor layer is spin-coated) on device parameters under 1 sun AM 1.5 illumination. The thinnest CdS layer considered was prepared by spin coating a 100 mg mL⁻¹ cadmium xanthate precursor layer at 6000 rpm and measured by profilometry to be ~20 nm thick. Also shown in Figure 58 is the best J-V response attained for a device without a CdS layer, which displays a notably reduced short-circuit current and open-circuit voltage with respect to those utilising the interlayer.

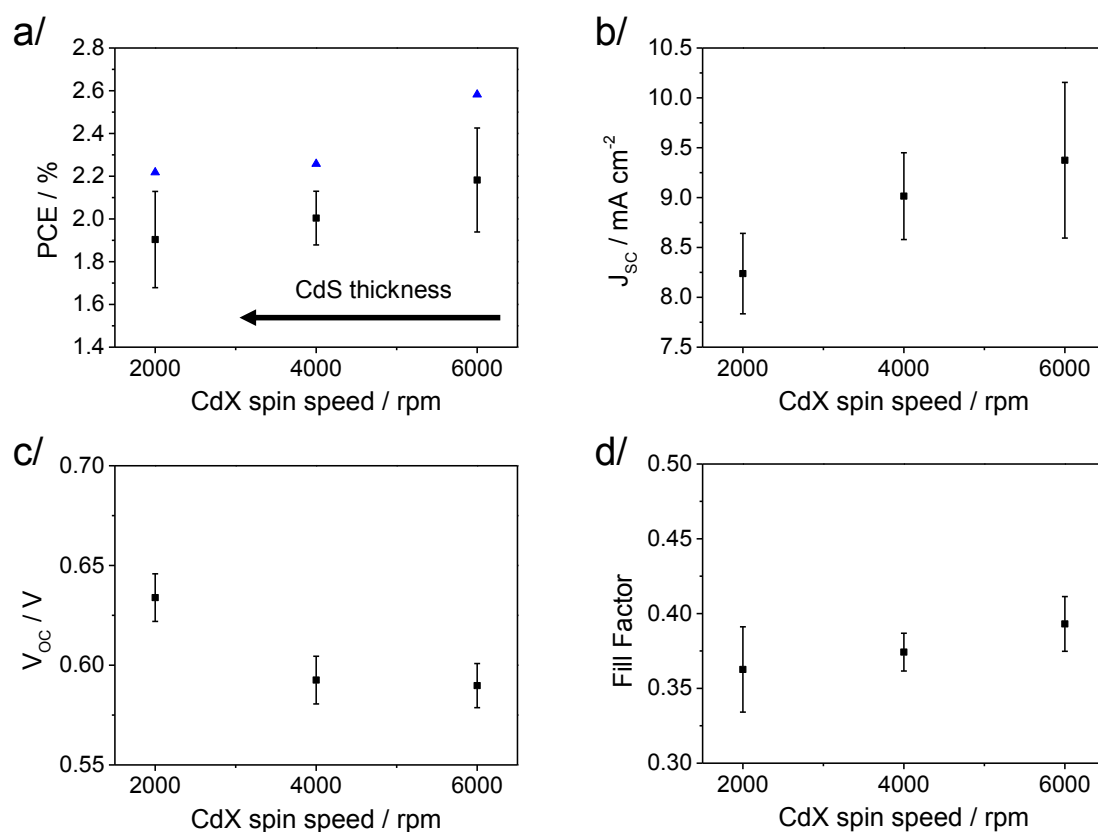


Figure 57 – Effect of CdS layer thickness in ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices: Cell performance under 100 mW cm⁻² AM 1.5 illumination as a function of CdX precursor solution spin-speed in chlorobenzene solution. Black squares represent an average over at least 12 separate devices with error bars representing the standard deviation and blue triangles corresponding to the most efficient device.

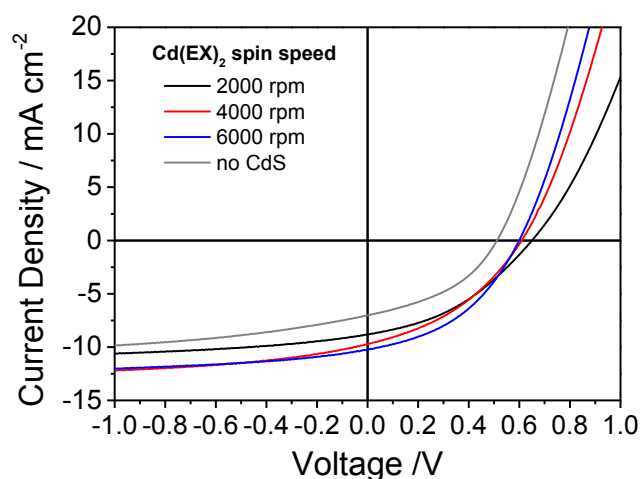


Figure 58 – Current density-voltage responses of best ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices under 100 mW cm⁻² AM 1.5 illumination as a function of CdS layer thickness, where the CdX precursor layer has been spin-coated at 2000 rpm (black), 4000 rpm (red) and 6000 rpm (blue) from a 100 mg mL⁻¹ chlorobenzene and annealed under N₂ at 160 °C for 30 minutes. Also shown is an analogous device without a CdS layer (grey).

CdX spin speed / rpm	J_{SC} / mA cm⁻²	V_{OC} / V	FF	PCE / %
2000	8.82	0.65	0.39	2.21
4000	9.71	0.61	0.38	2.26
6000	10.24	0.60	0.42	2.58
No CdS	7.01	0.51	0.41	1.48

Table 10 - J-V parameters of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices in Figure 58.

From Figure 57, it is clear that overall power conversion efficiency is reduced as the CdS layer is made thicker as a result of decreasing short-circuit current and fill-factor. This appears to be due to an increase in series resistance in the device when thicker CdS films are used (as evidenced by a reduction in the gradient of the respective J-V curves as they pass through V_{OC} - Figure 58) and confirms that photogenerated charge must pass through the CdS layer before being extracted. However, the negative influence of decreasing J_{SC} is partially offset by an increase in open-circuit voltage for the devices containing thicker CdS films. The increased V_{OC} may indicate that the CdS is indeed acting as a hole blocking layer and slowing recombination between electrons at the ITO/TiO₂ contact and holes in the Sb₂S₃ layer, as well as improving the physical interface between Sb₂S₃ and the substrate. Additionally, it is noted that there is only a very small photocurrent contribution from the light absorbed by the CdS layer itself (0.8 mA cm⁻², from Figure 42).

The majority of devices produced without a CdS layer were not rectifying diodes, probably due to the difficulty in controlling the structural quality of the Sb₂S₃ layers when depositing directly onto the TiO₂/ITO substrates (as described in Section 6.2). However, some limited success was achieved when the dense TiO₂ layer was cleaned by oxygen plasma treatment before the Sb(EX)₃ layer was deposited. The best of these achieved a power conversion efficiency of 1.48 % and is represented by the grey J-V curve in Figure 58. For this device, both J_{SC} and the V_{OC} are lower than when the thinnest CdS layer is incorporated. The low J_{SC} may be attributed to poor wetting of the Sb₂S₃ on the substrate, whilst the low voltage supports the suggestion that CdS is acting as a hole blocking layer and increasing the voltage. However, it is important to note that preparation of working devices without CdS was highly irreproducible, so it is difficult to separate the positive influence that the CdS layer has on the physical structure of the Sb₂S₃ thin film from the possible contribution it has towards the electrical properties of the device as a hole-blocking layer. Additionally, it is expected that the dense TiO₂ also present in the device architecture should act as a hole blocking layer, which raises the question as to why the presence of a second layer such layer should be beneficial. A more systematic comparison of devices with and without a CdS window layer would require the surface of the substrate to be treated in such a manner that good Sb₂S₃ coverage could reliably be achieved without the presence of CdS. Preliminary efforts in this regard, involving the use of alternative metal oxide blocking layers such as ZnO and the treatment of the metal oxide with a bifunctional linker molecule to bind to the metal sulfide has thus far proven unsuccessful.

6.3.6 Effects of Sb_2S_3 Oxidation

In section 6.3.2, it has been shown that $\text{Sb}_2\text{S}_3/\text{P3HT}$ bilayer device performance improves when films are light soaked in ambient conditions. The presence of oxygen is expected to be central to this effect, although it is unclear exactly which component(s) of the thin film assembly are affected.⁴ Whilst increased conductivity of the polymer as a result of oxygen induced doping seems a likely explanation, some interaction between oxygen and the Sb_2S_3 layer cannot be ruled out. Interestingly, Hodes and co-workers have found the presence of an antimony oxide interlayer at the metal sulfide/HTM in SSSC-type devices to be crucial to efficient performance.¹ The authors attribute this to an ability of the Sb_2O_3 to reduce recombination between electrons in the Sb_2S_3 and holes in the HTM and achieve oxidation by heating the films at 200 °C in ambient conditions. In addition, the presence of antimony oxide on the surface of thin films of Sb_2S_3 prepared by annealing a metal xanthate has recently been demonstrated using photoelectron spectroscopy.⁴⁵ In the present work, when $\text{Sb}(\text{EX})_3$ precursor layers are annealed in air at 300 °C, the films rapidly become completely transparent, indicating the production of antimony oxide and resulting devices do not generate photocurrent. This was even found to be the case when precursor layers were annealed at in a glovebox when oxygen levels were slightly high ($>\sim 50$ ppm), especially at elevated temperatures (e.g. 400 °C), highlighting the sensitivity of Sb_2S_3 to oxidation. This section considers whether (partial) oxidation of Sb_2S_3 can have a positive impact on bilayer device performance. In order to pursue this study in a systematic manner, it was first necessary to establish the minimum amount of time required by the initial $\text{Sb}(\text{EX})_3$ annealing step. In this manner, control devices would be exposed to as little uncontrolled and ill-defined oxidation as possible during precursor decomposition/metal sulfide crystallisation. Subsequently, a specific oxidation step can be used to study the process directly.

Figure 60 and Figure 61 show the effect of varying the amount of time that the $\text{Sb}(\text{EX})_3$ precursor layer is annealed (in a nitrogen glovebox at 300 °C) on solar cell performance. All devices were measured in nitrogen and without light-soaking, so as to minimise any unwanted oxygen-related effects. There is no decline in device performance as the annealing time is reduced and if anything, there appears to be a slight improvement with shorter precursor annealing times. As such, it is determined that annealing for 5 minutes limits the potential for oxidation in the glovebox, without inhibiting device performance and thus provides an improved starting point for the subsequent investigation of more controlled oxidation.

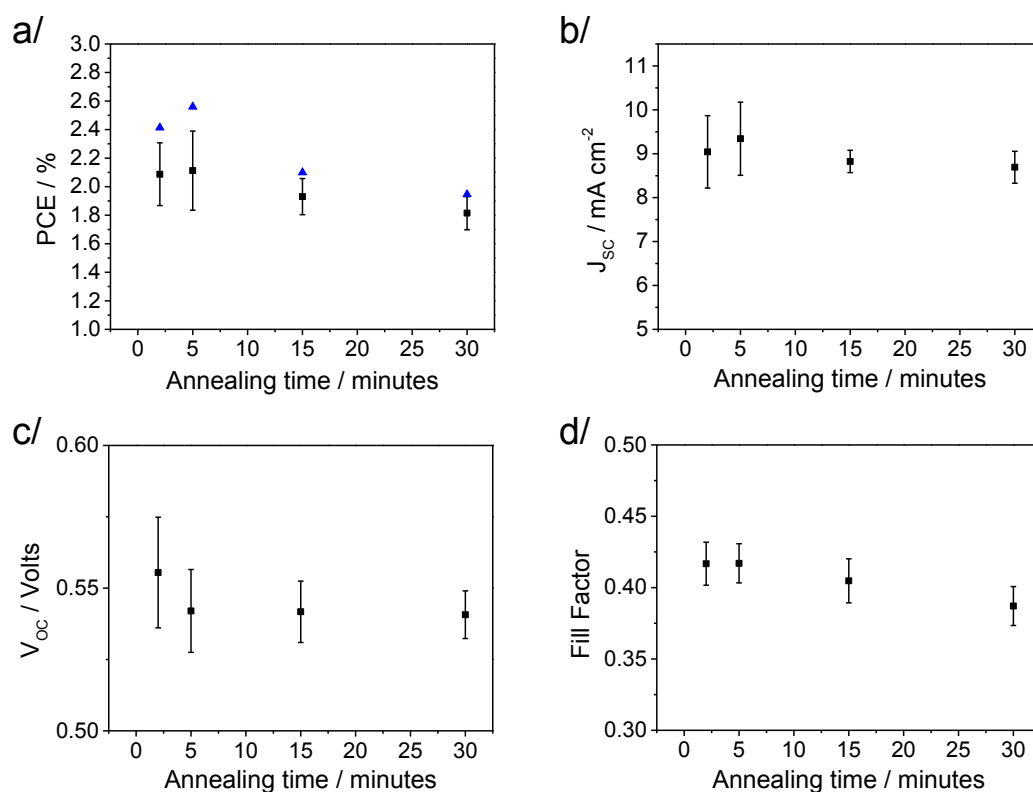


Figure 59 – Effect of $\text{Sb}(\text{EX})_3$ annealing time in ITO/ TiO_2 /CdS/ Sb_2S_3 /P3HT/ MoO_3 /Ag devices: Cell performance under 100 mW cm^{-2} AM 1.5 illumination as a function of time spent annealing the $\text{Sb}(\text{EX})_3$ precursor layer in N_2 at 300°C . Black squares represent an average over at least 5 separate devices with error bars representing the standard deviation and blue triangles corresponding to the most efficient device. All devices recorded as new (no light soaking).

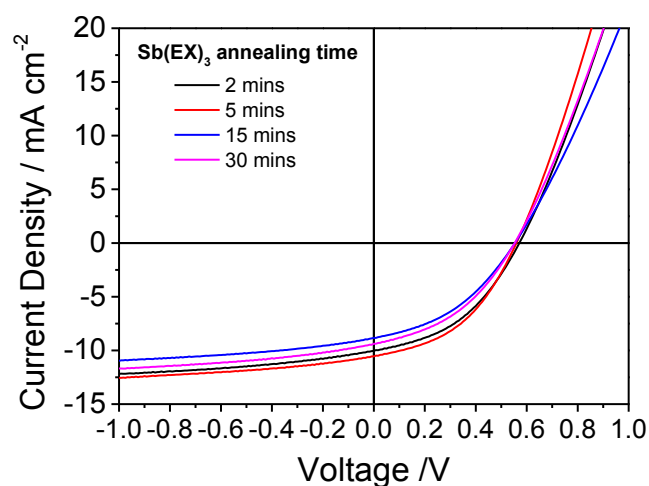


Figure 60 – Current density-voltage responses of typical ITO/ TiO_2 /CdS/ Sb_2S_3 /P3HT/ MoO_3 /Ag devices under 100 mW cm^{-2} AM 1.5 illumination as a function of time spent annealing the $\text{Sb}(\text{EX})_3$ precursor layer in N_2 at 300°C : 2 minutes (black), 5 minutes (red), 15 minutes (blue), 30 minute (pink).

Sb(EX)₃ annealing time / minutes	J_{SC} / mA cm⁻²	V_{OC} / V	FF	PCE / %
2	10.04	0.57	0.42	2.41
5	10.55	0.56	0.43	2.55
15	9.38	0.55	0.41	2.10
30	8.83	0.55	0.40	1.95

Table 11 – J-V parameters of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices in Figure 60.

In order to probe the effect of Sb₂S₃ oxidation at the heterojunction, films were prepared by annealing the Sb(EX)₃ precursor layer in a glovebox at 300 °C for 5 minutes, and immediately afterwards put on a hot-plate in ambient conditions at 200 °C for varying amounts of time, as per the work of Itzhaik *et al.*¹ Subsequently, P3HT was spin-coated on top and the devices were completed as usual. The performance of the resulting solar cells is described in Figure 61 and Figure 62. Although control device efficiency is slightly lower than expected, a clear trend is revealed, whereby increasing oxidation time causes a decrease in J_{SC}, V_{OC} and FF, significantly limiting device performance. This may be because Sb₂O₃ at the inorganic-organic interface acts as an insulating layer and also the oxidation of Sb₂S₃ reduces the amount of light absorbed by the device. It is clear that the positive effect reported for Sb₂S₃-based ETA cells is not reflected in the bilayer architecture. Furthermore, it is likely that even small fluctuations in the amount of oxygen contained in the local environment when annealing the Sb(EX)₃ precursor would influence device performance and thus act as a central cause of irreproducibility.

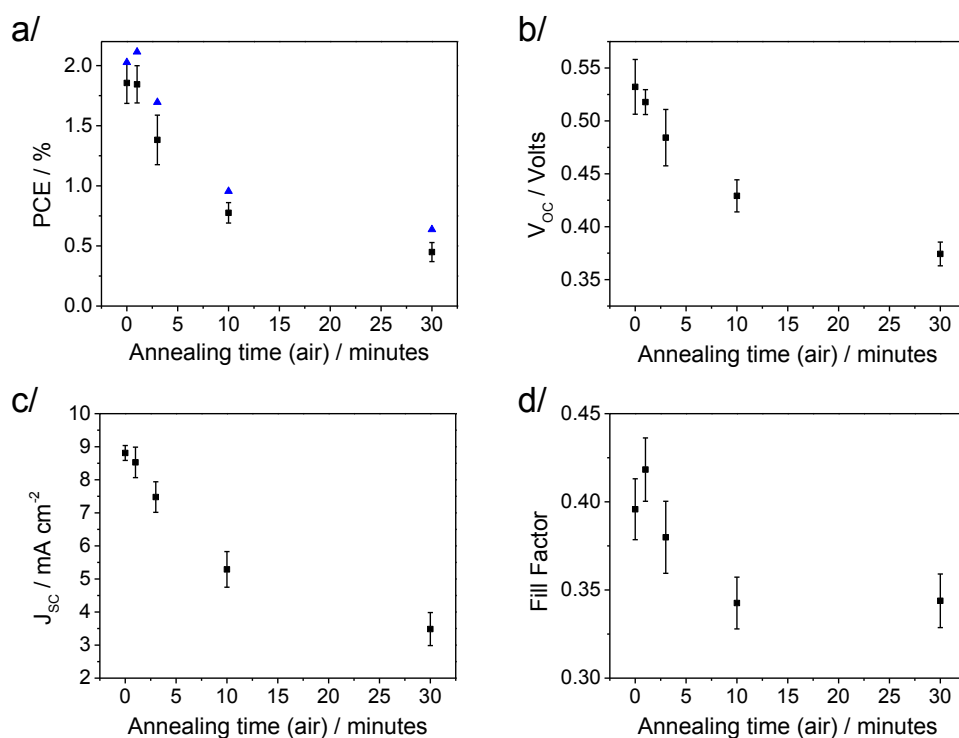


Figure 61 – Effect of Sb_2S_3 oxidation in ITO/ TiO_2 /CdS/ Sb_2S_3 /P3HT/ MoO_3 /Ag devices: Cell performance under 100 mW cm^{-2} AM 1.5 illumination as a function of time spent annealing the Sb_2S_3 layer in air at 200°C . All $\text{Sb}(\text{EX})_3$ precursor layers had previously been decomposed in N_2 at 300°C for 5 minutes. Black squares represent an average over at least 5 separate devices with error bars representing the standard deviation and blue triangles corresponding to the most efficient device. All devices recorded as new (no light soaking).

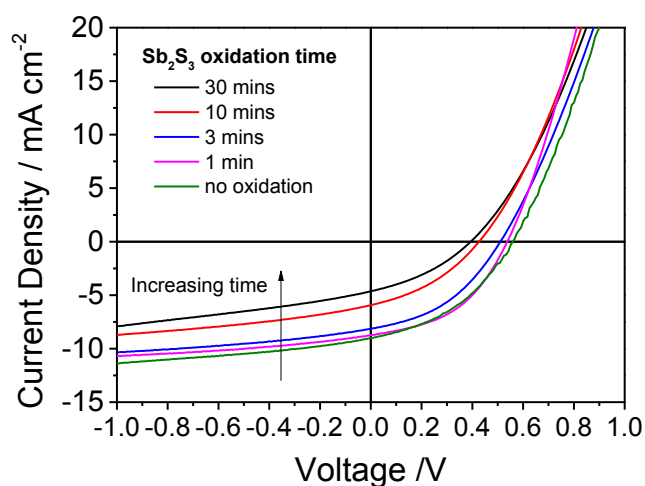


Figure 62 - Current density-voltage responses of typical ITO/ TiO_2 /CdS/ Sb_2S_3 /P3HT/ MoO_3 /Ag devices under 100 mW cm^{-2} AM 1.5 illumination as a function of time spent annealing the Sb_2S_3 layer in air at 200°C after initial precursor decomposition: 30 minutes (black), 10 minutes (red), 3 minutes (blue), 1 minute (pink) and no subsequent annealing (green). All $\text{Sb}(\text{EX})_3$ precursor layers had previously been decomposed in N_2 at 300°C for 5 minutes.

Sb₂S₃ oxidation time (200 °C, air) / minutes	J_{SC} / mA cm⁻²	V_{OC} / V	FF	PCE / %
0	9.04	0.56	0.40	2.02
1	8.74	0.54	0.45	2.11
3	8.15	0.51	0.41	1.69
10	5.94	0.43	0.36	0.92
30	4.65	0.39	0.35	0.64

Table 12 – J-V parameters of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag devices in Figure 62.

6.3.7 Champion Sb_2S_3 /P3HT Bilayer Device

A number of processing parameters have been shown to significantly influence the efficiency of Sb_2S_3 /P3HT bilayer devices, allowing for elucidation of the following design rules:

- The benefit of improved photocurrent and fill-factor when Sb_2S_3 is in the crystalline phase outweighs that of the higher V_{OC} achieved with the amorphous material.
- Light soaking in the presence of oxygen is required to achieve optimal performance.
- The presence of a very thin CdS layer enhances device performance by improving interfacial contact between Sb_2S_3 and the substrate and possibly blocking interfacial recombination.
- A ~ 100 nm thick Sb_2S_3 absorber layer appears to provide the best balance between strong light absorption and efficient charge photogeneration and extraction.
- Very little photocurrent is achieved when light is absorbed by the polymer such that it may be acting as a parasitic light filter. Improvements in device efficiency might be realised by use of a transparent HTM, or one whose absorption spectrum overlaps less strongly with Sb_2S_3 .
- Oxidation of Sb_2S_3 at the polymer heterojunction is detrimental to device performance.

By applying these criteria to the preparation of functioning devices, a maximum power conversion efficiency of 3.28 % has been achieved (Figure 63). The efficiency of this device was found to rise to almost 4 % under 0.1 sun illumination, which is quite remarkable for a flat hybrid bilayer.

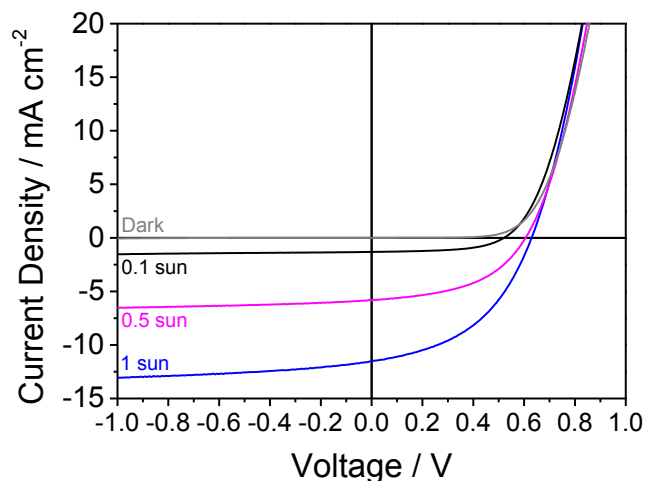


Figure 63 - Current density-voltage response of best ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag device under 100 mW cm⁻² illumination (blue), 50 mW cm⁻² (pink), 10 mW cm⁻² (black) and in the dark (grey), where CdEX₂ layer has been spin-coated at 6000 rpm from a 100 mg mL⁻¹ chlorobenzene solution and annealed at 160 °C in N₂. Sb(EX)₃ was spin-coated at 2000 rpm from a 400 mg mL⁻¹ chlorobenzene solution and annealed at 300 °C in N₂. P3HT was spin-coated at 2500 rpm from a 25 mg mL⁻¹ chlorobenzene solution. Measurement conducted following light-soaking in air under 100 mW cm⁻² illumination for 180 minutes.

Illumination intensity / mW cm⁻²	J_{SC} / mA cm⁻²	V_{OC} / V	FF	PCE / %
100	11.54	0.63	0.45	3.28
50	5.84	0.60	0.48	3.40
10	1.31	0.52	0.55	3.89

Table 13 – J-V parameters of ITO/TiO₂/CdS/Sb₂S₃/P3HT/MoO₃/Ag device in Figure 63 at different light intensities.

6.4 Comparison with Mesoporous Devices

In this section, preliminary spectroscopic and optoelectronic studies of the optimised bilayer devices are presented. These results are compared with those obtained for optimised extremely thin absorber-type systems, where the metal oxide has been sensitised with Sb_2S_3 via decomposition of the xanthate precursor, to determine the similarities and differences between the two systems, particularly in terms of the mechanisms of charge separation.

An attractive feature of xanthate decomposition for the preparation of metal sulfide nanocrystals is the associated versatility, which is evidenced by the fabrication of Sb_2S_3 -based extremely thin absorber (ETA)-type devices in parallel to the present work. For these systems, $\text{Sb}(\text{EX})_3$ is spin-coated onto the surface of mesoporous TiO_2 and thermally annealed to yield a sensitised metal oxide electrode.⁴⁶ Figure 64a shows a cross-sectional scanning electron micrograph of an Sb_2S_3 -sensitised TiO_2 film on a silicon substrate, highlighting the mesoporous structure. Despite the fact that the film is macroscopically dark brown in colour, the Sb_2S_3 layer is not clearly distinguished from the TiO_2 nanoparticles in the electron micrograph, suggesting the presence of a conformal thin coating. Figure 64b shows the absorption profile of a sensitised mesoporous film before (grey trace) and after (black trace) annealing at 300 °C for 30 minutes in a nitrogen glovebox.

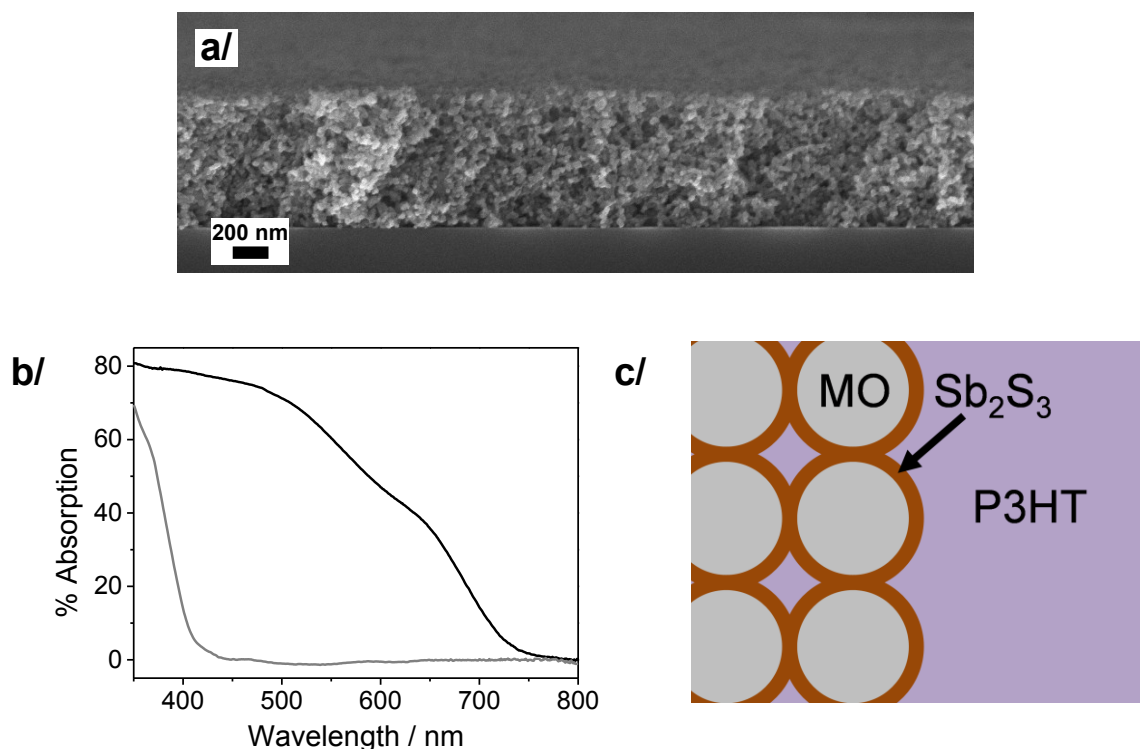


Figure 64 – a/ Cross-sectional scanning electron micrograph of an Sb₂S₃-sensitised mesoporous TiO₂ electrode. Film was prepared by Dr. Ute Cappel at Imperial College London. b/ UV-visible absorption spectra of the spin-coated Sb(EX)₃ precursor (grey) and the mesoporous TiO₂/Sb₂S₃ assembly (black). c/ Illustration of cell structure, where MO represents the metal oxide nanocrystals.

For the mesoporous system as for the bilayers, P3HT can be introduced as a hole transport material (HTM). The current-voltage responses of cell in this configuration under 1 sun illumination and in the dark are presented in Figure 65. For comparison, that of the optimised Sb₂S₃/P3HT bilayer cell described in Section 6.3.7 is also shown. Device parameters for the two systems are summarised in Table 14. It is found that although these devices are structurally very different, overall performance is remarkably similar. This observation contrasts with previous comparisons of the performance of mesoporous and flat Sb₂S₃ solar cells, where the studied bilayer-based devices have been limited to efficiencies below ~1.5 %.^{21,22,26}

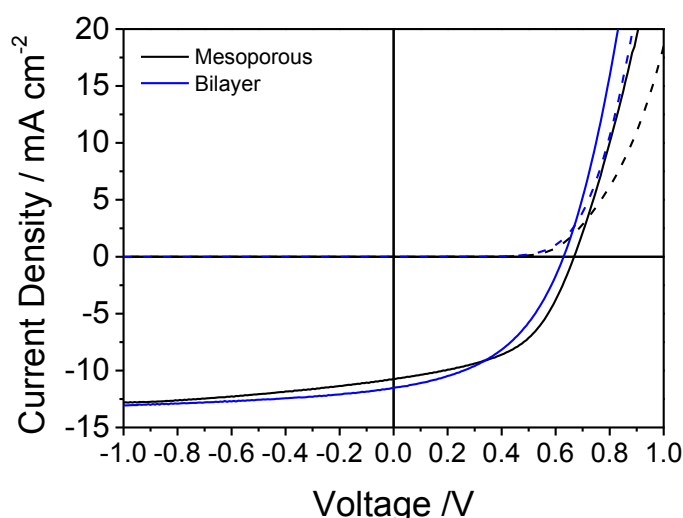


Figure 65 – Current-voltage response in the dark (dashed lines) and under 100 mW cm⁻² AM 1.5 illumination (solid lines) of an optimised mesoporous TiO₂/Sb₂S₃/P3HT solar cell (black) and an optimised Sb₂S₃/P3HT bilayer solar cell (blue).

Illumination intensity / mW cm ⁻²	J _{SC} / mA cm ⁻²	V _{OC} / V	FF	PCE / %
Bilayer	11.54	0.63	0.45	3.28
Mesoporous	10.7	0.67	0.51	3.62

Table 14 - J-V parameters of optimised mesoporous and bilayer Sb₂S₃/P3HT devices in Figure 65.

The similarity of overall performance not only highlights the impressive efficiency of the thin-film assembly, but also draws into question the importance of meso-scale morphological control and its effect on the charge photogeneration. It is also interesting to find that a slightly higher voltage is achieved with the mesoporous device. This seems to contradict initial expectations as in the ETA cell, extraction of charges in the Sb₂S₃ layer requires the photogenerated hole to be transferred to the HTM and the electron to the metal oxide. Both of these processes have an energetic cost associated with them, which is the thermodynamic driving force for interfacial separation reaction. In contrast, the bilayer system is only expected to rely upon a single interfacial charge separation reaction (hole transfer to the polymer), reducing the potential for losses. It is noted that although both types of device contain a dense TiO₂ underlayer, this is not believed to limit V_{OC} in either case, as bilayers cells utilising an amorphous Sb₂S₃ absorber layer (but still using the TiO₂ underlayer) achieve open-circuit voltages in excess of 850 mV (as described in Section 6.3.1). To compare and contrast the ways in which the two systems function, transient absorption spectroscopy is employed to study the yields and lifetime of long-lived charge separation in each system.

In Chapter 4, it was shown using pump-probe transient absorption spectroscopy that for the mesoporous system, charge separation can be instigated by hole transfer to P3HT, regardless of whether or not electron transfer to the metal oxide can take place. In order to show this, the Sb_2S_3 was selectively excited by pumping the sample beyond the absorption edge of the polymer ($\lambda_{\text{pump}} = 700 \text{ nm}$) whilst probing the characteristic spectrum of the long-lived P3HT polaron. Both mesoporous TiO_2 and ZrO_2 electrodes were used, with the latter acting as a control in which potential photoinduced electron injection from the sensitizer is prohibited. These results are reproduced in Figure 66a, where the black and the red traces represent the $10 \mu\text{s}$ transient absorption spectra of the mesoporous (mp-) $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$ and $\text{ZrO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$ films respectively. Also shown is the transient absorption spectrum of a $\text{Sb}_2\text{S}_3/\text{P3HT}$ bilayer (blue trace) recorded under the same conditions. The bilayer film contains the dense, flat TiO_2 and CdS underlayers used in the functioning devices. All signals have been scaled to account for small differences in ground state absorption at the probe wavelength and as such, are representative of the relative yields of hole transfer across the $\text{Sb}_2\text{S}_3/\text{P3HT}$ heterojunction per photon absorbed. This is confirmed in Figure 66b, which compares the time resolved change in absorbance at 980 nm for the different systems with (main figure) and without (inset) the P3HT hole conductor. The fact that very little signal is recorded in the absence of P3HT confirms that the signals presented in the main figures are indeed associated with interfacial charge separation.

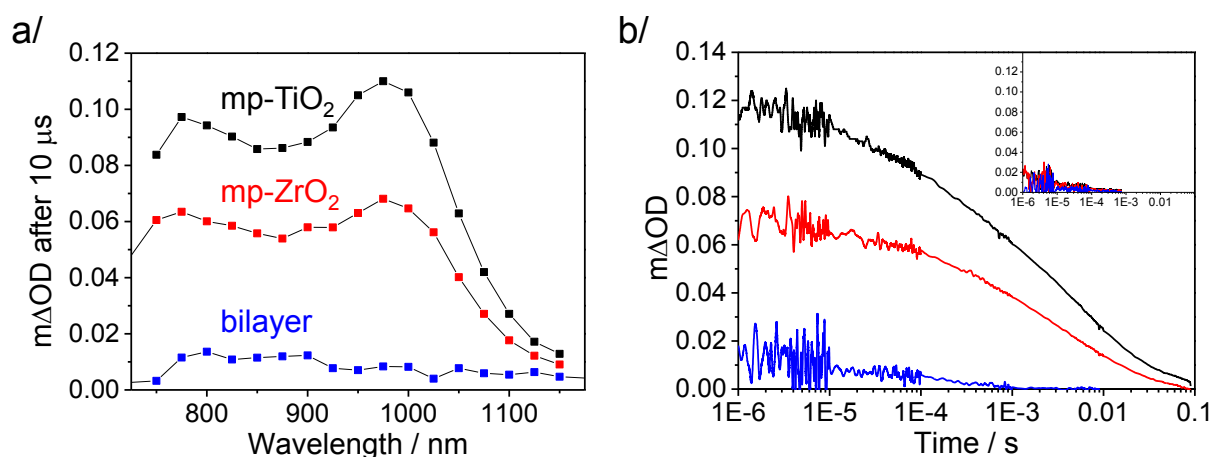


Figure 66 – a/ Transient absorption spectra of glass/mp- $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$ (black), glass/mp- $\text{ZrO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$ (red) and glass/dense $\text{TiO}_2/\text{CdS}/\text{Sb}_2\text{S}_3/\text{P3HT}$ (bilayer - blue)

Unlike the mesoporous systems, very little transient absorption associated with the P3HT hole polaron is observed for the $\text{Sb}_2\text{S}_3/\text{P3HT}$ bilayer, indicating a low yield of long-lived charge separation across this flat interface. This is consistent with results presented in Chapter 5, where the yield of hole transfer was found to decline with decreasing $\text{Sb}_2\text{S}_3/\text{P3HT}$ interface area.¹² However, for both the mesoporous and flat devices to function, holes must ultimately be transferred to the P3HT in order to

reach the hole collecting contact and contribute to the photocurrent. Given that short circuit currents in excess of 11 mA cm^{-2} are achieved with the $\text{Sb}_2\text{S}_3/\text{P3HT}$ bilayer system, it is surprising that no charge separation is seen to occur across the heterojunction in the spectroscopic study here. This indicates fundamental differences in the operating mechanisms of the mesoporous and flat devices. For the mesoporous films, it is likely that all photogenerated charges are produced in relatively close proximity to the HTM interface, such that only a short distance needs to be travelled before interfacial charge separation can occur. This results in relatively high yields of hole transfer in the films studied here with transient absorption spectroscopy. In contrast, for the bilayers, where a $\sim 100 \text{ nm}$ thick Sb_2S_3 layer is employed, most photogenerated holes will have to travel a more substantial distance through the absorber layer before they can be transferred to the polymer. For some reason, it would appear that this process proceeds with a reasonably high yield in a complete bilayer device, but not in the films prepared for spectroscopy.

Two possible explanations for the absence of the P3HT hole polaron transient absorption signal present themselves: 1/ for the bilayer system, interfacial charge separation does occur efficiently, but all charges recombine very quickly (on sub-microsecond timescales) and thus fall outside the time resolution of our system; 2/ the interfacial separation of charges requires an electric field, which exists in the functioning devices (at least away from V_{OC}) but not in the non-contacted films prepared for spectroscopy. In order to consider the first of these possibilities, transient photovoltage measurements have been performed to gain some measure of recombination lifetimes in the functioning device. With this technique, the device is held at open-circuit voltage under varying white light illumination intensities and a small perturbation in the voltage is induced by the flash of a laser diode. The rate of decay of the voltage perturbation is measured, which is indicative of the rate of recombination of photogenerated carriers in the device.⁴⁷ Figure 67a shows the variation in small perturbation lifetime as a function of light intensity for a bilayer device (blue) and for a mesoporous TiO_2 -based device (black). Figure 67b shows the variation in open-circuit voltage with light intensity for both devices.

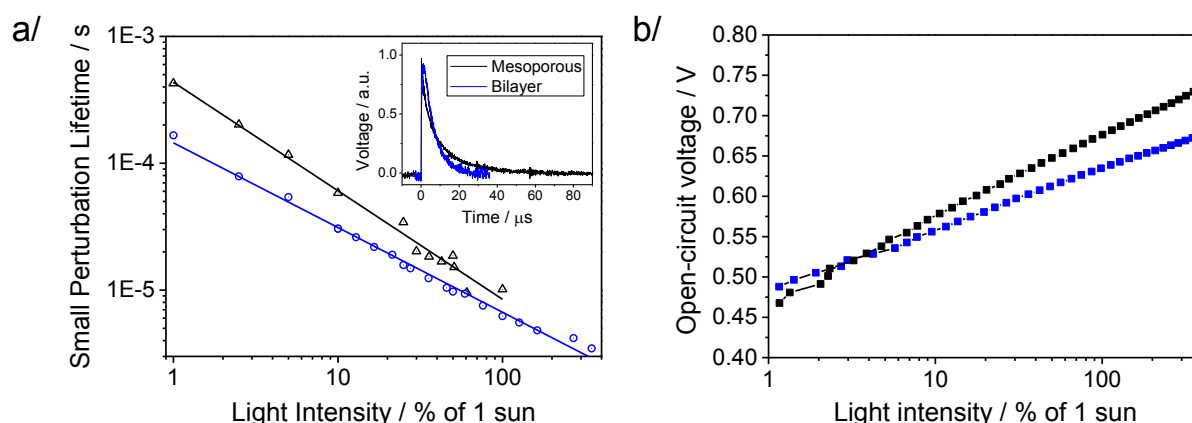


Figure 67 – a/ Main figure shows small perturbation transient photovoltage decay lifetimes of mp-TiO₂/Sb₂S₃/P3HT (black) and flat TiO₂/CdS/Sb₂S₃/P3HT-based (blue) devices as a function of light intensity. Hollow shapes represent experimental data points and solid lines provide a line of best fit as a power law. Perturbation lifetimes calculated from a monoexponential fit of the raw decays. Inset shows the normalized photovoltage transients under 1 sun equivalent illumination. Laser diode excitation at 520 nm. b/ Variation in open-circuit voltage with light intensity of mesoporous (black) and bilayer (blue) devices. Data collected in collaboration with Florent Deledalle and James Durrant at Imperial College London.

From the data shown in Figure 67a, it is clear that although carrier lifetimes are slightly increased in the mesoporous cells with respect to the bilayers, the difference between the two systems is relatively small (at least within the same orders of magnitudes).[‡] This suggests that fast recombination of interfacially separated charges is unlikely to account for the absence of transient absorption signal for the bilayer in Figure 66. On this basis, it appears likely that in the bilayer system, the development and maintenance of an electric field is required to separate charges generated in the Sb₂S₃ layer. This is not required when the heterojunction is mesostructured, thus demonstrating a link between interface morphology and the mechanisms of charge separation in Sb₂S₃-based hybrid photovoltaics. This may account for the reduced fill-factor recorded for the bilayer device with respect to the ETA-type cells.⁵¹

At present, it is only possible to speculate as to why an electric field may be required for effective interfacial charge separation in the bilayer system. It may indicate that the devices are limited by the minority (hole) carrier diffusion length within the Sb₂S₃ layer. In the mesostructured systems, charges

[‡] A possible explanation for the slightly increased carrier lifetimes in the mesoporous system is that negative charge builds up within the relatively thick mesoporous TiO₂ layer, from which the rate of recombination is likely to be governed by the trapping and de-trapping of electrons.⁴⁸⁻⁵⁰ In the bilayers, some equivalent charge may build up within the Sb₂S₃ layer and such that recombination with holes in the P3HT is faster. A more complete understanding of this effect would require a detailed knowledge of exactly where charge builds up in the respective cells, which is beyond the scope of the present work.

are always generated in close proximity to an interface and are thus able to separate rapidly, whereas for a flat bilayer, limited diffusion would restrict the number of photogenerated carriers that can reach the interface and be transferred. When an electric field exists, minority carriers would be able to drift through the depletion region to the interface and separate, increasing the effective optical depth. Moving from J_{SC} to V_{OC} , the width of the depletion region would be expected to reduce, limiting the yield of interfacial charge separation. This theory is consistent with work conducted on depleted-heterojunction colloidal quantum dot (CQD) solar cells.^{52,53} In these devices, thin films of densely packed p-type CQDs, typically PbS, are used as light absorbers and hole transport materials, and coupled with a metal oxide electron transporter such as TiO_2 to form a flat heterojunction. It has been shown that the generation of photocurrent in such systems largely relies upon the establishment of a depletion region in the CQD layer.^{51,54} This process is not normally retained at the maximum power point and thus negatively impacts the fill factor. It may also be expected to limit V_{OC} .

In the greater scheme of things, although it has been shown that reasonably high photocurrents have been achieved with Sb_2S_3 bilayer devices, if the diffusion lengths of photogenerated carriers are low enough that an electric field is required to drive efficient charge separation, the potential of Sb_2S_3 in a non-mesostructured photovoltaic system is ultimately limited. Therefore, the identification of solution-processable ambipolar absorbers is key to the achievement of high efficiencies with this type of non-structured photovoltaic system. This has recently been demonstrated by the emergence of organic lead halide perovskites-based solar cells.^{55,56} These materials have been shown to possess electron-hole diffusion lengths of more than 1 μm , well in excess of the optical absorption depth^{57,58} and simple solution-processed hybrid bilayer devices have achieved efficiencies in excess of 15 %.⁵⁹ Indeed, high efficiencies have been achieved with these absorbers in a range of device architectures, interfacially structured and otherwise.^{31,32,60} Some of the relative benefits of these different systems are discussed in Chapter 7. However, the requirement for true ambipolarity significantly limits the size of the library of potential materials. As such, the use of thin absorber layers and interface structuring is likely to be a valuable means of encouraging high yields of charge separation with materials in which electron and/or hole diffusion is limited.

It is noted that the above hypothesis appears to be challenged by the recent work of Christians *et al.*, who determine that kinetic limitations on the actual interfacial hole transfer reaction restrict the optimal absorber layer thickness to only 50 nm when using CuSCN as an HTM.⁶¹ If this is the case, one possible explanation for the apparent contradiction with the present work is that the dynamics of hole transfer to P3HT are faster than to CuSCN. This would be expected to alter the optimum layer thickness (and indeed Im *et al.*, have shown that a specific chemical interaction between the thiophene units in P3HT and the Sb_2S_3 crystal lattice result in higher quantum efficiencies than systems employing HTMs without these functional moieties)⁶. Additionally, the photocurrents achieved in the

literature for the bilayer devices are significantly lower than those reported here ($\sim 5 \text{ mA cm}^{-2}$ as opposed to $>11 \text{ mA cm}^{-2}$), which may indicate fundamental differences in the respective systems. Nonetheless, the possibility cannot be ruled out that the presence of an electric field increases the rate of interfacial hole transfer, rather than just assisting the transport of holes from the Sb_2S_3 bulk to the interface. This would reduce the kinetic competitiveness of recombination within the Sb_2S_3 layer and therefore increase the yield of interfacial separation. It is suggested that further efforts to test the validity of the above hypotheses might use bias-dependent transient absorption spectroscopy of full devices and thickness dependent optoelectronic measurements to determine the specific effect of electric field on the charge separation process.

6.5 Conclusions

In conclusion, a novel and facile deposition approach to the preparation of thin films of Sb_2S_3 has been developed, in which a single-source precursor is thermally decomposed to yield the crystalline metal sulfide. By coupling Sb_2S_3 layers prepared in this manner with a conducting polymer and optimising processing conditions in an iterative and systematic manner, it has been shown that Sb_2S_3 can be used as a light absorber and electron transport material to generate significant amounts of photocurrent in non-mesostructured hybrid photovoltaic devices. This not only represents another hybrid device architecture in which Sb_2S_3 shows significant promise, but the high performance begins to draw into question the importance of interfacial structuring in the design of such systems.

Preliminary transient absorption and optoelectronic transient photovoltage measurements have been used to compare the optimised bilayer devices with ETA cells prepared in a similar manner. It is determined that the mechanism of charge separation in Sb_2S_3 -based bilayer systems differs to that which drives photocurrent generation in mesostructured ETA-type cells. Specifically, the former system is believed to require the presence of an electric field in order for high yields of interfacial hole transfer to be achieved. This work highlights a link between interface structure and the mechanisms of charge separation for Sb_2S_3 -based hybrid photovoltaics and is anticipated to inform the development of design rules targeted at improving device efficiency.

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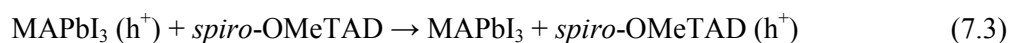
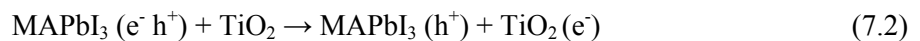
7 The Importance of Photoexcited Electron Extraction for Sustained Organic Lead Halide Perovskite Photovoltaic Performance

Impressive hybrid photovoltaic performance has been realised with the methylammonium lead triiodide (MAPbI₃) perovskite absorber in a wide range of device architectures. However, the question as to which of these systems represents the most commercially viable long-term prospect is yet to be answered conclusively. In this chapter, transient absorption spectroscopy is used to probe the effects of surrounding environmental conditions on the yields of long-lived charge separation for the three major device configurations: MAPbI₃-sensitised mesoporous TiO₂, MAPbI₃-coated mesoporous Al₂O₃ and a thin film bilayer. It is found that in the bilayer and mesoporous Al₂O₃ films, where no electron injection can take place, hole transfer is rapidly and critically inhibited by exposure to ambient conditions, with no accompanying change in ground state absorbance. This degradation process is determined to require the presence of both light and air, but not moisture. In contrast, significantly increased stability is achieved when MAPbI₃ is used to photosensitise mesoporous TiO₂. A key consequence of this effect is seen in the tolerance of the different systems to the processing environment; sensitised TiO₂ systems display no adverse effects when spin-coated and annealed in atmospheric conditions, whereas hole transfer appears to be limited when both the coated Al₂O₃ and thin-film devices are not prepared in glovebox. The present findings indicate that the reaction of the excited state in the perovskite layer – probably with molecular oxygen – can potentially destabilise the photovoltaic assembly. The introduction of an electron acceptor, such as mesoporous TiO₂, may act to rapidly quench the sensitiser excited state and thus reduce the likelihood of degradation. Preliminary investigations indicate that the impact of these observations extends to the fabrication of functioning photovoltaic devices. It is demonstrated that high conversion efficiency can be achieved with mesoporous TiO₂-based cells when prepared entirely in ambient conditions, whereas production of functioning bilayers appears to require processing in an oxygen deficient environment. This work highlights a significant advantage of retaining mesoscale morphological control in the preparation of efficient, low cost and stable hybrid photovoltaics.

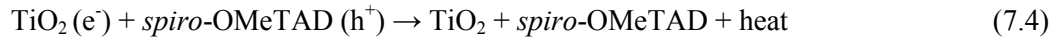
The work presented in this chapter has come as a result of an ongoing collaboration with the groups of Prof. Mohammed Nazeeruddin at École polytechnique fédérale de Lausanne (EPFL), Switzerland and Dr. Brian O'Regan at Imperial College London. All films and devices were fabricated in these laboratories according to literature procedures^{1,2} by either Cameron Jellett at Imperial College or Dr. Yong Hui Lee at EPFL; their contributions are gratefully acknowledged. All of the characterisation, spectroscopy and analysis described herein is the author's own work.

7.1 Introduction

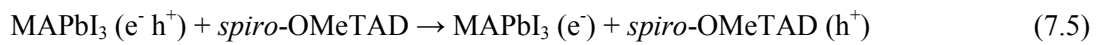
Organic lead halide perovskites, such as methylammonium lead tri-iodide MAPbI₃ and its mixed halide analogue MAPbI₂Cl are currently generating enormous interest and excitement with respect to their application in low-cost, solution-processable photovoltaics. Initially, these materials were employed as thin sensitiser layers for mesoporous (mp) TiO₂.^{3,4} However, in much the same way as described for Sb₂S₃ in the preceding chapters, it has been demonstrated that hole transfer can occur independently of electron injection.^{1,5,6} As a result, these materials demonstrate remarkable architectural versatility, with high efficiencies achieved in a wide range of configurations, including as a sensitiser for mesoporous TiO₂ (15 %),² a structured absorber and electron transport material on an electrically inert mesoporous scaffold (10.9 %),^{6,7} and in a planar thin-film configuration (15.4 %).⁸⁻¹⁰ This versatility also causes new questions to be posed; namely, what are the merits and shortcomings of the respective systems and which architecture is most promising in terms of long-term commercial viability. To consider these issues, and in the hope of improving understanding of the way in which the different systems work, transient absorption spectroscopy is used to compare and contrast the interfacial charge separation processes at the operational heart of device function. When the perovskite is used as a sensitiser for mesoporous TiO₂, ultrafast electron injection is expected to take place from the MAPbI₃ to the TiO₂ in a similar manner to in a dye-sensitised solar cell (DSSC).^{11,12} Subsequently, hole transfer from the sensitiser to *spiro*-OMeTAD regenerates the absorber ground state:



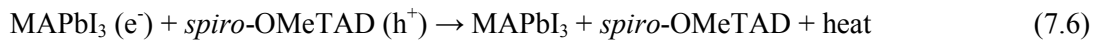
Electron and hole transport occurs through the TiO_2 and *spiro*-OMeTAD respectively and will compete kinetically with interfacial recombination of the charge separated states:



When TiO_2 is replaced with an otherwise analogous Al_2O_3 mesostructure, electron injection is blocked by virtue of the high energy conduction band of the latter metal oxide. In this case, interfacial charge separation is effected by hole transfer.^{1,6} For the non-structured thin film, again no electron injection takes place, but photogenerated holes are likely to have further to travel before reaching the interface with *spiro*-OMeTAD and separating across the heterojunction:



Thereafter, electrons are transported through the perovskite phase and holes through the *spiro*-OMeTAD. The competing recombination process is thus:



These different device architectures are illustrated in Figure 68.

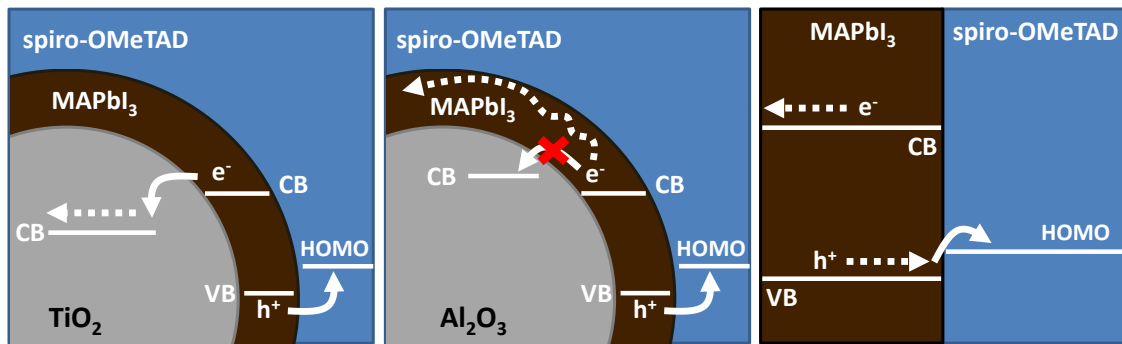


Figure 68 – Schematic to illustrate charge photogeneration in various device architectures incorporating MAPbI_3 as an absorber.

7.2 Interfacial Charge Separation

Figure 69 shows the steady-state photoluminescence spectra of mesoporous metal oxide/MAPbI₃ films, with (red traces) and without (black traces) the *spiro*-OMeTAD hole conductor. For Al₂O₃/MAPbI₃, where no charge separation is expected at the heterojunction, photoexcited states in the perovskite recombine emissively to yield a peak at ~770 nm. Comparing the pristine metal oxide/MAPbI₃ films, it is clear that substantial emission quenching is seen when Al₂O₃ is replaced with TiO₂. This confirms that charge separation occurs at the TiO₂/MAPbI₃ interface, where electron injection is energetically favourable. When *spiro*-OMeTAD is introduced, the perovskite emission is quenched on both metal oxides, confirming that hole transfer can take place even when electron injection does not.

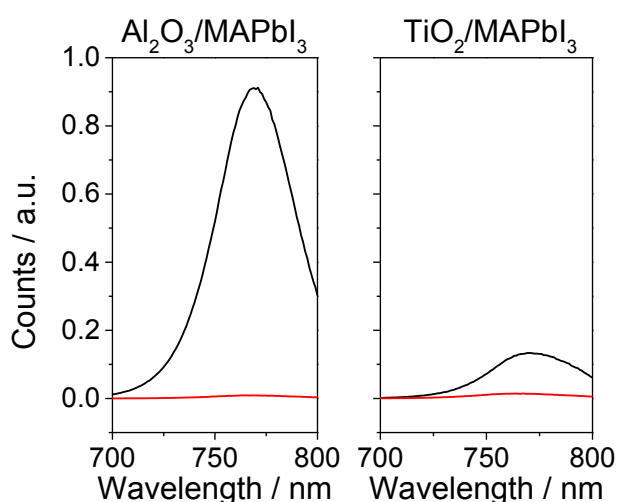


Figure 69 – Steady state emission spectra of mesoporous metal oxide/MAPbI₃ films with (black) and without (red) the *spiro*-OMeTAD hole transport material. Photoexcitation was at 450 nm.

To gain more insight into the fundamental differences between the device architectures, transient absorption spectroscopy is employed to study the yields and lifetimes of long-lived interfacial charge separation in the various films. The requirement that hole transfer ultimately takes places from MAPbI₃ to *spiro*-OMeTAD is common to all systems. As such, the transient existence of photooxidised *spiro*-OMeTAD, which is known to absorb strongly in the near-infrared,^{1,5} is a useful indicator of successful charge separation. Figure 70 shows the transient absorption spectra of a mesoporous TiO₂/MAPbI₃/*spiro*-OMeTAD film (Figure 70a) and an equivalent Al₂O₃/MAPbI₃/*spiro*-OMeTAD film (Figure 70b), recorded 10 μs after a 567 nm pulsed laser excitation. Both spectra reflect the characteristic absorption profile of oxidised *spiro*-OMeTAD, as shown by the similarity of shape with the absorption spectrum of a chemically oxidised solution of *spiro*-OMeTAD (blue dashed line in Figure 70a).¹³ The sharp negative peak seen at ~750 nm for the Al₂O₃-based assembly is likely

to be a result of stimulated emission from the perovskite layer.¹⁴ When no *spiro*-OMeTAD is present and the pristine metal oxide/MAPbI₃ films are measured, no transient absorption signal is recorded at 1600 nm (grey traces - insets to Figure 70a/ and b/). These observations confirm that photoinduced hole transfer from the perovskite absorber to the hole transport material (HTM) occurs in both systems and that the transient products of the reaction absorb at 1600 nm. Therefore, the intensity of transient absorption at 1600 nm for a MAPbI₃/*spiro*-OMeTAD assembly provides a measure of the relative number of charge separated states at a given time.

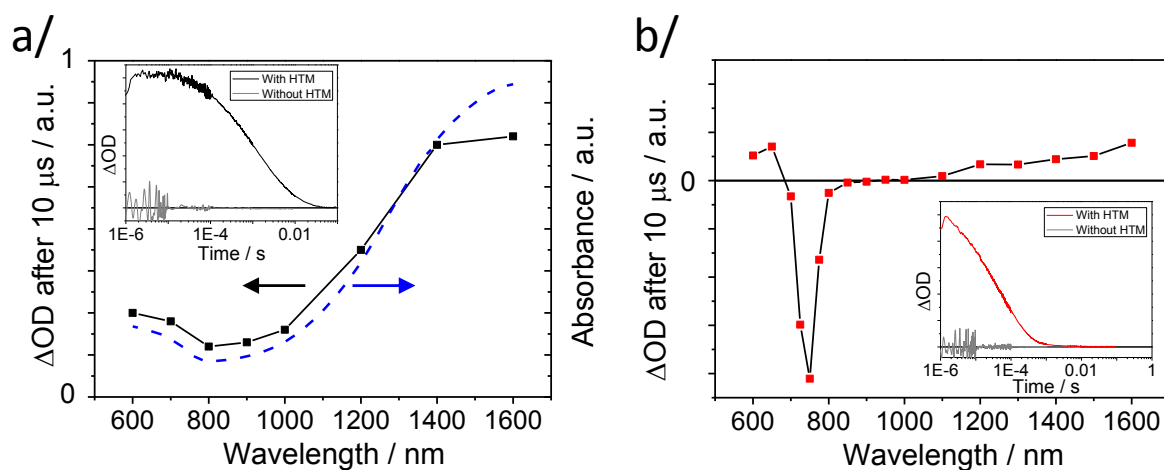


Figure 70 – Transient absorption spectra of a/ TiO₂/MAPbI₃/*spiro*-OMeTAD and b/ Al₂O₃/MAPbI₃/*spiro*-OMeTAD films. The blue trace in a/ represents the absorption spectrum of a solution of *spiro*-OMeTAD that has been chemically oxidised with N(PhBr)₃SbCl₆. The inset to each figure compares the transient absorption signal at 1600 nm for films prepared with (black/red traces) and without (grey traces) *spiro*-OMeTAD. Laser excitation energy density = 25 μJ cm⁻² at 567 nm.

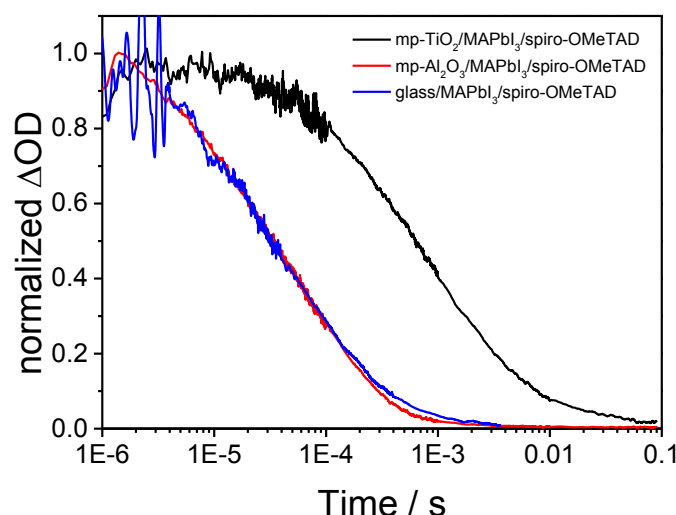


Figure 71 – Decay in transient absorption at 1600 nm for mp-TiO₂/MAPbI₃/*spiro*-OMeTAD (black), mp-Al₂O₃/MAPbI₃/*spiro*-OMeTAD (red) and bilayer MAPbI₃/*spiro*-OMeTAD (blue) following laser excitation at 567 nm (energy density = 25 μJ cm⁻²). All traces normalized to ΔOD = 1 at 1 μs to highlight differences in recombination kinetics.

In Figure 71, the yield of long-lived charge separation is monitored as a function of time after pulsed laser excitation by measuring the change in absorption (ΔOD) at 1600 nm for mp-TiO₂/MAPbI₃/*spiro*-OMeTAD (black), mp-Al₂O₃/MAPbI₃/*spiro*-OMeTAD (red) and bilayer MAPbI₃/*spiro*-OMeTAD (blue). At this wavelength, the intensity of the transient absorption signal is related to the yield of *spiro*-OMeTAD holes at a given time, as described above. The decay in signal thus represents the recombination of the charge separated states. In accordance with the work of Marchioro *et al.*,⁵ a much longer charge separation lifetime is seen for the mp-TiO₂-based assembly ($\tau_{1/2}$ (1 μs) = 1 ms) than for the mp-Al₂O₃ analogue ($\tau_{1/2}$ (1 μs) = 100 μs). This indicates that holes transferred to *spiro*-OMeTAD recombine more quickly with electrons in the MAPbI₃ (as on the Al₂O₃ scaffold) than with those in transferred to TiO₂. The lifetime of *spiro*-OMeTAD holes in the bilayer assembly appears almost identical to those in the mp-Al₂O₃ system. The differing dynamics of recombination may be a result of increased spatial separation between electrons and holes when the former are transferred to the TiO₂ (as opposed to remaining in the MAPbI₃), which would be expected to retard the reverse electron transfer process. Furthermore, recombination in the TiO₂-based system may be rate limited by the trapping and de-trapping of electrons in the metal oxide.¹⁵ This could further delay recombination compared to the cases in which no electron acceptor is present.

7.2.1 Photovoltaic Stability

Subsequent to measurement of the pristine films, the transient absorption response at 1600 nm was obtained at regular intervals over the course of 1 hour, with the films exposed to ambient light and air (but not the laser pulse or probe light) in the interim periods. The measurements themselves were conducted with the sample sealed under flowing nitrogen. On TiO_2 , the transient absorption signal remains relatively consistent over the ageing process, barring a small increase in intensity after a short period of exposure to atmospheric conditions. Figure 72 shows the initial amplitude of ΔOD (averaged between 2 and 5 μs) as a function of ageing time. The black markers represent the TiO_2 -based system, and are derived from the raw data presented in Figure 73a.

For the bilayer and mp- Al_2O_3 -based films, the initial signal amplitude decreases dramatically with ageing time, indicating a decline in the yield of long-lived *spiro*-OMeTAD holes (Figure 72 - red and blue data sets for Al_2O_3 and bilayer systems respectively; raw data shown in Figure 73). This suggests that hole transfer is rapidly and critically inhibited by the exposure of these systems to environmental conditions. Importantly, this process is not accompanied by any noticeable reduction in steady-state absorption (Figure 73 – right side figures), which would be expected if the water-soluble perovskite sensitiser were simply interacting with moisture in the air.¹⁶ For the Al_2O_3 -based system, the observed degradation process is also accompanied by an increase in transient lifetime (Figure 73b). It is unclear as to whether this long-lived component reflects an increase in the lifetime of the *spiro*-OMeTAD holes, or represents contribution of a product of the parasitic reaction.

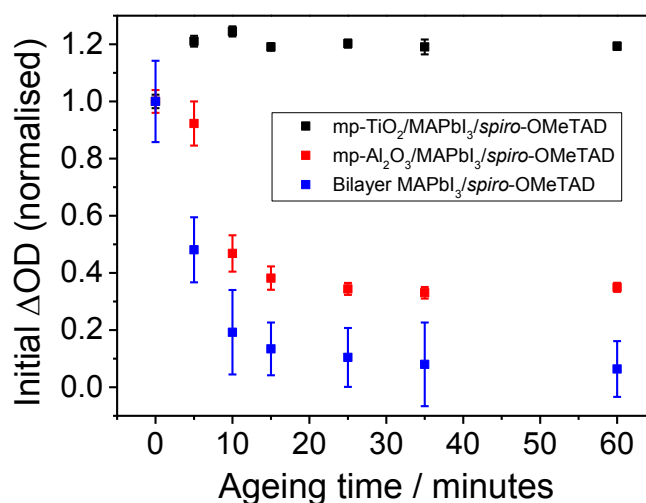


Figure 72 – Initial amplitude of ΔOD at 1600 nm as a function of ageing time in atmospheric conditions under ambient light for glass/mp- TiO_2 /MAPbI₃/*spiro*-OMeTAD (black), glass/mp- Al_2O_3 /MAPbI₃/*spiro*-OMeTAD (red) and glass/MAPbI₃/*spiro*-OMeTAD (blue). Data points determined from the mean value of ΔOD between 2 and 5 μs for each measurement. Films excited at 567 nm with a $25 \mu\text{J cm}^{-2}$ laser pulse.

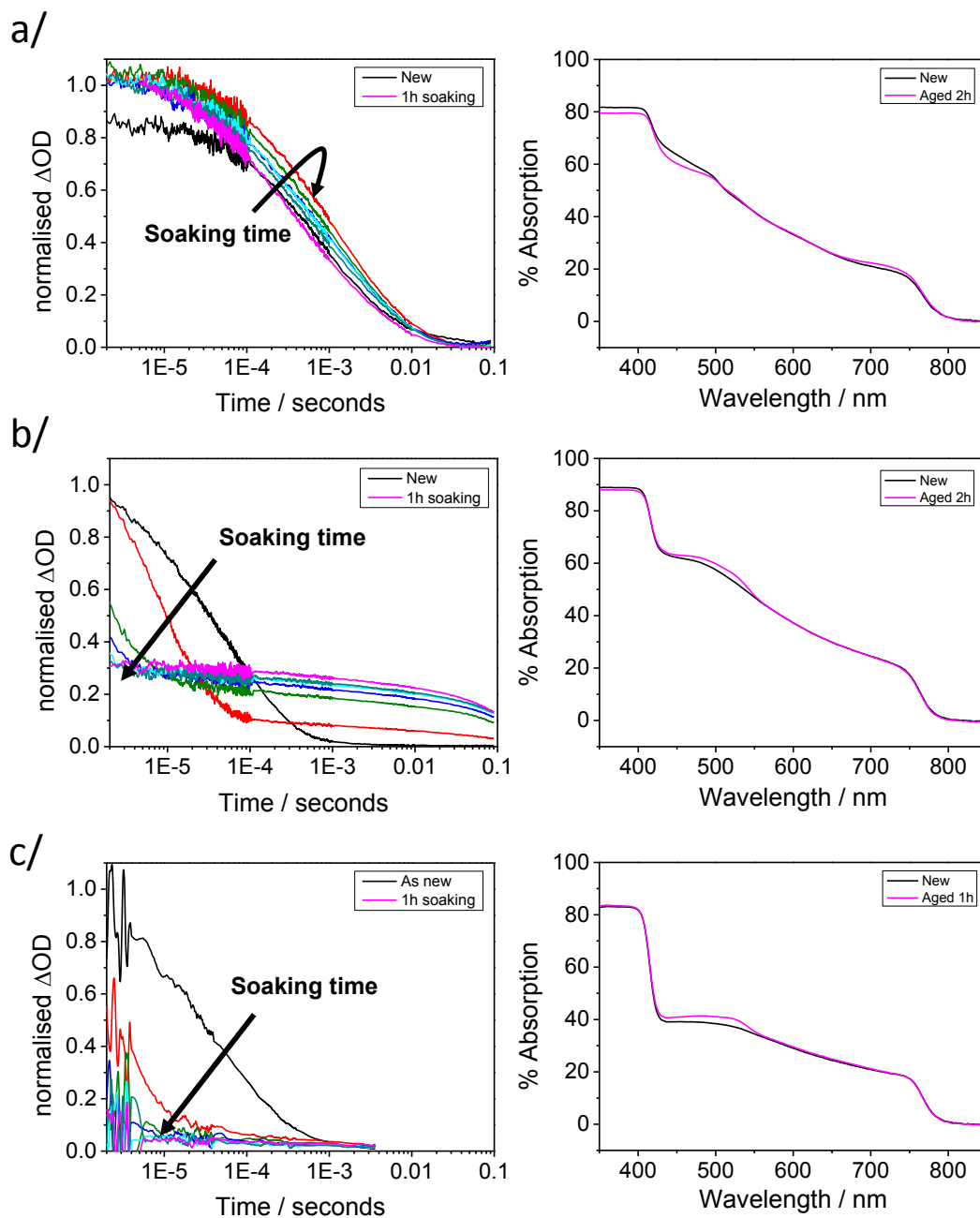


Figure 73 – Decay in transient absorption of *spiro*-OMeTAD holes at 1600 nm (left) and steady- state UV- vis absorption spectra (right) for a/ glass/mp-TiO₂/MAPbI₃/*spiro*-OMeTAD, b/ glass/mp-Al₂O₃/MAPbI₃/*spiro*-OMeTAD and c/ glass/MAPbI₃/*spiro*-OMeTAD as a function of soaking time in ambient light and air. All measurements recorded under flowing nitrogen. The black trace represents the pristine film, with red, green, blue, turquoise, pink and teal representing subsequent measurements recorded at regular intervals over the course of 1 hour. Laser photoexcitation was at 567 nm with an energy density of 24.5 $\mu\text{J cm}^{-2}$.

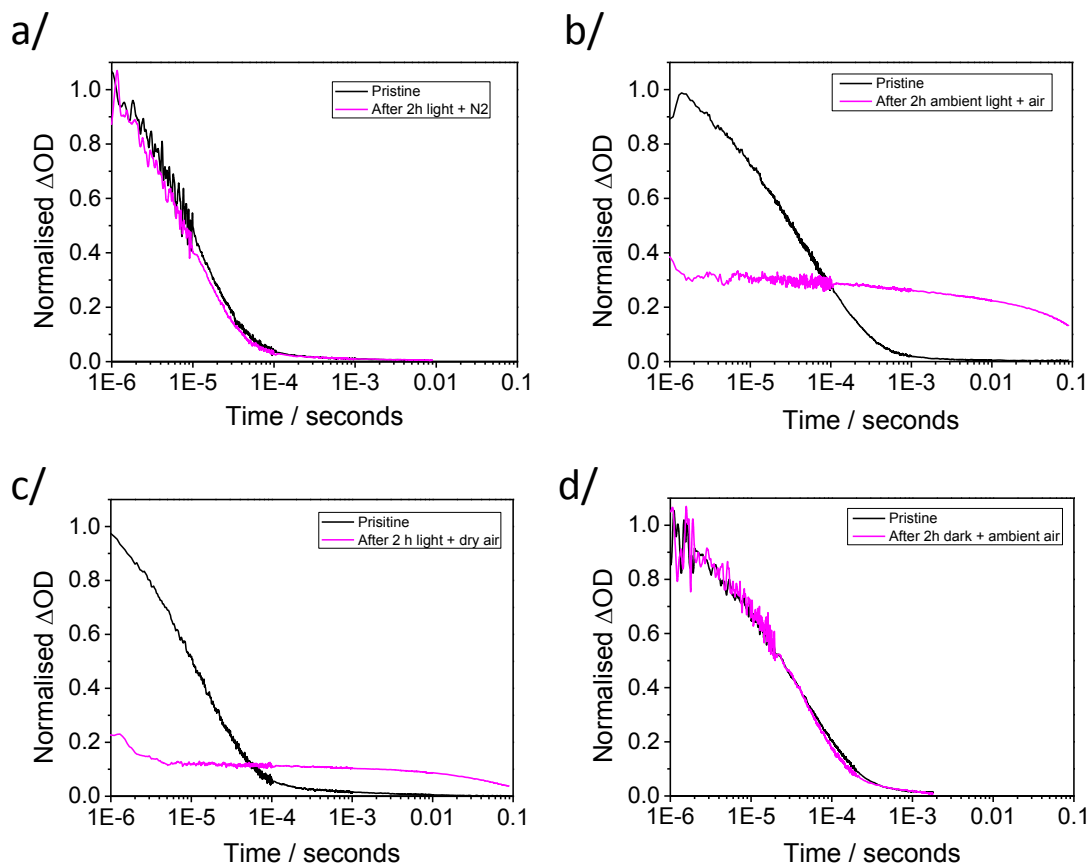


Figure 74 – Effect of exposure to varying environmental conditions for two hours on the transient absorption signal at 1600 nm for a mesoporous $\text{Al}_2\text{O}_3/\text{MAPbI}_3/\text{spiro-OMeTAD}$ film: a/ ambient light, sealed under flowing N_2 , b/ ambient light, non-sealed, c/ ambient light, sealed under flowing dry air ($\text{H}_2\text{O} < 2$ vpm), d/ dark, non-sealed. Laser excitation energy density = $25 \mu\text{J cm}^{-2}$ at 567 nm.

In order to try and identify what causes the decay in the yield of long-lived charge separation for Al_2O_3 -based and bilayer systems, the effects of film ageing in different environmental conditions are investigated. Figure 74 shows the time-resolved transient absorption signals for an $\text{Al}_2\text{O}_3/\text{MAPbI}_3/\text{spiro-OMeTAD}$ at 1600 nm before (black) and after (pink) 90 minutes of ageing in controlled conditions (where a/ is exposed to ambient light and sealed under flowing N_2 , b/ is in light and ambient air, c/ is in light and dry air (UN 1002, BOC, $\text{H}_2\text{O} < 2$ ppmV) and d/ is in the dark and ambient air). It is determined that in ambient light, a decline in long-lived interfacial charge separation occurs when the sample is sealed under flowing dry air, but not under flowing nitrogen. In the dark, no degradation occurs in any of the environmental conditions considered. It can thus be concluded that the degradation process is light-induced and as it is independent of moisture, is likely to be due to reaction of the perovskite sensitiser with oxygen.

The next question that arises relates to why the degradation process occurs on Al_2O_3 and in a bilayer, but not on mesoporous TiO_2 . The most fundamental difference between using a mesostructured TiO_2 electrode and an insulating scaffold is that in the former case, ultrafast electron injection to the TiO_2 is able to rapidly quench the excited state of the sensitiser.¹⁷ When no electron acceptor is present, photogenerated electrons remain within the sensitiser layer until they either reach a contact and are extracted or recombine. For dye-sensitised solar cells, from which the present perovskite systems have evolved, it has long been established that extending the lifetime of the sensitiser excited state increases the probability of a destructive side-reaction taking place and that this can cause significant photovoltaic instability.¹⁸ For example, Kohle *et al.*, have shown that the N3 dye is fundamentally unstable under extended illumination in ethanolic solution, as the photoexcited electron reacts with oxygen and causes the system to degrade.¹⁹ However, when anchored to an electron accepting TiO_2 surface, rapid deactivation of the dye excited state via interfacial electron injection precludes the parasitic side reaction and the assembly displays remarkable photostability. It may therefore be expected that the increased perovskite excited state lifetime experienced in the Al_2O_3 -based and bilayer systems increases the probability of reaction with external species, such as molecular oxygen, and thus destabilises the system. At present, the mechanism by which this degradation process proceeds is unclear, although studies aimed at resolving its nature are expected to form the basis of future work.

In a functioning device, the electrical extraction of photogenerated electrons from the perovskite layer will also contribute to defining the kinetic competitiveness of potential side-reactions and may thus delay the degradation process. However, an important consequence of the reported effects is the sensitivity of the different systems to processing environment. All of the films considered thus far have been prepared by spin-coating and annealing the MAPbI_3 layer in a nitrogen glove box. When the $\text{Al}_2\text{O}_3/\text{MAPbI}_3/\text{spiro-OMeTAD}$ and bilayer films are prepared in ambient conditions, transient absorption spectroscopy of the as-new films already reveals significant signs of decay (Figure 75). Conversely, the equivalent TiO_2 -based films are much more tolerant to processing conditions and even show signs of improvement when prepared in air.

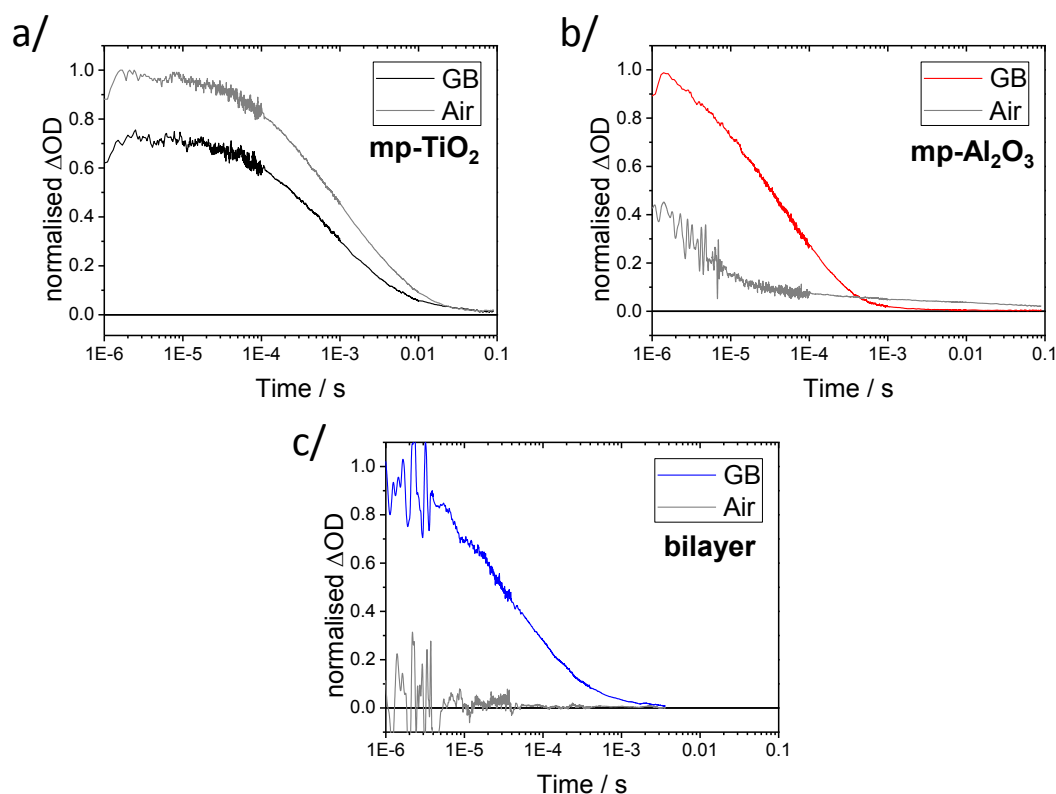


Figure 75 – Transient absorption signal at 1600 nm of as new MAPbI₃/*spiro*-OMeTAD films prepared in a glovebox (coloured) and in ambient conditions (grey) for the following architectures: a/ mesoporous TiO₂/ MAPbI₃/*spiro*-OMeTAD, b/ Al₂O₃/MAPbI₃/*spiro*-OMeTAD, MAPbI₃/*spiro*-OMeTAD bilayer. Laser excitation energy density = 25 μJ cm⁻² at 567 nm.

In order to test the practical implications of the observed effects, preliminary studies of photovoltaic devices in the two architectural extremes (in terms of likely perovskite excited state lifetime) have been considered: the TiO₂-sensitised system, where the excited state is expected to be rapidly quenched by electron injection to the metal oxide,⁵ and the bilayer, where photogenerated charges must diffuse to the *spiro*-OMeTAD interface before charge separation can take place via hole transfer. Figure 76 shows the current-voltage responses of two solution-processed MAPbI₃/*spiro*-OMeTAD bilayer devices, under 1 sun AM 1.5 illumination, prepared under the same processing conditions, except that the blue trace represents a device where the perovskite layer has been spin-coated and annealed in ambient conditions and the grey trace represents a device prepared in a nitrogen glovebox. Also shown is an mp-TiO₂-based device prepared entirely in ambient conditions (black trace). These data suggest that highly efficient performance can be achieved with the sensitised TiO₂ device under much less exacting conditions than for the bilayers. For the latter system, a profound sensitivity to ambient conditions would be expected to levy a costly toll on the economy of large-scale device production, whilst also imposing the need for more stringent and expensive standards of encapsulation. These observations suggest that meso-scale morphology is of great benefit in solar cells utilising organic lead halide perovskite absorbers, as the rapid quenching of the sensitiser excited state by electron injection helps ensure photovoltaic stability.

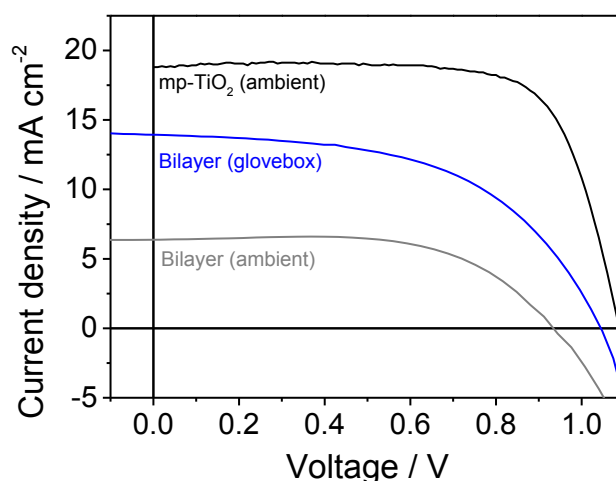


Figure 76 – Current density voltage response under 1 sun illumination of a mp-TiO₂/MAPbI₃/*spiro*-OMeTAD device prepared in ambient conditions (black), a bilayer MAPbI₃/*spiro*-OMeTAD device prepared in a nitrogen glovebox (blue) and a bilayer MAPbI₃/*spiro*-OMeTAD device prepared in ambient conditions (grey). Bilayer devices were prepared and tested by Cameron Jellett at Imperial College London and mp-TiO₂ devices were prepared and tested by Dr. Yong Hui Lee at EPFL.

	$J_{SC} / \text{mA cm}^{-2}$	V_{OC} / V	FF	PCE / %
mp-TiO₂ (ambient)	19.1	1.08	0.74	15.73
Bilayer (glovebox)	13.9	1.05	0.57	8.32
Bilayer (ambient)	6.3	0.93	0.64	3.72

Table 15 – J-V parameters of devices shown in Figure 76.

7.3 Conclusions

In conclusion, transient absorption spectroscopy has been used to probe yields and lifetimes of photoinduced, long-lived charge separation in the three major architectural variations of MAPbI₃-sensitised solar cells. It is confirmed that hole transfer to *spiro*-OMeTAD takes place in all cases and can therefore occur independently of electron extraction. When exposed to ambient conditions, the coated mp-Al₂O₃ and bilayer systems show a rapid and significant degradation in the yield of long-lived charge separation. This process, which does not affect sensitised mesoporous TiO₂ films, is only found to occur when both light and oxygen are present. It is therefore thought to be a result of parasitic reactions taking place between photoexcited electrons in the sensitiser and molecular oxygen. Preliminary investigations of functioning photovoltaic devices indicate that the effect may impose increasingly stringent requirements on processing conditions for the devices which do not

employ a specific electron acceptor. This work indicates a potential benefit of retaining mesoscale morphological control in hybrid photovoltaics, even when it is not required for the achievement of initially high intrinsic yields of charge separation.

7.4 References

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8 Conclusions and Outlook

For a number of years, metal chalcogenide-based extremely thin absorber (ETA) photovoltaics have relied upon antimony sulfide to achieve their record efficiencies. However, the operational mechanisms of these systems have been relatively poorly understood and introduction of Sb_2S_3 into alternative hybrid device architectures has been limited. One of the main aims of this project has been to improve understanding of the way in which Sb_2S_3 -based ETA devices work and to use the findings of these studies to selectively introduce Sb_2S_3 into different device configurations.

It has been determined that when Sb_2S_3 is used as a sensitizer material in an ETA cell, interfacial hole transfer to an appropriate hole transport material (HTM) can take place without the prerequisite that photogenerated electrons first be extracted. This points to the importance of the hole transfer reaction not simply as a means of regenerating the sensitizer, but rather as an integral part of the charge separation process. It is anticipated that this finding will aid the development of design-rules and structure-function relationships for the preparation of increasingly efficient Sb_2S_3 -based ETA cells, as well as the introduction of Sb_2S_3 to alternative hybrid device configurations.

On the basis of this observation and given that Sb_2S_3 is known to be an n-type semiconductor, a novel hybrid device architecture has been developed in which Sb_2S_3 assumes the structural, optical and electrical roles of a sensitised metal oxide. When coupled with an HTM, interfacial charge separation is effected by hole transfer and photogenerated electrons are transported through the inorganic phase. To achieve this, mesoporous films of highly crystalline Sb_2S_3 are prepared via a processing route in which a metal xanthate precursor layer is doctor bladed from a paste and thermally annealed at low temperature. The size of the absorber crystals and thus the size of the pores in the film can be controlled by changing the temperature of this annealing step. Transient absorption spectroscopy is used to show that photoinduced hole transfer does occur at the inorganic/organic heterojunction. It is found that the yield of long-lived charge separation is highly sensitive to interface area. Preliminary solar cell devices, which deliver short-circuit photocurrents of $\sim 5 \text{ mA cm}^{-2}$, provide evidence for electrical conductivity of the nanocrystals.

In order to consider the question of whether a structured interface is required for Sb_2S_3 -based hybrid photovoltaics to deliver photocurrent, thin film solar cells based on a Sb_2S_3 /P3HT heterojunction have also been studied. To facilitate the preparation of these devices, a novel method for the deposition of Sb_2S_3 thin films has been developed, whereby a single-source metal xanthate precursor is spin-coated

and thermally decomposed to yield the crystalline metal sulfide. Through systematic study and optimisation of processing parameters, the bilayer devices have been shown to deliver power conversion efficiencies in excess of 3.2 % under 1 sun illumination, and almost 4 % at 0.1 sun. Comparison of the bilayer devices with ETA-type cells prepared in an analogous manner revealed that despite the significant structural differences of the two systems, overall performance is relatively similar. This highlights the impressive performance of the bilayer system and draws into question the importance of mesoscale morphological control. Transient absorption spectroscopy and transient photovoltage measurements indicate that charge separation in the bilayer system requires the presence of an electric field, but occurs spontaneously at the structured interface. This may be associated with limited intrinsic diffusion lengths of electrons and holes in Sb_2S_3 and is expected to limit device performance. For absorber materials that are not sufficiently ambipolar, interface structuring is therefore likely to be beneficial as it can ensure rapid transfer of relatively immobile charge carriers to a specific transport material. It is expected that study of the formation and distribution of electric fields in devices such as these will be key to revealing more of the link between interface structure and the processes of interfacial charge separation.

For photovoltaic absorbers with high electron and hole diffusion lengths, it seems unlikely that interfacial structuring is required to achieve high yields of interfacial charge separation. This has been demonstrated by the development of solution-processed organic lead halide perovskite-based photovoltaic devices, where high power conversion efficiencies can be achieved in both planar and mesostructured interface configurations. In order to consider the question of whether the need to mesostructure is rendered obsolete by the selection of suitably ambipolar materials, transient absorption spectroscopy has been used to compare and contrast the interfacial charge transfer reactions that can govern the efficiency of the different perovskite-based devices. It is found that under exposure to ambient conditions, high yields of long-lived charge separation are readily sustained when a mesostructured electron accepting material is used. Without a specific electron acceptor, a rapid degradation in the yield of interfacial hole transfer is observed. It is suggested that this decay can be attributed to the reaction of photoexcited electrons in the absorber with oxygen in the air. When an electron acceptor is present, the rapid quenching of the absorber excited state by electron injection may preclude these parasitic side reactions and impart relative stability. These observations indicate a benefit to interfacial structuring beyond the initial concern of achieving maximum power conversion efficiencies.

