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(54) Title: SOLID-STATE HETEROJUNCTION DEVICE

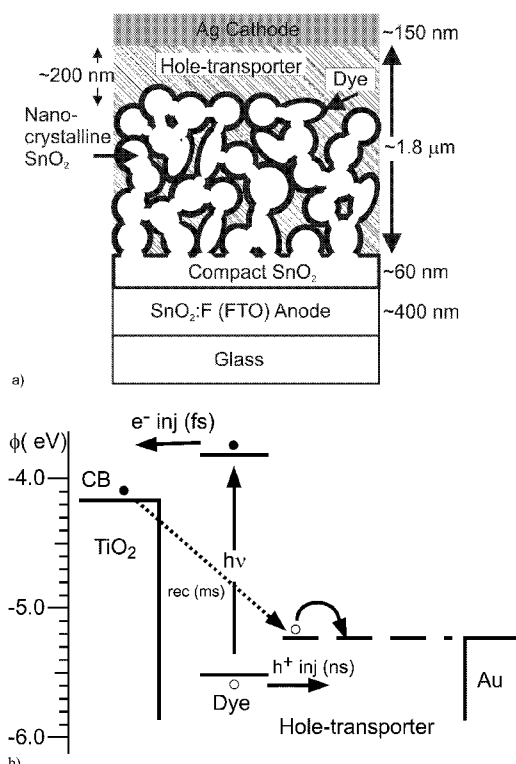


Figure 1. a) A schematic illustration of a cross section of a solid-state dye-sensitized solar cell using SnO_2 as the n-type metal oxide. b) An illustrative energy level diagram for a conventional solid-state dye sensitized solar cell.

(57) Abstract: The present invention relates to a solid-state p-n heterojunction such as in a solar cell comprising an organic p-type material in contact with a porous layer of n-type material, characterised in that the thickness of the porous layer of n-type material is 2 μm or greater. The invention also relates to a solid-state p-n heterojunction such as in a solar cell comprising an organic p-type material in contact with a porous layer of n-type material, characterised in that the pore-filling-fraction of the porous layer of n-type material by the organic p-type material is no more than 50%. The invention further comprises devices such as solar cells or photodetector devices formed from such heterojunctions, methods of forming the same and the use of a polymeric p-type material in such a device or method.



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Solid State Heterojunction Device

The present invention relates to a solid-state p-n heterojunction and to its use in optoelectronic devices, in particular in solid-state solar cells (SSCs) and corresponding light sensing devices. Most particularly, the present invention relates to optoelectronic devices having a polymeric hole transporting material and methods by which this material can be introduced.

The junction of an n-type semiconductor material (known as an electron transporter) with a p-type semiconductor material (known as a hole-transporter) is perhaps the most fundamental structure in modern electronics. This so-called "p-n heterojunction" forms the basis of most modern diodes, transistors and related devices including opto-electronic devices such as light emitting diodes (LEDs), photovoltaic cells, and electronic photo-sensors.

A realization of the pressing need to secure sustainable future energy supplies has led to a recent explosion of interest in photovoltaics (PV). Conventional semiconductor based solar cells are reasonably efficient at converting solar to electrical energy. However, it is generally accepted that further major cost reductions are necessary to enable widespread uptake of solar electricity generation, especially on a larger scale. Solid-state solar cells such as dye-sensitized solar cells (DSCs) and Polymer Oxide Solar Cells (POSCs) offer a promising solution to the need for low-cost, large-area photovoltaics.

Typically, currently known DSCs are composed of mesoporous TiO_2 (electron transporter) sensitized with a light-absorbing molecular dye, which in turn is contacted by a redox-active hole-transporting medium (electrolyte). Photo-excitation of the sensitizer leads to the transfer (injection) of electrons from the excited dye into the conduction band of the TiO_2 . These photo-generated electrons are subsequently transported to and collected at the anode. The oxidized dye is regenerated via hole-transfer to the redox active medium with the holes being transported through this medium to the cathode.

The most efficient DSCs are composed of TiO_2 in combination with a redox active liquid electrolyte, or a "gel" type semi-solid electrolyte. Those incorporating an

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iodide/triiodide redox couple in a volatile solvent can convert over 12% of the solar energy into electrical energy. However, this efficiency is far from optimum. Even the most effective sensitizer/electrolyte combination which uses a ruthenium complex with an iodide/triiodide redox couple sacrifices approx. 600 mV in order to drive the dye regeneration/iodide oxidation reaction. Furthermore, such systems are optimised to operate with sensitizers which predominantly absorb in the visible region of the spectrum thereby losing out on significant photocurrent and energy conversion. Even in the most efficiently optimised liquid electrolyte-based DSCs, photons which are not absorbed between 600 and 800 nm amount to an equivalent of 7 mA/cm⁻² loss in photocurrent under full sun conditions. Other problems with the use of liquid electrolytes are that these are corrosive and often prone to leakage, factors which become particularly problematical for larger-scale installations or over longer time periods.

More recent work has focused on creating gel or solid-state electrolytes, or entirely replacing the electrolyte with a solid-state molecular hole-transporter, which transports the charge by movement of electrons rather than electrolytes, which rely on movement of ions. Solid phase organic hole-transporters are much more appealing for large scale processing and durability due to their lack of corrosive properties and saving in potential by avoiding the need to drive the redox couple. However, there are a number of obstacles that need to be overcome if organic hole transporting materials can be used efficiently.

Polymeric organic hole transporters offer the potential of high efficiency charge transfer but are considered to be of limited application because it is difficult to cause the polymer to penetrate and fill the porous network of the n-type material (such as mesoporous metal oxide). As a result various workarounds have been proposed, such as the use of monomers that can be polymerised within the device after incorporation and the use of a molecular hole-transporters which dissolve to provide low viscosity solutions and can be incorporated readily into the device.

Since the amount of energy available in a solar cell is fundamentally limited by the amount of solar energy absorbed, the inability to form thick devices means that dyes which absorb very strongly must be used in order harvest that energy over a short path-length. In certain applications, however, it would be advantageous to

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use a broader range of dyes even where the absorption was less strong, or to use several dyes with overlapping absorption bands where not all of these absorb very strongly. Furthermore, a ideal polymer-oxide solar cell might utilise the absorption of the polymer itself to perform at least part of the light-harvesting function. Several
5 of these applications require a greater path-length than could be provided by currently known polymer-oxide devices.

A measure of the degree to which a p-type material such as a hole-transporting polymer fills the voids within the n-type material is the "pore filling fraction" (PFF).

10 This relates the total volume of the pores to that volume occupied by the p-type material. It is widely believed and reported in the literature that polymeric hole transporters cannot achieve a sufficient filling of the pores of an n-type material. Consequently, various methods have been proposed to overcome this limitation. Methods for overcoming a low PFF with polymeric p-type materials include the use
15 of in-situ polymerisation (e.g. Liu *et al.* Adv. Mater. 22 E1-E6 (2010)) or use of non-polymerised alternatives such as molecular hole transporters (Snaith H. J., Humphry-Baker R., Chen P., Cesar I., Zakeeruddin S. M., Gratzel M., Nanotechnology 2008, 19.). Evidently, polymerisation *in situ* requires additional processing steps at the manufacturing stage and it is yet to be determined whether
20 materials which are activated to polymerise under irradiation can withstand full sun conditions for a potential lifetime of many years. Similarly, although molecular hole transporting material has a great deal of promise, an optimised polymeric p-type material should be capable of faster hole transport with lower resistance.

25 In view of the above, the use of polymeric p-type materials in solid-state heterojunctions, such as solar cells, has generally been restricted to very thin devices with research effort directed towards providing higher pore filling factors or use of alternatives such as *in-situ* polymerisation. It would be a considerable advantage, however, if solid-state heterojunction devices, such as solid-state solar
30 cells, could be made with a polymeric p-type material without being restricted to very thin devices (such as devices below 2 μm in thickness) and without requiring specialist techniques such as in-situ polymerisation.

The present inventors have taken the unusual step of questioning the long-held
35 view in the art that polymeric p-type materials require specialised techniques and

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have attempted to make solid-state devices using a simple solution of polymer. Unexpectedly, they have now established that by doing this, heterojunction devices, such as solar cells can be constructed which function with good efficiency even when much thicker than expected (e.g. when 2 μm or greater). Furthermore, the present inventors have now established that contrary to the previously held belief, a high pore filling fraction (PFF) is not necessary in order to achieve good performance in a solid-state heterojunction device, such as solid state solar cell.

In a first aspect, the present invention therefore provides a solid-state p-n heterojunction (e.g. in a solar cell) comprising an organic p-type material in contact with a porous layer of n-type material, characterised in that the thickness of the porous layer of n-type material is 2 μm or greater.

In a second aspect, the present invention also provides a solid-state p-n heterojunction (e.g. in a solar cell) comprising an organic p-type material in contact with a porous layer of n-type material, characterised in that the pore-filling-fraction of the porous layer of n-type material by the organic p-type material is no more than 50%. In such a heterojunction, it is preferable that the p-type material should form an electrically continuous layer over the internal surface of the pores of the n-type material. This will preferably be the case even when the overall PFF is no more than 50%.

All references to a heterojunction herein may be taken to refer equally to an optoelectronic device, including referring to a solar cell or to a photo-detector where context allows. Similarly, while solid-state polymer-oxide solar cells are frequently used herein as illustration, it will be appreciated that such heterojunctions may equally be applied to other corresponding optoelectronic devices including all those described in all sections herein.

Generally in all heterojunctions and devices as well as all other aspects of the invention indicated herein, the organic p-type material will preferably be an organic polymer, more preferably a conducting polymer or a semi-conducting polymer. The categories of polymer and individual polymers indicated herein are particularly suitable.

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A particularly suitable application of the heterojunctions of the present invention (as well as applying to all other aspects of the invention) is in optoelectronic devices. In a further aspect, the present invention therefore provides an optoelectronic device comprising at least one solid state p-n heterojunction as indicated in any
5 embodiment of the present invention and/or formable by any indicated method. Most appropriate optoelectronic devices include all those indicated herein, such as photo-detectors, solid-state polymer-oxide solar cells, solid state dye sensitised solar cells and/or solid state polymer sensitised solar cells.

10 As noted above, solutions of polymers have previously not been considered appropriate for the formation of heterojunctions (e.g. in solar cells) of $2\mu\text{m}$ or greater in thickness because the relatively low pore filling fraction was considered to render such devices useless. However, by establishing that such devices can be highly effective, the present invention provides, in a further aspect, the use of a
15 solution of polymeric organic p-type material in the formation of a solid-state p-n heterojunction wherein said p-n heterojunction comprises a porous layer of n-type material having a thickness of $2\mu\text{m}$ or greater.

Furthermore, in a still further embodiment, the present invention provides the use of
20 a solution of polymeric organic p-type material in the formation of a solid-state p-n heterojunction wherein said p-n heterojunction comprises a porous layer of n-type material and wherein said polymerised organic p-type material fills the pores of said n-type material with a pore filling fraction of 50% or less.

25 The present inventors have furthermore established that by use of an appropriate method a heterojunction (e.g. in a solar cell) may be formed having at least one of the advantageous properties indicated herein. In a still further aspect, the present invention therefore provides a method for the manufacture of a solid-state p-n heterojunction (such as in a solar cell) comprising an organic p-type material in
30 contact with a porous layer of n-type material, said method characterised by;

a) coating an anode, preferably a transparent anode (e.g. a Fluorine doped Tin Oxide - FTO cathode) with a compact layer of an n-type semiconductor material (such as any of those described herein);

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- b) forming a porous (preferably mesoporous) layer of an n-type semiconductor material (such as any of those described herein) on said compact layer,
- c) optionally surface sensitizing said compact layer and/or said porous layer of n-type material with at least one sensitizing agent;
- 5 d) optionally treating said compact layer and/or said porous layer of n-type material with at least one ionic material such as a lithium salt.
- e) optionally forming a porous barrier layer of an insulating material on said porous layer of n-type material;
- f) contacting said porous layer of n-type material with at least one solution of
- 10 at least one polymeric organic p-type semiconductor material whereby to form a layer of polymeric organic p-type semiconductor in contact with said porous layer of an n-type material;
- g) forming a cathode, preferably a metal cathode (e.g. a silver or gold cathode) on said porous barrier layer, in contact with said p-type semiconductor material.

15

Without being bound by theory, it is believed that the use of an ionic material, such as a lithium salt at step d) enhances the generation of an electrically continuous layer of p-type material over the pore-surface within the n-type material. It is therefore preferable that step d) is included. It is more preferable that the ionic

20 material in step d) be a lithium salt and still more preferable that this be Li-TFSI or an analogue or derivative thereof (including any indicated in any section of this application). Devices formed or formable from any of the heterojunctions of the invention or by any of the methods, uses or process of the invention evidently also form additional aspects of the invention in themselves.

25

In a particularly preferred embodiment optional step d) comprises treating said compact layer and/or said porous layer of n-type material with a mixture of at least two ionic materials. Suitable ionic materials preferably include metal salts (especially lithium salts such as lithium bis(trifluoromethylsulfonyl)imide lithium salt)

30 in combination with ionic liquids (such as, 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide).

In all aspects and embodiments of the present invention, the term "ionic liquid" is used to indicate an ionic species with a melting point sufficiently low for convenient

35 processing in the formation of the heterojunctions and devices of the invention.

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Many suitable low melting-point salts are known and in one embodiment, salts having a melting point of 100°C or lower are preferable. Salts having a melting point of below 50°C or even below room temperature may be preferably used.

Some suitable ionic liquids, including 1-Ethyl-3-methylimidazolium

- 5 bis(trifluoromethylsulfonyl)imide have a melting point below 0°C. Highly preferable ionic liquids include those selected from 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Allyl-3-methylimidazolium
- 10 bis(trifluoromethylsulfonyl)imide, 1,3-Dihydroxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dimethoxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide and mixtures thereof.

Detailed Description

15

The functioning of a polymer oxide solar cell relies initially on the collection of solar light energy in the form of capture of solar photons by the polymer and/or by an additional sensitizer (typically a molecular, metal complex, or polymer dye). The effect of the light absorption is to raise an electron into a higher energy level in the

20 polymer and/or sensitizer. This excited electron will eventually decay back to its ground state, but in a solar cell, the n-type material in close proximity to the excited material provides an alternative (faster) route for the electron to leave its excited state, viz. by "injection" into the n-type semiconductor material. This injection can be direct or via an intermediate material but in all cases results in a charge

25 separation, whereby the n-type semiconductor has gained a net negative charge and the polymer has gained a net positive charge. Where a sensitizer or injecting material is present this may initially take the positive charge but it will rapidly be passed to the polymer charge carrier. This serves to "regenerate" the dye or portion of the polymer close to the heterojunction by passing the positive charge

30 ("hole") on through the p-type semiconductor material of the junction (the "hole transporter"). In a solid state polymer oxide device, this hole transporter is in direct contact with the n-type material and/or sensitizer material, while in the more common electrolytic dye sensitised photocells, a redox couple (typically iodide/triiodide) serves to regenerate a dye and transports the "hole species"

35 (triiodide) to the counter electrode. Once the electron is passed into the n-type

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material, it must then be transported away, with its charge contributing to the current generated by the solar cell.

While the above is a simplified summary of the ideal working of a polymer oxide solar cell, there are certain processes which occur in any practical device in competition with these desired steps and which serve to decrease the conversion of sunlight into useful electrical energy. Decay of the sensitizer back to its ground state was indicated above, but in addition to this, there is the natural tendency of two separated charges of opposite sign to re-combine. This can occur by return of the electron into a lower energy level of the sensitizer, or by recombination of the electron directly from the n-type material to quench the hole in the p-type material. In an electrolytic DSC, there is additionally the opportunity for the separated electron to leave the surface of the n-type material and directly reduce the iodide/iodine redox couple. Evidently, each of these competing pathways results in the loss of potentially useful current and thus a reduction in cell energy-conversion efficiency. It is therefore essential that each of the desired steps occurs at a rate which is considerably faster than the competing undesirable processes to avoid wasting potentially useful energy. It is also important that there is not too much of a disparity in the speeds of the various steps since a fast step followed by a slow step can lead to a build-up of a short-lived intermediate material which may then follow an energy-wasteful path. Thus it is particularly critical that the polymer hole-transporter is capable of effectively carrying charge away from the site of generation.

A schematic diagram indicating a typical structure of the solid-state DSC is given in attached Figure 1a and a diagram indicating some of the key steps in electrical power generation from a polymer oxide solar cell is given in attached Figure 1b .

Polymer-oxide solar cells, composed of mesoporous metal oxide electrodes infiltrated with (optionally light absorbing) semiconducting polymers and optionally also dye materials, have the potential to deliver high power conversion efficiencies while being compatible with low cost large area chemical processing. However, until recently solar-to-electrical power conversion efficiencies have remained below 1%. For efficient solar cell operation, a suitable fraction of sun light needs to be absorbed in the photoactive layer, excitons formed in the dye and/or polymer need

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to be ionised at the polymer-oxide heterojunction, and the photo-generated charges need to be separated and carried out of the solar cell to their respective electrodes. The latter requires effective percolation for both charge carriers, electrons and holes, in the oxide and polymer phases respectively. The two main issues thought to be responsible for the relatively poor operation of polymer-oxide solar cells have been an inability to effectively infiltrate semiconducting polymers into random porous networks and ineffective charge transport within the polymer phase due to non-crystalline, un-orientated polymer chains.

The present inventors have, however, questioned whether pore infiltration and charge transport do in fact fundamentally limit polymer-oxide solar cells, or if these issues can be resolved and the path to further improvement lies elsewhere. The Examples below detail a structural and electronic characterisation of certain polymer/oxide solar cells incorporating a suitable dye. Study of the pore infiltration of the mesostructured oxide by XPS depth profiling has revealed that in fact uniform pore filling of the polymer within the mesostructured oxide can be achieved to depths of over 4 μm . Though the pore filling is uniform, it is not complete and the pore filling fraction is below 50%. We estimate that the pore filling fraction is in a range between 1 and 45%, particularly between 5 and 35%, most preferably between 6 to 30% depending upon the polymer and processing conditions.

Despite having a low pore filling fraction, the present inventors have provided cells in which the polymer appears to form a "wetting film" over the entire internal surface of the dye-sensitized mesoporous electrode. Most surprisingly, and in defiance of the currently understood practice, this wetting layer, of only a few nm thick, is sufficiently capable of transporting the holes out of the device to make efficient solar cells. Charge collection efficiencies by the polymer film at the pore surface can be up to 98%, as estimated from transient electronic measurements. Beyond this, the inventors have found evidence to suggest that even in the thickest devices of over 7 μm thick, the charge collection is limited by electron transport through the mesoporous n-type material, even though the polymer "shell" may only have an average thickness of around 0.2 to 10 nm (e.g. around 1 nm).

The present invention may be applied to devices wherein the porous layer of n-type material is any thickness (e.g. 0.1 to 50 μm) but it is a particularly unexpected

development that heterojunctions having a layer of porous n-type material (as described herein) of significant thickness can be formed into an efficient solar cell with a polymeric p-type material, using the techniques described herein. Thus, the thickness of the porous layer of n-type material in all aspects of the invention may be 0.1 to 50 μm , but is typically greater than 1 μm , preferably 2 μm or greater (e.g. 2 to 20 μm) and more preferably 2.5 μm or greater (e.g. 2.5 to 10 μm). Devices of at least 7 μm have been shown to have efficient hole-conduction through the polymer material in the present invention. Thus the present invention is not limited to thin devices (e.g. 1 μm or less) as has previously been thought for polymer oxide solar cells absent special techniques such as *in situ* polymerisation.

It has previously been believed that in order to provide a high level of efficiency in a polymer oxide solar cell or dye-sensitized solar cell, a high degree of pore filling is required. This has driven workers in the field to develop complex techniques such as *in situ* polymerisation or to use less efficient charge transfer materials such as molecular hole transporters in order to boost this pore-filling factor. As described above, a further contribution provided by the work of the present inventors is to establish that providing a substantially continuous layer of polymer is present as a "film" on the pore surface, the filling of the bulk volume of the pore is not in fact essential to the effective functioning of a heterojunction device, such as a polymer oxide solar cell.

The present invention may therefore be applied to devices having any degree of pore filling fraction (PFF) (e.g. 0.1% to substantially 100%, such as 1% to 99.9%). However, in one embodiment of the present invention, which may be applied across all aspects of the invention as described herein, heterojunctions and corresponding devices (e.g. polymer oxide solar cells) are provided having a pore filling fraction of significantly less than 100%. This may be, for example, no more than 75% (e.g. 1 to 75%), or no more than 50% (e.g. 2 to 50%). A pore filling fraction of less than 50% (e.g. 0.1 to 49% or 1 to 40%) is particularly likely in prior work to be considered insufficient for effective function and it is thus a particularly important contribution of the present invention that the heterojunctions and devices are both effective and can have a PFF in this range and below (e.g. 0.5 to 30% or 1 to 20%).

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The present inventors have now established that in fact the pore filling fraction of a heterojunction or device is not an effective measure of the amount of *functional* p-type material present in the pores of the n-type oxide layer. In particular, a high PFF with a low degree of contact with the pore surface will be relatively ineffective
5 whereas even a low PFF can provide for an efficient device if the contact with the pore surface is high and the conductivity is good enough to transport the holes effectively away from the point of charge-separation and regenerate the oxidised sensitizer or polymer.

10 Charge collection efficiency (CCE) is a standard and established method for determining whether charge is effectively transported away from its site of generation and is typically measured with well-known methods of transient electronic measurement. In the present case, it is preferable that the CCE is no less than 50% in all cases, even where a "low" PFF such as those described in
15 certain embodiments of the invention are employed. It has not previously been appreciated that a CCE of up to 98% can be achieved in a polymer oxide solar cell even when the PFF is comparatively low. Thus, in one embodiment, the CCE of the heterojunctions or devices of the present invention, or in any aspect, may be at least 50% (e.g. 50 to 99%), preferably at least 60% (e.g. 60 to 98%) and more
20 preferably at least 70% (e.g. 70 to 98%).

The p-n heterojunctions of the invention, as well as those used with or generated by alternative aspects of the invention are light sensitive and as such include at least one light sensitizing agent (sensitizer). Referred to herein as the sensitizer or sensitizing agent, this material may be the (or one of the) polymer p-type material(s) itself, and/or may be one or more dyes, salts, films, particles, or any material which generates an electronic excitation as a result of photon absorption and which is capable of direct or indirect injection of the excited electron into the n-type material.

In one preferred aspect of the present invention, at least a part of the light absorbing capacity of the heterojunction or device is provided by the polymeric p-type material (or where that material is a mixture, by at least one component thereof). Polymeric p-type materials can be highly effective in absorbing certain frequencies in the electromagnetic spectrum useful for photovoltage generation and/or photo-detection. Thus, where possible, it is desirable to take advantage of

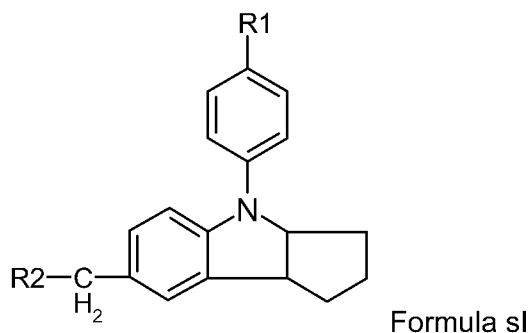
this property. Thus, as used herein, the term "sensitizer" may indicate, where context allows, a property of the polymeric p-type material (or at least one component thereof).

Alternatively or in addition to the above, one or more further sensitizers may be used in the devices of the present invention. These may be chosen, for example, in order to enhance the absorption of light at wavelengths not effectively absorbed by the p-type material of the polymer(s) and/or to act as one or more intermediaries serving to aid in transferring the excitation energy from the polymer and complete the charge separation and "injection". Where a "cascade" of sensitizers of this type is used then it is desirable that there be at least some overlap between the emission spectrum of a first dye and the absorption spectrum of a second so that a "resonance energy transfer" type effect may occur.

The most commonly used light sensitising materials in electrolytic DSCs are organic or metal-complexed dyes. These have been widely reported in the art and the skilled worker will be aware of many existing sensitizers, all of which are suitable in all appropriate aspects of the invention and consequently are reviewed here only briefly.

A common category of organic dye sensitizers are indolene based dyes, of which D102, D131 and D149 (shown below) are particular examples.

- 5 The general structure of indolene dyes is that of Formula sI below:



- 10 wherein R1 and R2 are independently optionally substituted alkyl, alkenyl, alkoxy, heterocyclic and/or aromatic groups, preferably with molecular weight less than

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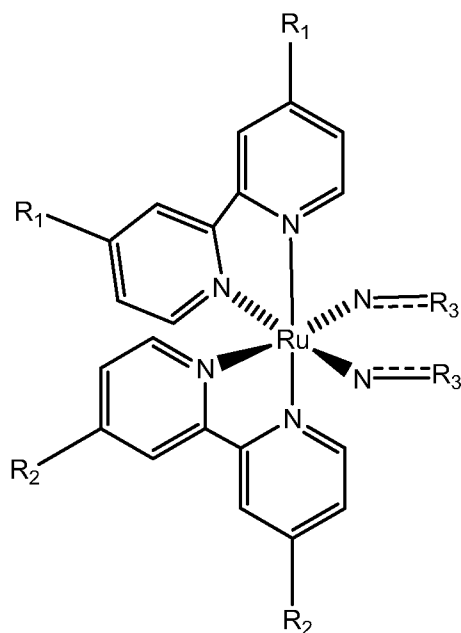
around 360 amu. Most preferably, R1 will comprise aralkyl, alkoxy, alkoxy aryl and/or aralkenyl groups (especially groups of formula $C_xH_yO_z$ where x, y and z are each 0 or a positive integer, $x+z$ is between 1 and 16 and y is between 1 and $2x+1$) including any of those indicated below for R1, and R2 will comprise optionally substituted carbocyclic, heterocyclic (especially S and/or N-containing heterocyclic) cycloalkyl, cycloalkenyl and/or aromatic groups, particularly those including a carboxylic acid group. All of the groups indicated below for R2 are highly suitable examples. One preferred embodiment of R2 adheres to the formula $C_xH_yO_zN_vS_w$ where x, y, z, v and w are each 0 or a positive integer, $x+z+w+v$ is between 1 and 22 and y is between 1 and $2x+v+1$. Most preferably, $z \geq 2$ and in particular, it is preferable that R2 comprises a carboxylic acid group. These R1 and R2 groups and especially those indicated below may be used in any combination, but highly preferred combinations include those indicated below:

15

Dye Name	R1	R ₂
D ₁₄₉	$Ph_2C=CH$	
D ₁₀₂	$Ph_2C=CH$	
D ₇₇	OMe	
D ₁₀₃		
D ₁₃₁	$Ph_2C=CH$	
D ₁₂₀	OMe	

Indolene dyes are discussed, for example, in Horiuchi et al. J Am. Chem. Soc. **126** 12218-12219 (2004), which is hereby incorporated by reference.

5 A further common category of sensitizers are ruthenium metal complexes, particularly those having two bipyridyl coordinating moieties. These are typically of formula sII below



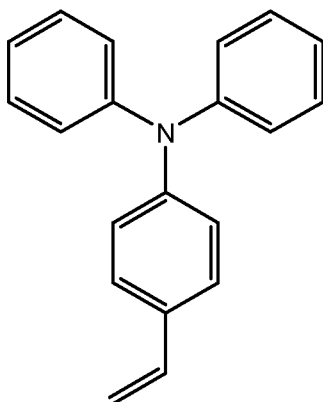
Formula sII

10 wherein each R1 group is independently a straight or branched chain alkyl or oligo alkoxy chain such as C_nH_{2n+1} where n is 1 to 20, preferably 5 to 15, most preferably 9, 10 or 11, or such as $C(-XC_nH_{2n-})_m-XC_pH_{2p+1}$, where n is 1, 2, 3 or 4, preferably 2, m is 0 to 10, preferably 2, 3 or 4, p is an integer from 1 to 15, preferably 1 to 10, most preferably 1 or 7, and each X is independently O, S or NH, preferably O; and
 15 wherein each R2 group is independently a carboxylic acid or alkyl carboxylic acid, or the salt of any such acid (e.g. the sodium, potassium salt etc) such as a $C_nH_{2n}COOY$ group, where n is 0, 1, 2 or 3, preferably 0 and Y is H or a suitable metal such as Na, K, or Li, preferably Na; and wherein each R3 group is single or double bonded to the attached N (preferably double bonded) and is of formula CH_a-Z or $C=Z$, where a is 0, 1 or 2 as appropriate, Z is a hetero atom or group such as S, O, SH or OH, or is an alkyl group (e.g. methylene, ethylene etc) bonded to any
 20 such a hetero atom or group as appropriate; R3 is preferably $=C=S$.

- 15 -

A preferred ruthenium sensitizer is of the above formula sII, wherein each R1 is nonyl, each R2 is a carboxylic acid or sodium salt thereof and each R3 is double-bonded to the attached N and of formula =C=S. R1 moieties of formula sII may also be of formula sIII below:

5



Formula sIII

10

Ruthenium dyes are discussed in many published documents including, for example, Kuang et al. Nano Letters **6** 769-773 (2006), Snaith et al. Angew. Chem. Int. Ed. **44** 6413-6417 (2005), Wang et al. Nature Materials **2**, 402-498 (2003), Kuang et al. Inorganica Chemica Acta **361** 699-706 (2008), and Snaith et al. J Phys, Chem. Lett. **112** 7562-7566 (2008), the disclosures of which are hereby incorporated herein by reference, as are the disclosures of all material cited herein.

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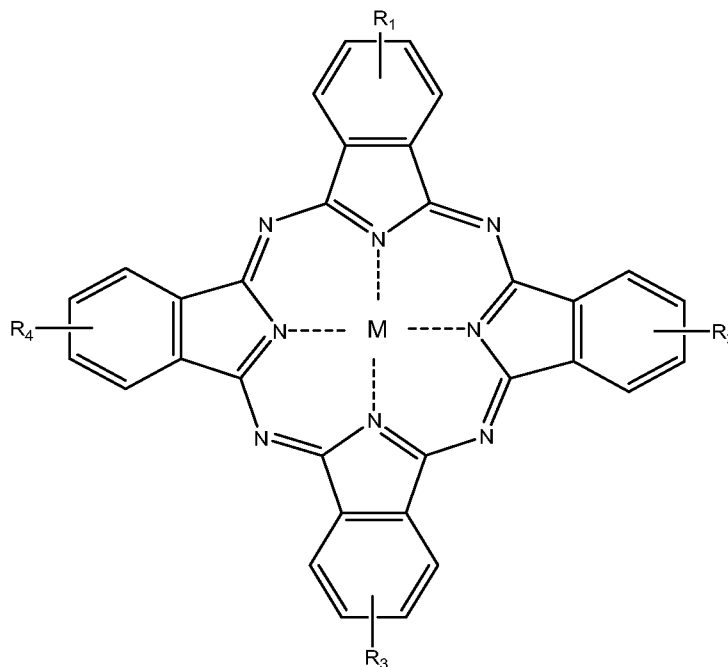
Other sensitizers which will be known to those of skill in the art include Metal-Phthalocyanine complexes such as zinc phthalocyanine PCH001, the synthesis and structure of which is described by Reddy *et al.* (Angew. Chem. Int. Ed. **46** 373-376 (2007)), the complete disclosure of which (particularly with reference to Scheme 1), is hereby incorporated by reference.

20

Some typical examples of metal phthalocyanine dyes suitable for use in the present invention include those having a structure as shown in formula sIV below:

25

- 16 -

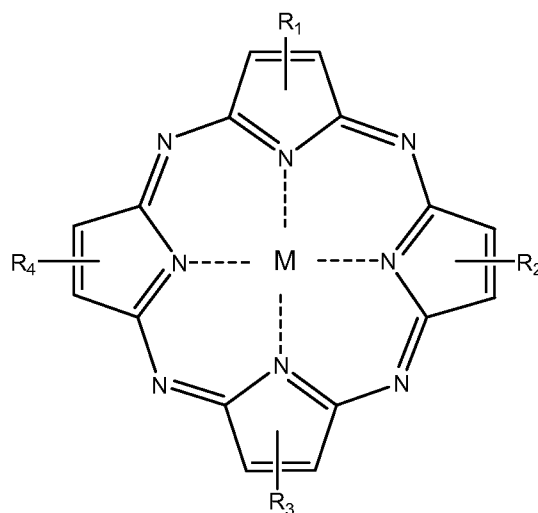


Formula sIV

Wherein M is a metal ion, such as a transition metal ion, and may be an ion of Co, Fe, Ru, Zn or a mixture thereof. Zinc ions are preferred. Each of R1 to R4, which
 5 may be the same or different is preferably straight or branched chain alkyl, alkoxy, carboxylic acid or ester groups such as C_nH_{2n+1} where n is 1 to 15, preferably 2 to 10, most preferably 3, 4 or 5, with butyl, such as tertiary butyl, groups being particularly preferred, or such as OX or CO_2X wherein X is H or a straight or
 10 branched chain alkyl group of those just described. In one preferred option, each of R1 to R3 is an alkyl group as described and R4 is a carboxylic acid CO_2H or ester CO_2X , where X is for example methyl, ethyl, iso- or n-propyl or tert-, iso-, sec- or n-butyl. For example, dye TT1 takes the structure of formula sIV, wherein R1 to R3 are t-butyl and R4 is CO_2H .

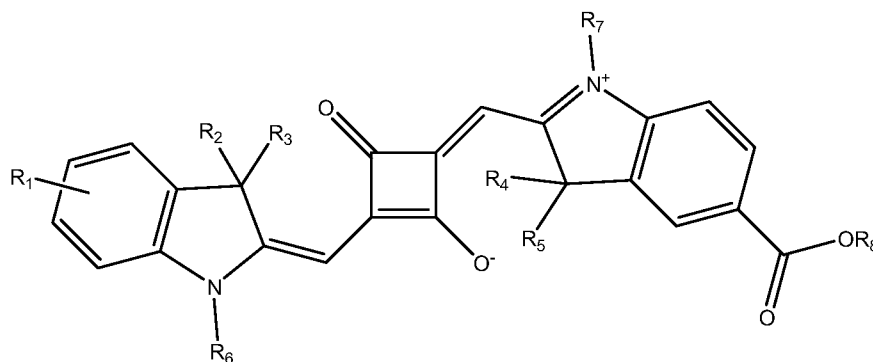
15 Further examples of suitable categories of dyes include Metal-Porphyrin complexes, Squaraine dyes, Thiophene based dyes, fluorine based dyes, molecular dyes and polymer dyes. Examples of Squaraine dyes may be found, for example in Burke et al., *Chem. Commun.* **2007**, 234, and examples of polyfluorene and polythiophene polymers in McNeill et al., *Appl. Phys. Lett.* **2007**, 90, both of which
 20 are incorporated herein by reference. Metal porphyrin complexes include, for example, those of formula sV and related structures, where each of M and R1 to R4 can be any appropriate group, such as those specified above for the related phthalocyanine dyes:

- 17 -



Formula sV

- 5 Squaraine dyes form a preferred category of dye for use in the present invention. The above Burke citation provides information on Squaraine dyes, but briefly, these may be, for example, of the following formula sVI



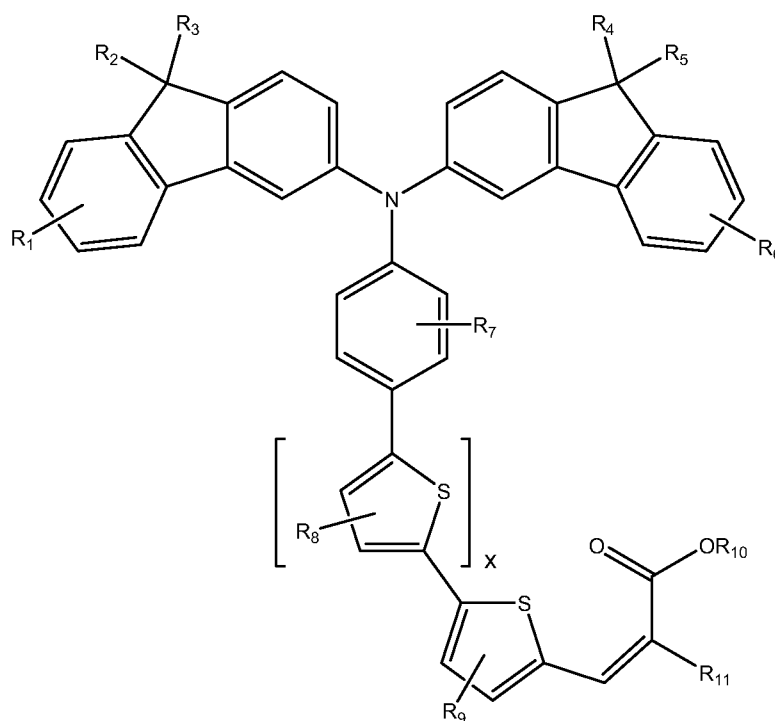
Formula sVI

10

- Wherein any of R1 to R8 may independently be a straight or branched chain alkyl group or any of R1 to R5 may independently be a straight or branched chain alkyloxy group such as C_nH_{2n+1} or $C_nH_{2n+1}O$ respectively where n is 1 to 20, preferably 1 to 12, more preferably 1 to 9. Preferably each R1 to R5 will be H, C_nH_{2n+1} or $C_nH_{2n+1}O$ wherein n is 1 to 8 preferably 1 to 3 more preferably 1 or two. Most preferably R1 is H and each R5 is methyl. Preferably each R6 to R8 group is H or C_nH_{2n+1} wherein n is 1 to 20, such as 1 to 12. For R6, n with preferably be 1 to 5 more preferably 1 to 3 and most preferably ethyl. For R7 n will preferably be 4 to 12, more preferably 6 to 10, most preferably 8, and for R8, preferred groups are H, methyl or ethyl. preferably H. One preferred squaraine dye referred to herein is
- 15
- 20

SQ02, which is of formula sVI wherein R1 and R8 are H, each of R2 to R5 is methyl, R6 is ethyl, and R7 is octyl (e.g. n-octyl).

- 5 A further example category of valuable sensitizers are polythiophene (e.g. dithiophene)-based dyes, which may take the structure indicated below as formula sVII



Formula sVII

- 10 Wherein x is an integer between 0 and 10, preferably 1, 2, 3, 4 or 5, more preferably 1, and wherein any of R1 to R10 may independently be hydrogen, a straight or branched chain alkyl group or any of R1 to R9 may independently be a straight or branched chain alkyloxy group such as C_nH_{2n+1} or $C_nH_{2n+1}O$ respectively where n is 1 to 20, preferably 1 to 12, more preferably 1 to 5. It is preferred that
- 15 each if R1 to R10 will independently be a hydrogen or C_nH_{2n+1} group where n is 1 to 5, preferably methyl, ethyl, n- or iso-propyl or n-, iso-, sec- or t-butyl. Most preferably, each of R2 to R4 will be methyl or ethyl and each of R1 and R6 to R10 will be hydrogen. The group R11 may be any small organic group (e.g. molecular weight less than 100) but will preferably be unsaturated and may be conjugated to
- 20 the extended pi-system of the dithiophene groups. Preferred R11 groups include alkenyl or alkynyl groups (such as C_nH_{2n-1} and C_nH_{2n-3} groups respectively, e.g. where n is 2 to 10, preferably 2 to 7), cyclic, including aromatic groups, such as substituted

or unsubstituted phenyl, piridyl, pyrimidyly, pyrrolyl or imidazyl groups, and unsaturated hetero-groups such as oxo, nitrile and cyano groups. A most preferred R11 group is cyano. One preferred dithiophene based dye is 2-cyanoacrylic acid-4-(bis-dimethylfluorene aniline)dithiophene, known as JK2.

5

No dye sensitizer is necessary for the functioning of the present invention since light may be absorbed either by the polymeric p-type material and/or by sensitizers of other types, such as inorganic films or nanoparticles. Where present, in one embodiment, only a single dye sensitizer will be employed in the p-n

10 heterojunctions herein described (and thus all compatible aspects of the invention), and this may serve to absorb over a broad range of wavelengths and/or may act to increase absorption in regions of the spectrum where the absorption of the polymer material is relatively low. In an alternative embodiment, two or more dye sensitizers may nevertheless be used. For example, all aspects of the present invention are

15 suitable for use with co-sensitisation using a plurality of (e.g. at least 2, such as 2, 3, 4 or 5) different sensitizing agents, including dye sensitizing agents. If two or more dye sensitizers are used, these may be chosen such that their respective emission and absorption spectra overlap. In this case, resonance energy transfer (RET) results in a cascade of transfers by which an electron excitation steps down

20 from one dye to another of lower energy, from which it is then injected into the n-type material. Alternatively, it may be preferred that the emission and absorption spectra of the individual dyes do not overlap to any significant extent. This ensures that all dye sensitizers are effective in the injection of electrons into the n-type material. Where two or more dye sensitizers are used, these will preferably have

25 complimentary absorption characteristics. Some complimentary parings include, for example, the near-infra red absorbing zinc phalocianine dyes referred to above in combination with indoline or ruthenuim-based sensitizers to absorb the bulk of the visible radiation. As an alternative, a polymeric or molecular visible light absorbing material may be used in conjunction with a near IR absorbing dye, such as a visible

30 light absorbing polyfluorene polymer with a near IR absorbing zinc phlaocianine or squaraine dye.

Other types of sensitizers may also be used in the various aspects of the present invention and in each case may form all or the bulk of the light-absorbing material

35 or may be used in conjunction with absorption from the polymeric p-type material and/or in combination with other sensitizers of the same or different types.

Preferred sensitizing agents include at least one inorganic light absorbing thin film or semiconductor nanoparticle layer, where the film or layer is formed from materials selected from, for example, PbS, PbSe, SnS, SnSe SbS, SbSe, CdSe, Ge, Si.

5 Although many of the dyes indicated above show broad spectrum absorption in the visible region, plasmonic nanoparticles allow injection of electrons which result from excitation of surface plasmon modes by lower energy solar photons including those of near infra-red frequencies. These are therefore advantageously combined with suitable dye sensitizers.

10

As referred to in the context of this patent, a p-type polymer is a material which exhibits good hole-transport characteristics and functions as a hole-transporter in the operating heterojunction (especially solar cell). Its function is to 1. Transfer an electron from the highest occupied molecular orbital (HOMO) level of the p-type
15 polymer to the HOMO level of the photo-oxidized dye or other sensitizer (where present - also known as dye regeneration). 2. Transfer an electron from photoexcitations directly on the p-type polymer to the n-type oxide resulting in generated charge. 3. Transport the holes remaining on the polymer to the cathode and into the external circuit.

In all aspects of the present invention, a polymerised material is used as the p-type material of the heterojunction or device. There are a number of polymeric p-type materials which have been used previously in reported polymer oxide solar cells and any of these may be used. Preferably, the polymeric p-type material is an organic polymer selected from poly thiophenes, poly p-phenylene vinylenes and mixtures, copolymers and derivatives thereof. A particularly effective example is poly(3-hexylthiophene) (P3HT).

20

In all aspects, the n-type semiconductor material for use in the solid state heterojunctions (e.g. DSCs) relating to the present invention may be any of those which are well known in the art. Oxides of Ti, Al, Sn, Mg and mixtures thereof are among those suitable. TiO₂ and Al₂O₃ are common examples, as are MgO and SnO₂. The n-type material is used in the form of a layer and will typically be
25 mesoporous providing a relatively thick layer of around 0.05 - 100 µm over which the second sensitizing agent may be absorbed at the surface.

In one optional but preferred embodiment, a thin surface coating of a high band-gap / high band gap edge (insulating) material, may be deposited on the surface of a lower band gap n-type semiconductor such as SnO_2 . This can greatly reduce the fast recombination from the n-type electrode, which is a much more severe issue in solid state DSCs than in the more widely investigated electrolyte utilising cells. Such a surface coating may be applied before the oxide particles (e.g. SnO_2) are sintered into a film or after sintering.

The n-type material of the solid state heterojunctions relating to all aspects of the present invention is generally a metal compound such as a metal oxide, compound metal oxide, doped metal oxide, selenide, telluride, and/or multicomponent semiconductor, any of which may be coated as described above. Suitable materials include single metal oxides such as Al_2O_3 , ZrO , ZnO , TiO_2 , SnO_2 , Ta_2O_5 , Nb_2O_5 , WO_3 , W_2O_5 , In_2O_3 , Ga_2O_3 , Nd_2O_3 , Sm_2O_3 , La_2O_3 , Sc_2O_3 , Y_2O_3 , NiO , MoO_3 , PbO , CdO and/or MnO ; compound metal oxides such as $\text{Zn}_x\text{Ti}_y\text{O}_z$, ZrTiO_4 , ZrW_2O_8 , $\text{SiAlO}_{3.5}$, $\text{Si}_2\text{AlO}_{5.5}$, SiTiO_4 and/or AlTiO_5 ; doped metal oxides such as any of the single or compound metal oxides indicated above doped with at least one of Al, F, Ge, S, N, In, Mg, Si, C, Pb and/or Sb; carbides such as Cs_2C_5 ; sulphides such as PbS , CdS , CuS ; selenides such as PbSe , CdSe ; tellurides such as CdTe ; nitrides such as TiN ; and/or multicomponent semiconductors such as ClGaS_2 .

It is common practice in the art to generate p-n heterojunctions, especially for optical applications, from a mesoporous layer of the n-type material so that light can interact with the junction at a greater surface than could be provided by a flat junction. In the present case, this mesoporous layer may be conveniently generated by sintering of appropriate semiconductor particles using methods well known in the art and described, for example in Green et al. (J. Phys. Chem. B **109** 12525-12533 (2005)) and Kay et al. (Chem. Mater. **17** 2930-2835 (2002)), which are both hereby incorporated by reference. With respect to the surface coatings, where present, these may be applied before the particles are sintered into a film, after sintering, or two or more layers may be applied at different stages.

Typical particle diameters for the semiconductors will be dependent upon the application of the device, but might typically be in the range of 5 to 1000nm, preferably 10 to 100 nm, more preferably still 10 to 30 nm, such as around 20 nm.

Surface areas of $1\text{-}1000\text{ m}^2\text{g}^{-1}$ are preferable in the finished film, more preferably $30\text{-}200\text{ m}^2\text{g}^{-1}$, such as $40\text{ - }100\text{ m}^2\text{g}^{-1}$. The film will preferably be electrically continuous (or at least substantially so) in order to allow the injected charge to be conducted out of the device. The thickness of the film will be dependent upon

5 factors such as the photon-capture efficiency of the photo-sensitizer, but may be in the range $0.05\text{ - }100\text{ }\mu\text{m}$, preferably $0.5\text{ to }20\text{ }\mu\text{m}$, more preferably $0.5\text{ -}10\text{ }\mu\text{m}$, e.g. $1\text{ to }5\text{ }\mu\text{m}$. In one alternative embodiment, the film is planar or substantially planar rather than highly porous, and for example has a surface area of $1\text{ to }20\text{ m}^2\text{g}^{-1}$ preferably $1\text{ to }10\text{ m}^2\text{g}^{-1}$. Such a substantially planar film may also or alternatively

10 have a thickness of $0.005\text{ to }5\text{ }\mu\text{m}$, preferably $0.025\text{ to }0.2\text{ }\mu\text{m}$, and more preferably $0.05\text{ to }0.1\text{ }\mu\text{m}$.

Where the n-type material is surface coated, materials which are suitable as the coating material (the "surface coating material") may have a conduction band edge

15 closer to or further from the vacuum level (vacuum energy) than that of the principal n-type semiconductor material, depending upon how the property of the material is to be tuned. They may have a conduction band edge relative to vacuum level of at around -4.8 eV , or higher (less negative) for example $-4.8\text{ or }-4.7\text{ to }-1\text{ eV}$, such as $-4.7\text{ to }-2.5\text{ eV}$, or $-4.5\text{ to }-3\text{ eV}$

20 Suitable coating materials, where present, include single metal oxides such as MgO , Al_2O_3 , ZrO , ZnO , HfO_2 , TiO_2 , Ta_2O_5 , Nb_2O_5 , WO_3 , W_2O_5 , In_2O_3 , Ga_2O_3 , Nd_2O_3 , Sm_2O_3 , La_2O_3 , Sc_2O_3 , Y_2O_3 , NiO , MoO_3 , PbO , CdO and/or MnO ; compound metal oxides such as $\text{Zn}_x\text{Ti}_y\text{O}_z$, ZrTiO_4 , ZrW_2O_8 , $\text{SiAlO}_{3.5}$, $\text{Si}_2\text{AlO}_{5.5}$, SiTiO_4 and/or AlTiO_5 ;

25 doped metal oxides such as any of the single or compound metal oxides indicated above doped with at least one of Al , F , Ge , S , N , In , Mg , Si , C , Pb and/or Sb ; carbonates such as Cs_2C_5 ; sulphides such as PbS , CdS , CuS ; selenides such as PbSe , CdSe ; telurides such as CdTe ; nitrides such as TiN ; and/or multicomponent semiconductors such as ClGaS_2 . Some suitable materials are discussed in Grätzel

30 (Nature **414** 338-344 (2001)). The most preferred surface coating material is MgO .

Where present, the coating on the n-type material will typically be formed by the deposition of a thin coating of material on the surface of the n-type semiconductor film or the particles which are to generate such a film. In most cases, however, the

35 material will be fired or sintered prior to use, and this may result in the complete or partial integration of the surface coating material into the bulk semiconductor. Thus

although the surface coating may be a fully discrete layer at the surface of the semiconductor film, the coating may equally be a surface region in which the semiconductor is merged, integrated, or co-dispersed with the coating material.

5 Since any coating on the n-type material may not be a fully discrete layer of material, it is difficult to indicate the exact thickness of an appropriate layer. The appropriate thickness will in any case be evident to the skilled worker from routine testing, since a sufficiently thick layer will retard electron-hole recombination without undue loss of charge injection into the n-type material. Coatings from a monolayer
10 to a few nm in thickness are appropriate in most cases (e.g. 0.1 to 100 nm, preferably 1 to 5 nm).

The bulk or "core" of the n-type material in all embodiments of the present invention may be essentially pure semiconductor material, e.g. having only unavoidable
15 impurities, or may alternatively be doped in order to optimise the function of the p-n-heterojunction device, for example by increasing or reducing the conductivity of the n-type semiconductor material or by matching the conduction band in the n-type semiconductor material to the excited state of the chosen sensitizer.

Thus the n-type semiconductor and oxides such as TiO_2 , ZnO , SnO_2 and WO_3 referred to herein (where context allows) may be essentially pure semiconductor (e.g. having only unavoidable impurities). Alternatively they may be doped throughout with at least one dopant material of greater valency than the bulk (to provide n-type doping) and/or may be doped with at least one dopant material of lower valency than the bulk (to give p-type doping). n-type doping will tend to increase the n-type character of the semiconductor material while p-type doping will tend to reduce the degree of the natural n-type state (e.g. due to defects).

20 Such doping may be made with any suitable element including F, Sb, N, Ge, Si, C, In, InO and/or Al. Suitable dopants and doping levels will be evident to those of skill in the art. Doping levels may range from 0.01 to 49% such as 0.5 to 20%, preferably in the range of 5 to 15%. All percentages indicated herein are by weight
25 where context allows, unless indicated otherwise.

In addition to the n-type, p-type and optional sensitizer components, an optional by preferable ionic material such as a lithium salt may also be included in all aspects of

the present invention. In one embodiment therefore, this ionic additive will be present. In a more preferable embodiment, this ionic additive will be present and will comprise a lithium salt or compound. Particularly preferable ionic additives are lithium salts such as lithium perchlorate or ionic liquids, such as 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dihydroxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dimethoxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide. Mixtures of such materials are also highly suitable.

The invention will now be further elaborated by reference to the following non-limiting examples and the enclosed figures, in which:

5 Figure 1. a) shows a schematic illustration of a cross section of a solid-state dye-sensitized solar cell using SnO_2 as the n-type metal oxide.

Figure 1 b) Shows an illustrative energy level diagram for a conventional solid-state dye sensitized solar cell.

10 Figure 2a shows a cross-section scanning electron microscopy (SEM) image of a $1\text{ }\mu\text{m}$ thick dye-sensitized polymer-oxide solar cell.

Figure 2b shows the XPS depth profiling for a $1\text{ }\mu\text{m}$ TiO_2 thick D131+P3HT device, showing the signals for the carbon, oxygen, titanium and tin.

15 Figure 2c. Shows the depth profile for the P3HT in bare TiO_2 device.

Figure 3 shows the UV-Vis absorption spectra for dye-sensitized TiO_2 coated with P3HT with and without pre-coating with Li-TFSI.

20 Figure 4 shows the current voltage curves for complete devices with the addition of Li-TFSI and tBP with thicknesses of 1, 2.5 and $4\text{ }\mu\text{m}$ measured under AM 1.5 simulated sun light of 100 mWcm^{-2} .

Figure 5 Shows that with P3HT employed as a hole transporter, specifically when used in combination with Li-TFSI, the conductivity increases to the range of 10^{-2} Scm^{-1}

5 Figure 6 shows the spectral response for the 2.5 μm thick device, along with the UV-Vis absorption spectra for a 1 μm thick TiO_2 film coated with dye (+ Li-TFSI), infiltrated with P3HT and both coated with dye (+ Li-TFSI) and P3HT.

Figure 7 shows the transport rate (left y-axis) and the charge collection efficiency (right y-axis) measured under conditions equivalent to full sun illumination at 100 mWcm^{-2} as a function of film thickness.

10

Figure 8 shows a cartoon to aid an intuitive explanation for ambipolar diffusion for P3HT (represented by the red phase) and TiO_2 (white pillar).

15

Examples

Example 1 - Solar Cell assembly:

20 Fluorine doped tin oxide (FTO) coated glass sheets ($15 \Omega/\square$ Pilkington) were etched with zinc powder and HCl (2 Molar) to obtain the required electrode pattern. The sheets were then washed with soap (2% Hellmanex in water), de-ionized water, acetone, methanol and finally treated under an oxygen plasma for 10 minutes to remove the last traces of organic residues. The FTO sheets were subsequently coated with a compact layer of TiO_2 (100 nm) by aerosol spray pyrolysis deposition at 450 $^\circ\text{C}$, using air as the carrier gas.

25

The standard Dyesol TiO_2 paste was previously diluted down 1:2 and 1:3.5 in anhydrous ethanol and stirred and ultrasonicated until complete mixing has occurred. The paste was then doctor-bladed by hand using 2 and 1 layer of scotch tape and a pipette on the TiO_2 compact layer coated FTO sheets to get a TiO_2 average thickness from 1 to 6 μm . The sheets were then slowly heated to 550 $^\circ\text{C}$ (ramped over 1 $\frac{1}{2}$ hours) and baked at this temperature for 30 minutes in air. After cooling, slides were cut down to size and soaked in a 15 mM of TiCl_4 in water bath

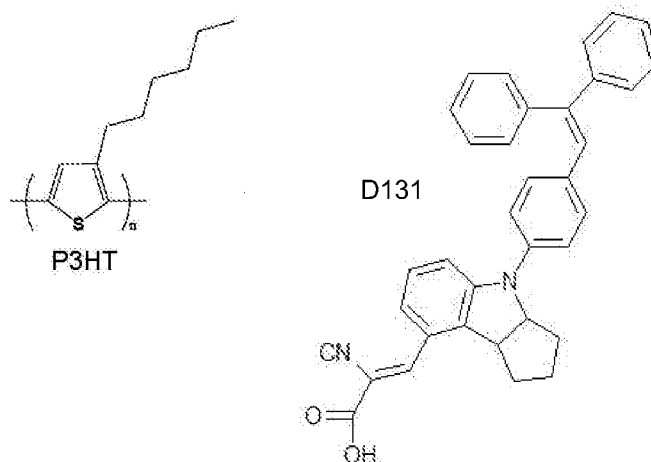
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and oven-baked for 1 hour at 70 °C. After rinsing with subsequently in water, ethanol and drying in air, they were subsequently baked once more at 550 °C for 45 min in air, then cooled down to 70 °C and finally introduced in a dye solution for 1 hour

5 A yellow indolene dye was used (D131) at 0.3 mM in a 1:1 volume ratio of tert-butanol and acetonitrile. P3HT was synthesised by according to the published route (ref: Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, 34, 4324-4333.). Briefly, to a 0.2M THF solution of 2,5-dibromo-3-hexylthiophene at 0°C was added 0.98 equivalents of a 0.98M solution of
10 n-Butylmagnesium chloride in THF. The mixture was allowed to warm to RT and then stirred for 1 h. The mixture was warmed to 50°C, and Ni(dppp)Cl₂ (1 mol%) was added directly as a powder, and the resulting mixture was refluxed for 4 h. The reaction was cooled and precipitated into a well stirred solution of methanol (160 mL)/25% HCl (40 mL). After stirring for 1 h, the resulting suspension was filtered
15 directly into a soxhlet funnel. This was extracted (soxhlet) with methanol (12 h), acetone (12 h) and hexane (until no further colour was removed ca. 16 h). The polymer was dried, dissolved in hot chlorobenzene, filtered and precipitated into acetone (twice). Number-average (M_n) and weight-average (M_w) were 27,500 g/mol and 35,000 g/mol respectively, as determined by Agilent Technologies 1200 series
20 GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. Regioregularity was determined to be greater than 97% by NMR integration of the methylene protons. P3HT (was dissolved in chlorobenzene at 3,5,7 wt% concentration and heated at 70 °C for 1 hour. An additive solution of Lithium
25 bis(trifluoromethylsulfonyl)imide salt (Li-TFSI) with 4-tert-butyl pyridine (*t*BP) in acetonitrile was prepared to treat the dyed-adsorbed TiO₂ surface prior P3HT spin-coating. The dyed films were rinsed briefly in acetonitrile and dried in air for 1 minute. Then a small quantity of salts additive solution (25 µl) was dispensed onto each substrate and left to wet the films for 20 s before spin-coating at 1000 rpm for
30 60 sec in air. Then P3HT was subsequently spun on each substrate using 3.5% P3HT solution for 1-4 µm TiO₂ thick films and 7% for 6.8 µm. The films were dried in air and then placed in a thermal evaporator where 150 nm thick silver electrodes were

- 27 -

deposited through a shadow mask under high vacuum (10^{-6} mbar). The active areas of the devices were defined by metal optical masks with a round aperture of 2.5 mm giving an area of 0.0491 cm^2 . We note that the masks used were single aperture and all light was excluded from entering the sides of devices by measuring them in a black box sample holder.



10

Example 2 - Cross-section SEM:

The cross-section SEM images were acquired with FEI XL30 Sirion SEM operated at an accelerating voltage of 5V.

15

Example 3 - XPS depth profiling:

XPS spectra were acquired with a PHI 5000 Versaprobe system using a microfocused (100 μm , 25 W) Al K_{α} X-ray beam with a photoelectron takeoff angle of 45° . A dual-beam charge neutralizer (10-V Ar^{+} and 30-V electron beam) was used to compensate the charge-up effect. Ar^{+} ion source was operated at 1 μA and 5 kV, with rastering on an area of 1 mm x 1 mm. In order to calculate the sputter rate, the film thicknesses were measured with a cross-section SEM image. The sputter rate was around 25 nm min^{-1} for all P3HT-infiltrated mesoporous TiO_2 films.

20

The carbon signal comes from both the dye and P3HT. To subtract the contribution of the dye, a TiO₂ film with only the dye and no polymer was first measured in XPS to quantify the carbon concentration. This concentration is subtracted from the other samples that contain both the dye and polymer

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Example 4 - pore filling

Figure 2a shows a cross-section scanning electron microscopy (SEM) image of a 1 µm thick dye-sensitized polymer-oxide solar cell. The layers from left to right are the silver electrode (bright), over-standing or capping layer of P3HT (dark), mesoporous TiO₂ infiltrated with P3HT, and fluorine doped tin oxide (FTO) transparent conducting electrode. We have used the carbon signal from the XPS in order to probe the presence of the P3HT. Unfortunately, the sulphur signal, unique to P3HT, was too weak to use reliably. The carbon signal arises from both the dye and the P3HT. Hence the average carbon signal from a dye sensitized film without polymer was used as a reference so that the carbon signal contribution from the dye can be subtracted. In **Figure 2b** we show the XPS depth profiling for a 1 µm TiO₂ thick D131+P3HT device, showing the signals for the carbon, oxygen, titanium and tin. As can be seen there is a significant reduction in the carbon signal when going from the capping layer into the mesoporous film. However, this signal remains significant and approximately constant throughout the entire depth down to the FTO electrode. The coincidence of the drop in the carbon signal, with the drop in the titanium and raise in the tin indicates that the observed carbon signal is not due to the "knock-in" effect from the Ar-ion beam. We repeated these measurements for devices with purely P3HT in TiO₂, P3HT in dye sensitized TiO₂ with and without the additives, and for devices with a range of thicknesses for two different P3HT starting solution concentrations. The average carbon content within the mesoporous section of the films, are summarised in **Table 1**.

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Table 1

	Electrode composition and P3HT solution concentration (mg/mL)	TiO ₂ 1 μm	TiO ₂ 2.5 μm	TiO ₂ 4 μm
Carbon content at bottom of film - as determined by Argon-ion milling and XPS	P3HT 30	3.9±0.8		
	D131	4.2±0.6	4.9±0.6	
	D131+P3HT 30	9.6±0.6	7.5±0.5	
	D131+Adds+P3HT 30	7.5±0.4	7.5±0.5	6.4±0.5
	D131+Adds+P3HT 50	9.6±0.7	7.9±0.7	7.1±0.5

- 5 All films showed uniform pore filling, apart from bare TiO₂ infiltrated with P3HT. The depth profile for the P3HT in bare TiO₂ device is shown in **Figure 2c**.

Example 5 - pore filling by UV-Vis absorption

- 10 Since XPS depth profiling cannot give a quantitative estimation of the pore filling fraction, we have employed UV-Vis absorption measurements, in combination with capping layer thickness measurements to estimate the pore filling fraction (PFF) in these films. In brief, the total equivalent thickness of P3HT in the film (d_{tot_P3HT}) is estimated by measuring the UV-Vis transmission spectra and
- 15 comparing this to a solid-film of known thickness. The capping, or over standing layer thickness (d_{os}) is estimated from cross-section SEM images, and subtracted from the total P3HT thickness to give the equivalent thickness of P3HT within the porous titania film. The pore filling fraction (PFF) is then calculated by dividing the product of the TiO₂ film thickness (d_{TiO_2}) times the TiO₂ porosity ($p_{TiO_2} \sim 0.6$) by the
- 20 equivalent thickness of P3HT within the pores (d_{pores}), obtained by subtracting from the total P3HT equivalent thickness (d_{tot_P3HT}), the polymer overlayer thickness (d_{os}). This is represented by the simple equation given below,

$$PFF = \frac{d_{tot_P3HT} - d_{os}}{p_{TiO_2} \cdot d_{TiO_2}} \quad (1)$$

In **Table 2** we show the total equivalent P3HT thickness, the over standing layer thickness and the pore filling fraction for films incorporating 1, 2.5 and 4 μm thick mesoporous TiO_2 , sensitized with D131 and coated with P3HT from a 30 mg/ml and 50 mg/ml solution spin-coated at 1000 rpm.

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Table 2

	Electrode composition and P3HT solution concentration (mg/mL)	TiO_2 1 μm		TiO_2 2.5 μm		TiO_2 4 μm	
P3HT overlayer (nm) —as determined by cross sectional ESEM (left column) P3HT d_{pores} (nm) — as determined by UV-vis absorption (right column)	P3HT 30	50	242.6	0	292.6	0	261.1
	D131+P3HT 30	177	63.6	102	235.9	40	211.9
	D131+AddS+P3HT 30	155	187.3	130	293.4	75	272.6
	D131+AddS+P3HT 50	405	152.7	432	490.6	340	581.1
Pore filling fraction (%) — as determined by UV-vis absorption	P3HT 30	30.9		20.8		10.1	
	D131+P3HT 30	8.1		9.5		6.7	
	D131+AddS+P3HT 30	23.8		11.6		7.6	
	D131+AddS+P3HT 50	19.4		4.1		9.3	

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Prior to P3HT coating the films were optionally coated with Li-TFSI (19 mg/ml in acetonitrile, coated at 1000 rpm), or tBP and Li-TFSI (17.5 $\mu\text{l}/\text{ml}$ and 19 mg/ml in acetonitrile, coated at 1000 rpm). The thickness of a P3HT film spin-coated upon a microscope slide at 1000 rpm from a 30 mg/ml and 50 mg/ml solution is also shown (respectively 263 nm and 485 nm). Interestingly the pore filling fraction appears to be enhanced by the pre-deposition of the Li-TFSI solution (**Table 2**).

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As spin-coating proceeds, the solvent evaporates and the polymer concentrates into the porous film, until it crashes out of solution at a concentration of what will become the pore filling fraction, and the remaining material which has not yet concentrated into the pores becomes the overstanding layer.[10] As the

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solvent continues to evaporate, voids remain within the porous film. The only means by which it is possible to get significantly more material into the porous film in the case of additives pre-treatment, is if either the viscosity of the P3HT solution is effected by the underlying substrate or the polymer concentrates more into the pores prior to spin-coating when Li-TFSI and tBP are pre-spun (the solution stands for 20 seconds following solution deposition.

In fact when the P3HT solution is deposited upon the film we let the solution rest for 20 seconds prior to spin-coating. This is to enable the solution to entirely wet the internal surface of the porous film. We varied this resting time from 5 to 80 seconds on dye-sensitized films incorporating Li-TFSI, but only saw marginal variations in the total equivalent thickness of P3HT (see additional information for details). This suggests that whatever process is occurring, polymer concentrating into the pores, or changes in viscosity, it is happening relatively quickly.

Example 6 - Light Absorption

When P3HT is p-doped, the oxidized polymer chains become more planar and rigid, resulting in a characteristic red shift in the ground state absorption and reduced solubility or gelling in a solution.[11] In **Figure 3** we show the UV-Vis absorption spectra for dye-sensitized TiO₂ coated with P3HT with and without pre-coating with Li-TFSI (changes in the absorption coefficient of the P3HT due to the doping have been taken into account for the determination of pore filling by absorption spectroscopy). For the film without Li-TFSI, there is the expected ground-state absorption from P3HT and the sensitizer D131, but no absorption in the infrared region. For the film with the addition of Li-TFSI there are also strong absorptions in the IR with peaks centred around 900 and 2000 nm characteristic of the absorption of oxidized P3HT.[12] There is negligible absorption in this region from the dye-sensitized films with the addition of Li-TFSI when no P3HT is added. We note that the TFSI is the component which would enable stabilisation of holes on oxidized P3HT.

We estimate a hole density (p) of $7.5 \times 10^{15} \text{ cm}^{-3}$ at 980 nm (averaged over the entire film including TiO_2 , open-pores and polymer), using the following relationship:

$$p = \frac{N_A \Delta OD}{1000 \cdot \varepsilon \cdot d} \quad (2)$$

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where d is the TiO_2 film thickness of the measured films in **Figure 3**, ΔOD is the difference in absorbance at 980 nm between a D131 film coated with 3% P3HT solution with and without pre-treatment with the Li-TFSI and ε is the extinction coefficient at that wavelength ($4 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) as estimated by Durrant et al.

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These observations are consistent with the Li-TFSI inducing p-doping of the P3HT, possibly benefiting from the presence of oxygen, resulting in an increase in the viscosity of the P3HT solution. The increased viscosity results in an increase in thickness of the layer during spin-coating, but remarkably does not inhibit uniform pore filling and even appears to increase the pore filling fraction. This counter intuitive observation, that increased viscosity is preferable for improved pore infiltration, suggests that capillary forces play a pivotal role in enabling the concentration of the polymer deep into the porous network.

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In **Table 2** we show the estimated pore filling fraction for the devices with a range of thicknesses, with and without dye and with and without the additives (Li-TFSI and tBP). The pore filling fraction is in qualitative agreement with the XPS depth profiling, in as much as there is little drop in the pore filling fraction with increasing TiO_2 thickness, and increasing the P3HT concentration from 30 to 50 mg/ml does not show any improvement on the pore filling. Notably however, the pore filling fraction is only between 6 to 23% for all the D131+P3HT films and it consistently increases with pre-treatment of the film with Li-TFSI. In the case of P3HT on bare TiO_2 the pore filling fraction reaches 30% and systematically decreases with TiO_2 increasing thickness. For simplicity, if we assume the pores to be cylindrical with 20 nm diameter and assume that the P3HT uniformly wets the pore walls, a pore filling fraction of 6 to 20% would result in a thin “shell” of P3HT.

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We have clearly demonstrated that thick porous films can be uniformly filled with semiconducting polymer, but since the filling fraction is relatively low, this does not directly imply that the devices will operate effectively. The critical questions are whether the thin shell of P3HT forms a sufficiently interconnected network of polymer chains to enable effective hole-transport out of the device, and whether the P3HT uniformly wets the dye-coated pore walls to enable effective dye regeneration (hole-transfer from the photoexcited dye).

Example 7 - Li salt

Dye-sensitized polymer-oxide solar cells operate most effectively when ionic salts (typically Li-TFSI) and a base (typically 4-tert-butyl pyridine, *t*BP) are added to the system. We have found that the best approach is to spin-coat an acetonitrile solution of the additives (Li-TFSI and *t*BP) upon the dye-sensitized film, directly prior to spin-coating the P3HT solution. The addition of Li-TFSI dramatically enhanced the charge generation efficiency from the photoexcited dye, and a detailed study of its electronic influence will be presented elsewhere. For this work regioregular P3HT (RR>97%, $M_n=27K$, $M_w=33.2K$) was dissolved in chlorobenzene at 30 or 50 mg/ml, deposited upon the mesoporous electrodes and spin-coated at 1000 rpm. In order to characterise the influence of the dye, the additives and the film thickness upon the mesopore infiltration with P3HT, we have performed XPS depth profiling.[9] XPS is sensitive to the surface composition of the film with depth sensitivity on the order of 5 nm. Since we can not be sure that the Ar-ion milling uniformly etches the TiO_2 and the polymer at the same rate, this technique can only be used to give a qualitative picture of the relative composition as a function of depth within the mesoporous films.

In **Figure 4** we show the current voltage curves for complete devices with the addition of Li-TFSI and *t*BP with thicknesses of 1, 2.5 and 4 μm measured under AM 1.5 simulated sun light of 100 $mWcm^{-2}$. Remarkably, all the devices generate a

similar photocurrent and have similar efficiencies, with the best device being 2.5 μm thick, with an overall power conversion efficiency of 2.8%.

We note that the high extinction coefficient dye employed (D131), and the P3HT within the pores absorb over 90% of the light over the active range within the first micron of the film. Hence we would not expect a gain in photocurrent with increasing the film thickness beyond one micron, and the comparable photocurrents suggest that the P3HT at the bottom of the pores in the 4 μm thick films is suitably uniformly wetting and suitably well interconnected to both regenerate the dye and transport the holes out of the device. We also note that with P3HT employed as a hole transporter, specifically when used in combination with Li-TFSI, the conductivity increases to the range of 10^{-2} Scm^{-1} (**Figure 5**). In this case edge effects are significant and it is essential to use an optical mask with a single aperture which only illuminates the active area and excludes light from entering the cell from the side where “light piping” and underestimations of the active area size can lead to an overestimation of the photocurrent by more than a factor of 2 in some instances. This should be taken into account when comparing these results (where the cells were entirely masked apart from a single aperture on the connected pixel) with those previously reported in literature for similar systems where all the device pixels were illuminated through a rectangular mask).

In **Figure 6** we show the spectral response for the 2.5 μm thick device, along with the UV-Vis absorption spectra for a 1 μm thick TiO_2 film coated with dye (+ Li-TFSI), infiltrated with P3HT and both coated with dye (+ Li-TFSI) and P3HT.

Example 8 - Transient photocurrent measurements

As a final part to this study, to understand in more detail the charge transport and charge collection in this hybrid composite, we have employed small perturbation transient photocurrent decay measurements. For these measurements we shone white light on to the solar cells, generated from an LED array, to create conditions similar to those under sun light at short-circuit. We simultaneously exposed the solar cells to

a short pulse (100 μ s) of green light, generated from green LEDs, in order to photoexcite the dye and measured the transient decay of the small perturbation in the photocurrent. As well as measuring the charge collection rate, we can estimate the charge recombination lifetime (τ_e), by holding a constant current through the cell and measuring the voltage perturbation to the light pulse. With knowledge of both the charge collection rate (k_{coll}) and the charge recombination rate ($k_{rec} = 1/\tau_e$) we can estimate the charge collection efficiency (η_{coll}) at short-circuit as $\eta_{coll} = k_{coll}/(k_{coll}+k_{rec})$. In **Figure 7** we show the transport rate (left y-axis) and the charge collection efficiency (right y-axis) measured under conditions equivalent to full sun illumination at 100mWcm⁻² as a function of film thickness.

The key observation here is that both the collection efficiency and the transport rate are relatively independent of film thickness over a range of 1 to 6.8 μ m. This simple observation has a number of significant implications. In this system most of the light is absorbed within the bottom 500 nm to 1 μ m, in the region close to the FTO electron collection electrode, from which the light is incident. If the charge transport was limited by hole-transport in the P3HT, we would expect the charge collection rate to decrease with increasing thickness of the film (d), since the holes would have further to travel. The way in which it decreases would depend on whether drift or diffusion currents were dominant in the bulk of the active layer, but with either of these conditions it should follow a trend on the order of $1/d^2$. Since the charge collection rate does not slow down with increasing thickness we can directly infer that the electrons in the TiO₂ are the transport limiting carriers, despite the holes having to travel in an exceptionally thin shell of P3HT, and much further.

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As a final consideration, though we have demonstrated that the transport limiting carrier appears to be the electron, the charge diffusion is still ambipolar, and the ambipolar diffusion coefficient (D_{amb}) has the following relationship:

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$$D_{amb} = \frac{n + p}{\left(\frac{n}{D_p} + \frac{p}{D_n} \right)} \quad (3)$$

where n is the free electron density, p is the free hole density and D_n and D_p are the diffusion coefficients for electrons and holes respectively. For a situation where there is a considerable excess of one carrier type, in this instance holes, then the weighting for charge density is such that the ambipolar diffusion coefficient can still closely match D_n even if $D_n > D_p$. A cartoon to aid an intuitive explanation for ambipolar diffusion for P3HT (represented by the red phase) and TiO₂ (white pillar) is shown in **Figure 8**: considering the requirement for current continuity, all the holes represented in the red region (P3HT) can collectively move a small distance to have one hole leaving the system at the top. However, the lone electron illustrated in the gray region (TiO₂) has to move the entire length of the cylinder within the same timeframe to exit the system at the bottom. Hence, a balanced flux of electrons at the bottom and holes at the top can be achieved with the holes diffusing much slower than the electrons. With this in mind, the ability to employ a heavily doped hole-transporter within this system implies that the required mobility of the hole-transporter could be very low, and significantly lower than the mobility of the TiO₂, which is probably in the region of 10^{-3} cm²/Vs. We do note however, that for this system incorporating P3HT without the addition of Li-TFSI, which is the component inducing chemical oxidization, the charge collection rates remain similar, suggesting that D_p is not smaller than D_n and that the thin shell of P3HT is sufficiently interconnected to enable faster hole-transport than electron transport in this system. We also note that we have not presented the charge recombination lifetime data, since it is not central to the discussion, but the charge lifetimes also remain relatively invariant for the range of film thicknesses studied.

Claims

- 1) A solid-state p-n heterojunction comprising an organic p-type material in contact with a porous layer of n-type material, characterised in that the thickness of the porous layer of n-type material is 2 μm or greater.
- 2) A solid-state p-n heterojunction comprising an organic p-type material in contact with a porous layer of n-type material, characterised in that the pore-filling-fraction of the porous layer of n-type material by the organic p-type material is no more than 50%.
- 3) A solid-state p-n heterojunction as claimed in claim 1 or claim 2, wherein said organic p-type material is an organic polymer, preferably a conducting polymer or a semi-conducting polymer.
- 4) A solid-state p-n heterojunction as claimed in preceding claim wherein said heterojunction is sensitised by at least one sensitizing agent.
- 5) A solid state p-n heterojunction as claimed in any preceding claim wherein said sensitizing agent comprises at least one dye selected from a ruthenium complex dye, a metal-phalocianine complex dye, a metal-porphyrin complex dye, a squaraine dye, a thiophene based dye, a fluorine based dye, a polymer dye, and mixtures thereof.
- 6) A solid state p-n heterojunction as claimed in any preceding claim wherein said sensitizing agent comprises at least one inorganic light absorbing thin film or semiconductor nanoparticle layer formed from a material selected from PbS, PbSe, SnS, SnSe SbS, SbSe, CdSe, Ge, Si.
- 7) A solid-state p-n heterojunction as claimed in preceding claim wherein said heterojunction comprises at least one ionic additive.
- 8) A solid-state p-n heterojunction as claimed in claim 7 wherein said ionic additive is a lithium salt such as lithium bis(trifluoromethylsulphonyl)imide salt (Li-TFSI) or Li perchlorate.

- 9) A solid-state p-n heterojunction as claimed in claim 7 or claim 8 wherein said ionic additive is a mixture of a metal salt and an ionic liquid.
- 5 10) A solid-state p-n heterojunction as claimed in any of claims 7 to 9 wherein said ionic additive comprises or consists of an ionic liquid, selected from 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-Allyl-3-methylimidazolium
10 bis(trifluoromethylsulfonyl)imide, 1,3-Dihydroxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-Dimethoxy-2-methylimidazolium bis(trifluoromethylsulfonyl)imide and mixtures thereof.
- 11) A solid-state p-n heterojunction as claimed in preceding claim wherein said
15 p-type material is an organic polymer selected from – poly thiophenes, poly p-phenylene vinylenes, mixtures, derivatives and copolymers thereof.
- 12) A solid-state p-n heterojunction as claimed in preceding claim wherein said
20 p-type material is an organic polymer, preferably a poly thiophene or mixture thereof.
- 13) A solid-state p-n heterojunction as claimed in preceding claim wherein said
25 p-type material is an organic polymer having a molecular weight Mn of greater than 15,000.
- 14) A solid-state p-n heterojunction as claimed in preceding claim wherein said
p-type material is substantially electrically continuous throughout the mesoporous film.
- 30 15) A solid-state p-n heterojunction as claimed in preceding claim wherein said n-type semiconductor material comprises at least one single metal oxide, compound metal oxide, doped metal oxide, carbonate, sulphide, selenide, teluride, nitrides and/or multicomponent semiconductor, most preferably TiO₂, SnO₂ or ZnO.

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- 16) A solid state p-n heterojunction as claimed in preceding claim wherein said n-type material has a surface area of $1\text{-}1000\text{ m}^2\text{g}^{-1}$ and preferably in the form of an electrically continuous layer.
- 5 17) A solid state p-n heterojunction as claimed in preceding claim wherein said n-type material has a thickness of 2 to 30 μm , preferably 2 to 5 μm , more preferably 2 to 3 μm .
- 10 18) A solid-state p-n heterojunction as claimed in preceding claim wherein said n-type material is selected from oxides of Ti, Zn, Sn, W and mixtures thereof, and wherein said n-type material is optionally surface coated.
- 15 19) An optoelectronic device comprising at least one solid state p-n heterojunction as claimed in preceding claim.
- 20 20) An optoelectronic device as claimed in claim 16 wherein said device is a solar cell or photo-detector, preferably a solid state dye sensitised solar cell and/or solid state polymer sensitised solar cell.
- 25 21) An optoelectronic device as claimed in claim 20 wherein said device is encapsulated so as to be substantially isolated from atmospheric oxygen.
- 22) Use of a solution of polymerised organic p-type material in the formation of a solid-state p-n heterojunction wherein said p-n heterojunction comprises a porous layer of n-type material having a thickness of 2 μm or greater.
- 30 23) Use of a solution of polymerised organic p-type material in the formation of a solid-state p-n heterojunction wherein said p-n heterojunction comprises a porous layer of n-type material and wherein said polymerised organic p-type material fills the pores of said n-type material with a pore filling fraction of 50% or less.
- 24) Use of a solution of polymerised organic p-type material in the formation of a solid-state p-n heterojunction as claimed in any of claims 1 to 18 or an optoelectronic device as claimed in any of claims 19 to 21.

- 40 -

25) Use as claimed in claim 23 or claim 24 in the formation of a solar cell.

26) A method for the manufacture of a solid-state p-n heterojunction comprising an organic p-type material in contact with a porous layer of n-type material, said
5 method characterised by;

a) coating an anode, preferably a transparent anode (e.g. a Fluorine doped Tin Oxide - FTO anode) with a compact layer of an n-type semiconductor material (such as any of those described herein);

10 b) forming a porous (preferably mesoporous) layer of an n-type semiconductor material (such as any of those described herein) on said compact layer,

c) optionally surface sensitizing said compact layer and/or said porous layer of n-type material with at least one sensitizing agent;

15 d) optionally treating said compact layer and/or said porous layer of n-type material with at least one ionic material such as a lithium salt.

e) optionally forming a porous barrier layer of an insulating material on said porous layer of n-type material;

20 f) contacting said porous layer of n-type material with at least one solution of at least one polymeric organic p-type semiconductor material whereby to form a layer of polymeric organic p-type semiconductor interpenetrating the said porous layer of an n-type material;

f2) optionally treating said layer produced in "f" by coating on top with a solution of ionic material, such as Li-TFSI.

25 g) forming a cathode, preferably a metal cathode (e.g. a silver or gold cathode) in contact with said p-type semiconductor material.

27) A method as claimed in claim 26 wherein optional step d) is included and comprises treating said compact layer and/or said porous layer of n-type material with a mixture of at least two ionic materials.

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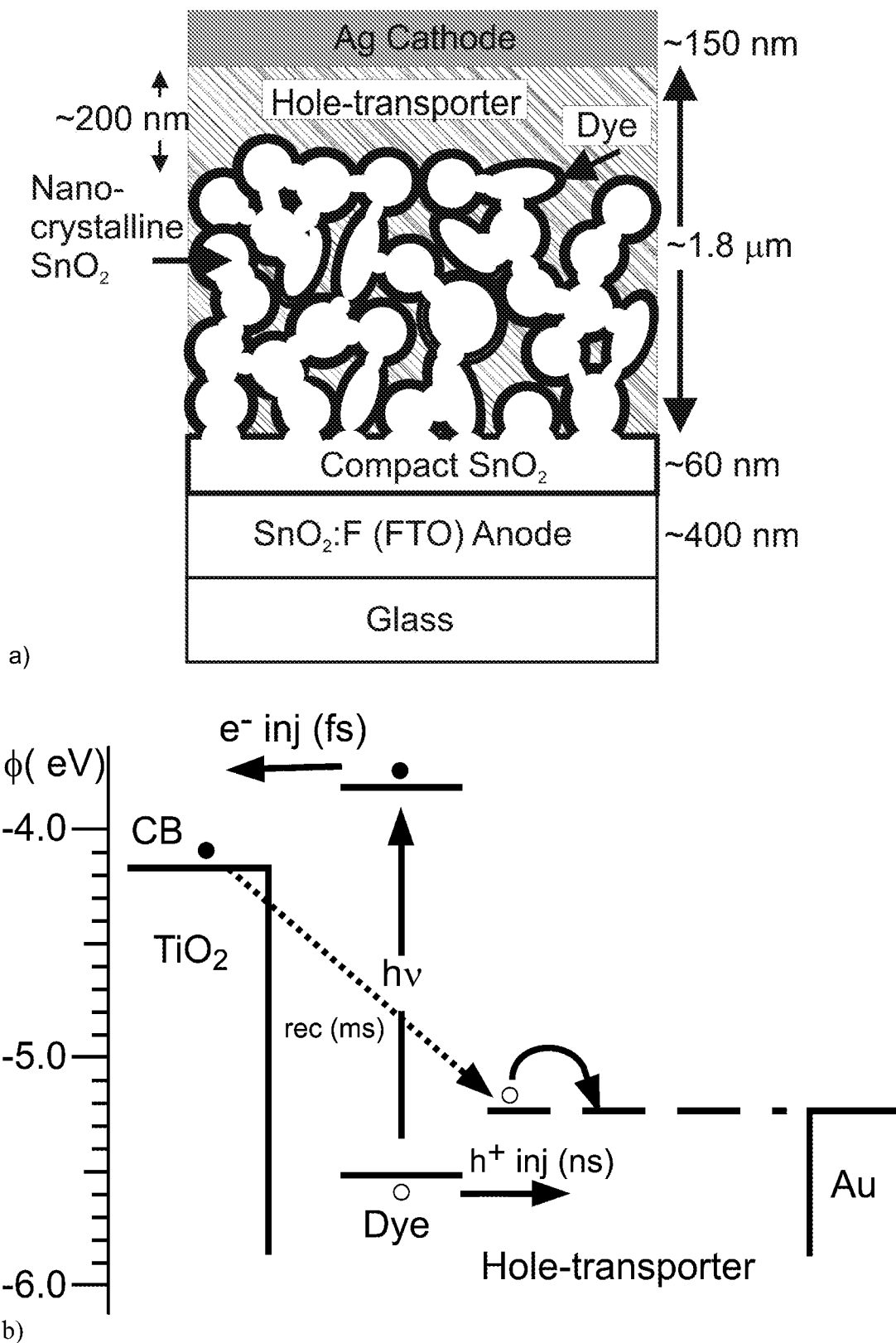
28) A method as claimed in claim 27 wherein said ionic materials comprise at least one metal salt, preferably at least one lithium salt, and at least one ionic liquid, preferably 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

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29) A method as claimed in any of claims 26 to 28 wherein step d) takes place and comprises contacting the porous layer of n-type material with a solution of Li-TFSI.

- 5 30) An optoelectronic device such as a photovoltaic cell or light sensing device comprising at least one solid-state p-n heterojunction formed or formable by the method of and of claims 26 to 29.

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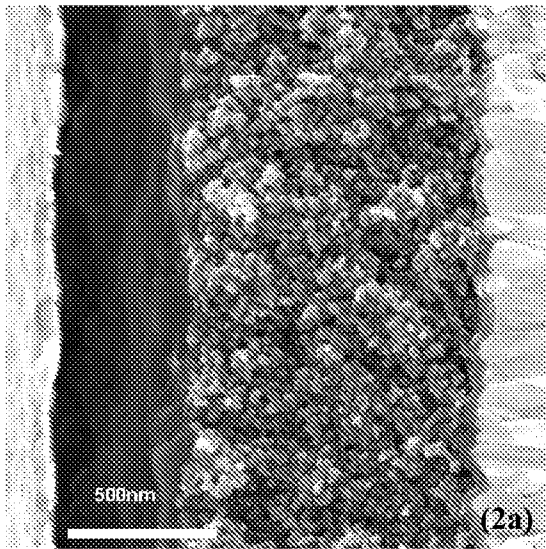
5 Figure 1. a) A schematic illustration of a cross section of a solid-state dye-sensitized solar cell using SnO_2 as the n-type metal oxide. B) An illustrative energy level diagram for a conventional solid-state dye sensitized solar cell.

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2a)

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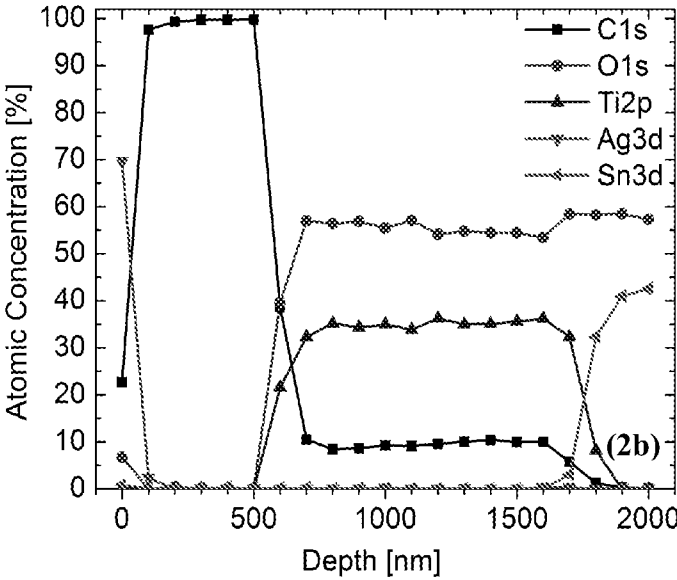
TiO₂+D131+Additives+P3HT (1μm, 5% P3HT)

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2b)

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TiO₂+P3HT (2.5μm, 3% P3HT)

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2c)

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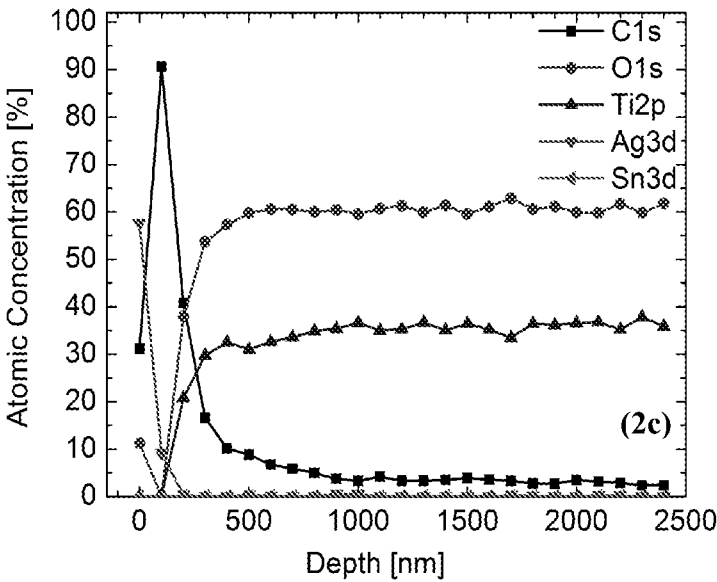


Figure 2

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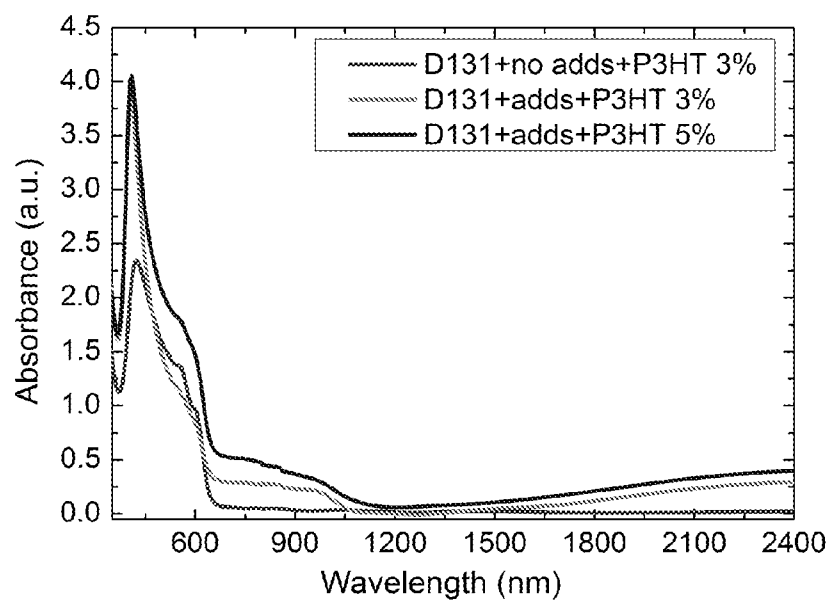
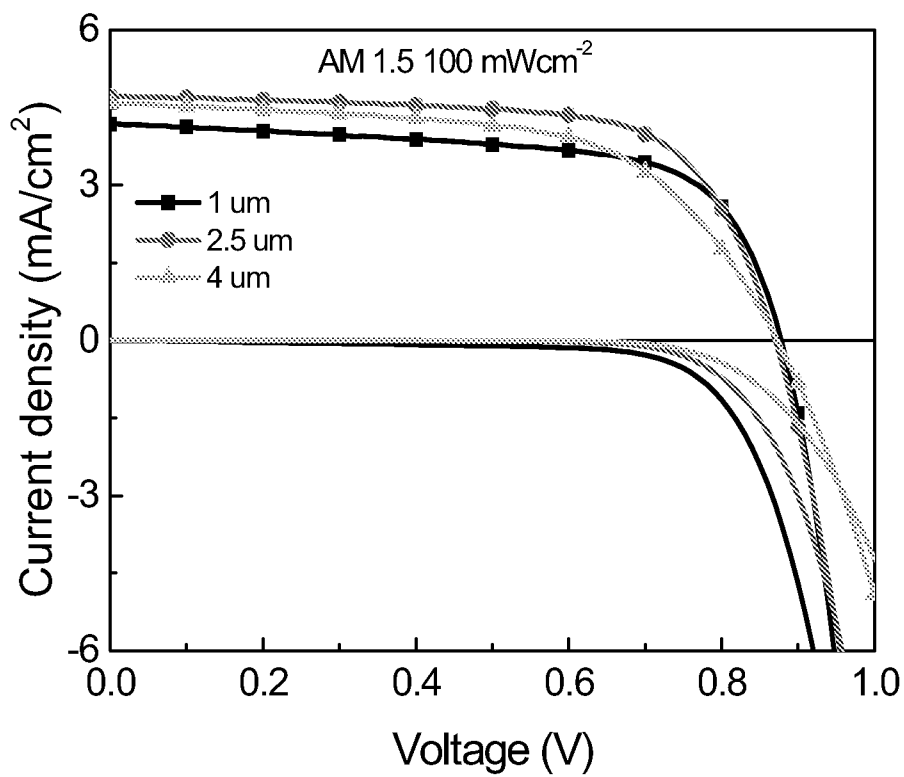


Figure 3



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Figure 4

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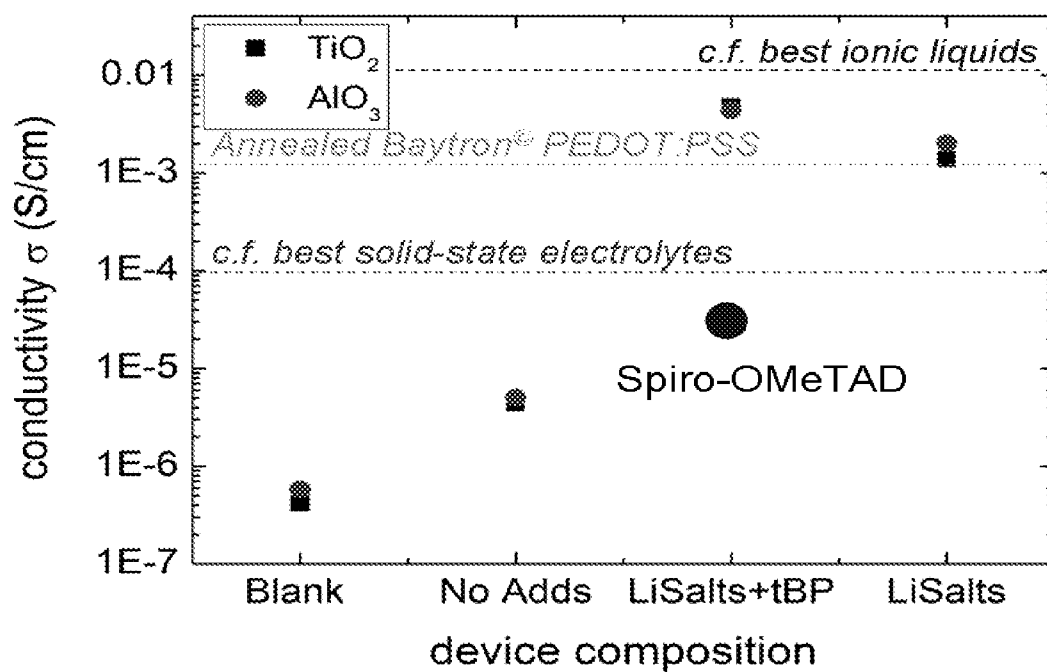


Figure 5

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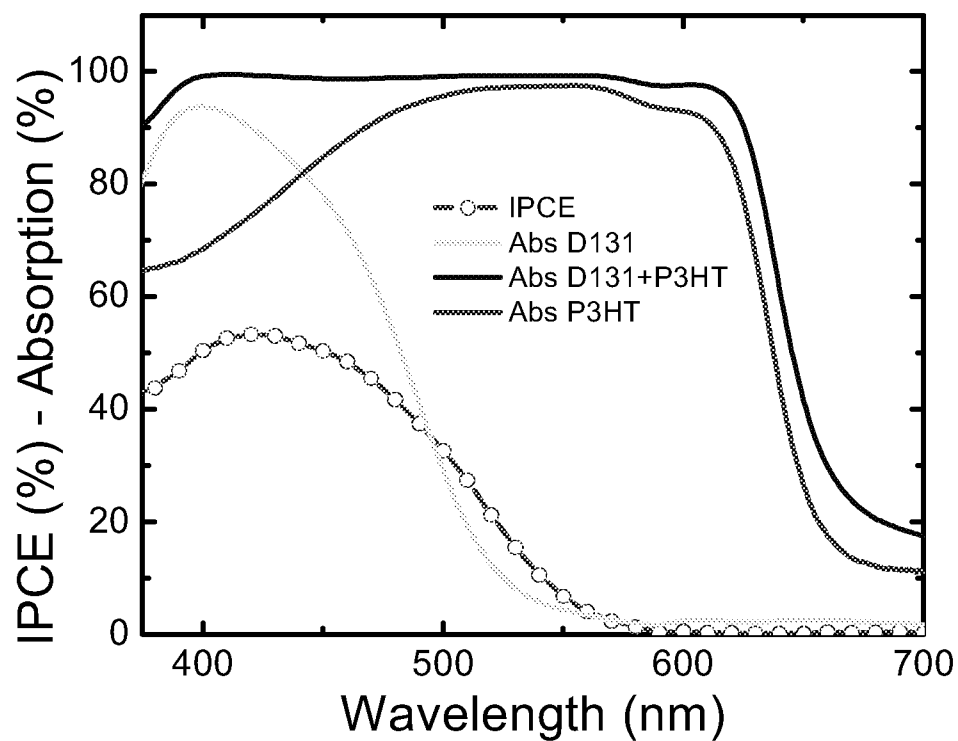


FIGURE 6

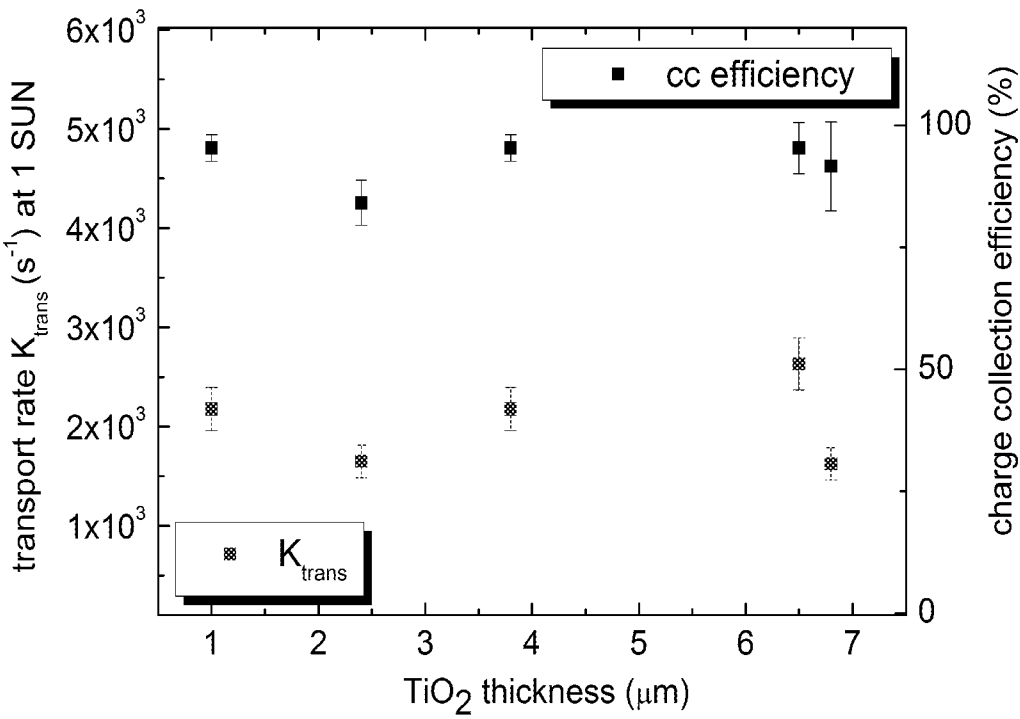


FIGURE 7

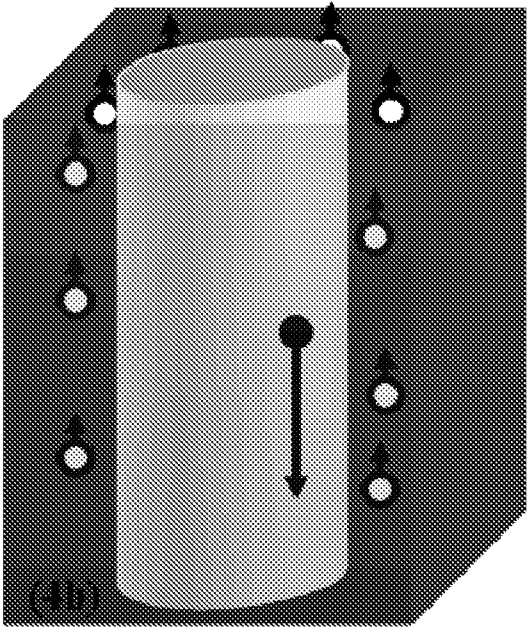


FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2011/052347

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L51/42

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JIANG K-J ET AL: "Photovoltaics Based on Hybridization of Effective Dye-Sensitized Titanium Oxide and Hole-Conductive Polymer P3HT", ADVANCED FUNCTIONAL MATERIALS, WILEY - V C H VERLAG GMBH & CO. KGAA, DE, vol. 19, no. 15, 10 August 2009 (2009-08-10), pages 2481-2485, XP001548758, ISSN: 1616-301X, DOI: 10.1002/ADFM.200900283 the whole document ----- -/--	1,3-22, 24-30



Further documents are listed in the continuation of Box C.



See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 January 2012

Date of mailing of the international search report

16/05/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Wolfbauer, Georg

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2011/052347

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NOGUEIRA A F ET AL: "ENHANCED PHOTORESPONSE OF POLY(3-METHYLTHIOPHENE) SUPPORTED ON TiO₂", ELECTROCHEMISTRY COMMUNICATIONS, ELSEVIER, AMSTERDAM, NL, vol. 1, no. 7, 1 July 1999 (1999-07-01), pages 262-265, XP001023578, ISSN: 1388-2481, DOI: 10.1016/S1388-2481(99)00051-X the whole document	1,3-22, 24-30
X	----- GEBEYEHU D ET AL: "SOLID STATE DYE-SENSITIZED TiO₂ SOLAR CELLS WITH POLY (3-OCTYLTHIOPHENE) AS HOLE TRANSPORT LAYER", SYNTHETIC METALS, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 121, no. 1-03, 15 March 2001 (2001-03-15), pages 1549-1550, XP001023526, ISSN: 0379-6779, DOI: 10.1016/S0379-6779(00)01239-X the whole document	1,3-6, 11-26,30
X	----- WO 2010/008294 A1 (STICHTING ENERGIE [NL]; PEX PETRUS PAULUS ANTONIUS CAT [NL]; SOMMELING) 21 January 2010 (2010-01-21) page 10	1,3-6, 11-22, 24-26,30
X,P	----- AGNESE ABRUSCI ET AL: "Facile infiltration of semiconducting polymer into mesoporous electrodes for hybrid solar cells", ENERGY & ENVIRONMENTAL SCIENCE, vol. 4, no. 8, 1 January 2011 (2011-01-01), pages 3051-3058, XP055016666, ISSN: 1754-5692, DOI: 10.1039/c1ee01135a the whole document -----	1-30

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2011/052347

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1, 22(completely); 3-21, 24-30(partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1, 22(completely); 3-21, 24-30(partially)

A solid state p-n heterojunction with a thickness of the nanoporous n-type material layer of 2 microns or greater.

2. claims: 2, 23(completely); 3-21, 24-30(partially)

A solid state p-n heterojunction with the nanoporous n-type material filled with the p-type material of 50% or less.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2011/052347

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010008294 A1	21-01-2010	AU 2009271786 A1	21-01-2010
		EP 2308114 A1	13-04-2011
		JP 2011528486 A	17-11-2011
		NL 2001815 C2	19-01-2010
		US 2011186126 A1	04-08-2011
		WO 2010008294 A1	21-01-2010
