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(54) Title: SOLID STATE P-N HETEROJUNCTION COMPRISING METAL NANOPARTICLES HAVING A SURFACE PLASMON MODE

(57) Abstract: The invention provides a solid-state p-n heterojunction comprising an organic p-type material in contact with an n-type material wherein said heterojunction is sensitised by at least one sensitizing agent wherein said sensitizing agent comprises coated nanoparticles of at least one metal, and wherein the coated metal nanoparticles have at least one surface plasmon mode in the visible to infra-red regions of the electromagnetic spectrum. Optionally more than one sensitizing agent is employed, where the 2<sup>nd</sup> sensitizing agent comprises at least one molecular, metal complex or polymeric sensitizing agent. Also provided are optoelectronic devices such as solar cells or photo-sensors comprising such a p-n heterojunction, and methods for the manufacture of such a heterojunction or device.



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## **SOLID STATE P-N HETEROJUNCTION COMPRISING METAL NANOPARTICLES HAVING A SURFACE PLASMON MODE**

The present invention relates to a solid-state p-n heterojunction and to its use in optoelectronic devices, in particular in solid-state dye-sensitized solar cells (SDSCs) and corresponding light sensing devices. Most particularly, the present invention relates to optoelectronic devices having enhanced light to electrical power conversion efficiency.

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 semi-conductor 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. Dye-sensitized solar cells (DSCs), for example, offer a promising solution to the need for low-cost, large-area photovoltaics. Typically, DSCs are composed of flat or mesoporous  $\text{TiO}_2$  (electron transporter) sensitized with a light-absorbing molecular dye, which in turn is contacted by a redox-active hole-transporting medium. Photo-excitation of the sensitizer leads to the transfer (injection) of electrons from the excited dye into the conduction band of the  $\text{TiO}_2$ . 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  $\text{TiO}_2$  in combination with a redox active liquid electrolyte. Those incorporating an 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  $7 \text{ mA/cm}^2$  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

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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 polymeric or molecular hole-transporter which is much more appealing for large scale processing and durability. Of these alternatives, the use of a molecular hole-transporter appears to be the most promising. Though these solid-state DSCs (SDSCs) are a proven concept, the most efficient still only convert just over 5% of the solar energy into usable electrical power. This is still a long way off the efficiency of the liquid based cells and will require further optimisation before SDSCs can become a viable commercial prospect in routine applications.

The rates of many of the charge-transfer steps in a DSC-type optoelectronic device are highly dependent upon the environment in which the relevant materials are held. For example, although the "injection" step of transferring an excited electron from a sensitizer to the n-type material is essentially quantitative in electrolyte-based DSCs, in solid state devices this step is relatively slow and a significant proportion of electrons are quenched by other pathways before they can be transferred to the n-type material. Similarly, the characteristics of such devices are also controlled by the components which are required to form them and so, for example, in cells containing the aggressively corrosive iodide/triiodide redox couple, certain components must be physically isolated from this electrolyte if the cell is to have a significant working lifetime. In a solid-state device, however, this aggressive environment is removed and so correspondingly is the need for physical isolation of the redox active medium from other cell components. As a result of these and other factors, many of the approaches used to improve the efficiency of electrolyte-type DSCs are not applicable in the solid state devices.

Although thicker layers of n-type semiconductor allow for more surface for dye loading, losses at the semiconductor junction mean that thick layers of n-type material result in impaired efficiency. This is particularly the case in SDSCs, where the molecular hole transporter cannot effectively be introduced into a layer of n-type material having a thickness over about 2  $\mu\text{m}$ . As a result, the more densely a dye can be loaded and the greater its extinction coefficient the better because this allows the thickness of the n-type material to be minimised. Thus, for highest efficiency, it is preferable for as much light as possible to be absorbed at the surfaces of an n-type material layer only a few  $\mu\text{m}$  deep at most. This absorbed light would then result in more excited electrons which could be transferred to the n-type material.

One route which has been investigated in order to enhance the absorption in thin dye-sensitized films is the use of larger  $\pi$ -conjugated systems. However, even the best absorbing dyes cannot

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effectively harvest more than a fraction of the available photons at the layer thicknesses and dye loading levels so far achieved. For example, the optical absorption spectrum for a conventional Ru-complex dye such as "Z907" (an NCS bipyridyl complex) is highest at the absorption peak of about 500 nm, but decreases at longer wavelengths. The inability of such dyes to harvest photons in the red region of the visible spectrum has a significant impact on the efficiency of the cell. Furthermore, larger  $\pi$ -conjugated dyes which exhibit very high molar extinction coefficients, often undergo aggregation which in many instances also reduces their electron transfer efficiency (see Wenger, *et al.* J. Am. Chem. Soc. 2005, **127**, 12150-12151).

One approach which has been investigated in solution solar cells is the use of metal nanoparticles to boost the light absorption efficiency of a thin layer junction. For example, Ishikawa *et al.* (Journal of Chemical Engineering of Japan, Vol. 37, No. 5, 645-649, 2004) investigated the incorporation of silver nanoparticles into dye-sensitized electrolyte-containing cells and found an increase in performance, at least at low dye loading levels.

The absorption cross-section of a material is proportional to the number of electrons involved in the optical transition. Metal nanoparticles thus provide a method by which hundreds of electrons can be utilised in light absorption due to the coupling of light with a coherent excitation of free electrons on the surface of the metal structure. This coupling is termed a "surface plasmon polariton". In a nanoparticle, the surface plasmon modes can be excited by light incident at any angle and will potentially absorb a relatively broad band of wavelengths. The energy from this light absorption is not typically injected directly into the heterojunction, but may be transferred to an additional sensitizing agent (e.g. a dye sensitizer or polymeric material) by near- and/or far-field effects and thus serves to amplify the absorption of the other material (e.g. dye). In this way, the surface plasmon resonance of a nanoparticle may be used to enhance the optical absorption of a dye sensitizer at longer wavelengths. Although a "dye" is indicated here as illustration, it will be evident that any other material which could absorb light may similarly be used in combination with a metal nanoparticle and this may include other organic, inorganic or polymeric materials including the n-type and p-type materials of the heterojunction itself.

Such methods have so far not been applied in the solid-state dye-sensitized solar cell. Indeed, when the present inventors attempted to incorporate metal nanoparticles into solid-state DSCs the efficiency of such cells was remarkably low, with the cells being much less efficient than corresponding cells containing only the dye sensitizer. Although the metal nanoparticles would absorb light effectively, the transfer of energy to the dye sensitizer and subsequent injection of charge into the n-type material was found to be close to zero. Essentially all that was achieved was that the nanoparticles absorbed and wasted some of the light that would otherwise have usefully been absorbed by the dye. Thus, based on this finding, it seemed that the use of

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nanoparticles as sensitizers in solid-state devices was not simply useless, but positively disastrous. This is in direct contrast to the better known electrolyte-containing cells where nanoparticles are known to be useful. Evidently, therefore, these two systems are far from comparable with respect to the use of nanoparticles.

The present inventors have, however, now established that by coating of metal nanoparticles having appropriate surface plasmon modes with a suitable material to electrically isolate the nanoparticles from the hole transporter, such nanoparticles can be effectively incorporated into a solid-state DSC without destroying the efficiency of the cell. Furthermore, the present inventors have established that this incorporation can have a very positive effect on the light conversion efficiency of a solid-state DSC. Such an effect may in fact be significantly greater than any effect previously reported when using metal nanoparticles in electrolyte-based DSCs.

In a first aspect, the present invention therefore provides a solid-state p-n heterojunction comprising an organic p-type material in contact with an n-type material (organic or inorganic) wherein said heterojunction is sensitised by at least one sensitizing agent comprising coated nanoparticles of at least one metal wherein the coated metal nanoparticles have at least one surface plasmon mode in the visible to infra-red regions of the electromagnetic spectrum.

In a second aspect, the present invention provides a solid-state p-n heterojunction comprising an organic p-type material in contact with an n-type material (organic or inorganic) wherein said heterojunction is sensitised by at least two sensitizing agents comprising a first sensitizing agent and a second sensitizing agent, wherein said first sensitizing agent comprises coated nanoparticles of at least one metal and said second sensitizing agent comprises at least one molecular or polymeric sensitizing agent, and wherein the coated metal nanoparticles have at least one surface plasmon mode in the visible to infra-red regions of the electromagnetic spectrum.

Suitable molecular or polymeric “second” sensitizing agents will be well known in the art and include all of the materials currently known to be useful in sensitizing solar cells (such as DSCs, including SDSCs). This will evidently include the p-type and n-type materials of the devices themselves, where these are capable of at least some light absorption and/or capable of converting the energy absorbed by the coated nanoparticles to injected electrons. Thus, molecular, ionic, inorganic and/or polymeric dyes may be suitable second sensitizing agents, as may molecular, ionic, inorganic and/or polymeric p-type, materials, n-type materials, electron transporters and/or hole transporters. The “second” sensitizing agent as used herein will preferably not comprise metal nanoparticles.

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The junction will preferably comprise a solid p-type material (hole transporter) in the form of an organic semiconductor, such as a molecular, oligomeric or polymeric hole transporter. In one embodiment the p-type material is an optionally amorphous molecular organic compound. As indicated above, this material may also form all or part of the “second” sensitizing agent.

The coating of the metal nanoparticles of the first sensitizing agent is a key aspect of the invention. This coating should be of a material and thickness that will help to electrically isolate the nanoparticle from the other components of the heterojunction. Such materials include semiconductor and particularly insulating materials of nanometre thickness as described herein. Although the coating material may potentially be any appropriate insulating or semiconducting material, they are preferably inorganic materials such as metal oxides, (including doped metal oxides), metal carbides, metal sulphides such as PbS, CdS, CuS; metal selenides, metal tellurides; metal nitrides or a mixture thereof. Metal oxides, particularly wide band-gap metal oxides are highly preferable and very highly preferred examples include SiO<sub>2</sub>, MgO, Y<sub>2</sub>O<sub>5</sub>, NbO, ZrO, HfO, Al<sub>2</sub>O<sub>3</sub> and combinations thereof. Most preferred is SiO<sub>2</sub>.

The solid-state p-n heterojunctions of the present invention are particularly suitable for use in solar cells, photo-detectors and other optoelectronic devices. In a second aspect, the present invention therefore provides an optoelectronic device comprising at least one solid state p-n heterojunction of the invention, as described herein. 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 DSCs 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.

In a corresponding further aspect, the present invention additionally provides the use of first and second sensitizing agents in a solid-state p-n heterojunction wherein said first sensitizing agent comprises coated nanoparticles of at least one metal and said second sensitizing agent comprises at least one molecular or polymeric sensitizing agent, and wherein the coated metal nanoparticles have at least one surface plasmon mode in the visible to infra-red regions of the electromagnetic spectrum. This will preferably be a heterojunction of the present invention as described herein. All preferred features of the heterojunctions described herein apply correspondingly to the use aspect of the invention.

The use in all appropriate aspects of the invention will preferably be a use of the first sensitizing agent to generate increased light energy conversion efficiency in the solid-state p-n heterojunction in comparison with the second sensitizing agent (dye sensitizer) when used as sole sensitizer in an equivalent heterojunction. In particular, the use will preferably be to bring

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about such an increase at least partially by near- and/or far-field energy transfer between the plasmon modes of the nanoparticle sensitizer (first sensitizing agent) and the dye sensitizer (second sensitizing agent, including the p- and/or n-type material where these act at least partially as a dye or sensitizer).

The use in all appropriate aspects of the invention will preferably be in an optoelectronic device such as any of those described herein, e.g. in a solar cell or photodetector.

In a still further aspect, the present invention provides a method for the manufacture of a solid-state p-n heterojunction incorporating a first sensitizing agent which comprises coated nanoparticles of at least one metal (such as any of those nanoparticles described herein) and a second sensitizing agent which comprises at least one molecular or polymeric sensitizing agent (such as any of those described herein), said method comprising:

- a) coating a cathode, preferably a transparent cathode (e.g. a Fluorinated Tin Oxide - FTO cathode) with a compact layer of an n-type semiconductor material (such as any of those described herein);
- b) optionally forming a porous (preferably mesoporous) layer of an n-type semiconductor material (such as any of those described herein) on said compact layer,
- c) surface sensitizing said compact layer or, where present, said porous layer with said second sensitizing agent;
- d) forming a layer of a solid state p-type semiconductor material (preferably an organic hole transporting material such as any of those described herein) in contact with said compact layer or, where present, said porous layer of an n-type semiconductor material; and
- e) forming an anode, preferably a metal anode (e.g. a silver or gold anode) on said p-type semiconductor material;

wherein said first sensitizing agent is incorporated before step a), before step b), during step b), before step c), during step c), before step d), during step d), and/or before step e).

Where the second sensitizing agent is formed at least partially from the p-type and/or n-type material or the heterojunction, step c) becomes an optional step which may be used if additional second sensitizing material(s) is required.

Typically the method of the invention will involve the formation of a porous layer of an n-type semiconductor material due its increased surface area. Although the n-type semiconductor material used to form the porous layer may be different to that which is used to form the underlying compact layer, generally these materials will be formed from the same n-type

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semiconductors. Suitable n-type semiconductor materials for use in forming the compact and porous layers are described herein. Highly preferred for use as the n-type semiconductor material in both the compact and porous layers are  $\text{TiO}_2$  and  $\text{SnO}_2$ .  $\text{TiO}_2$  is most preferred. In a preferred embodiment of the invention, the coated nanoparticles are incorporated into the p-n heterojunction during step b). For example, these may be applied to the compact layer by means of a paste having dispersed therein the desired n-type semiconductor material and the coated nanoparticles. Sintering of the resulting film provides the desired mesoporous structure having a plurality of pores in which the coated nanoparticles are disposed.

The surface sensitizing of the layer (e.g. porous layer) of n-type semiconductor material is preferably by surface absorption of the second sensitizing agent. This sensitizing agent may be absorbed by contact of the surface with a solution of the desired sensitizing agent. Where the first sensitizing agent is incorporated during step c), the first and second sensitizing agents may be co-absorbed by contact with a solution containing appropriate concentrations of both of the desired sensitizing agents.

The solid-state p-n heterojunction formed or formable by any of the methods described herein evidently constitutes a further aspect of the invention, as do optoelectronic devices such as photovoltaic cells or light sensing devices comprising at least one such heterojunction.

The functioning of a DSC relies initially on the collection of solar light energy in the form of capture of solar photons by a sensitizer (typically a molecular (including metal complex), or polymer dye). The effect of the light absorption is to raise an electron into a higher energy level in the sensitizer. This excited electron will eventually decay back to its ground state, but in a DSC, the n-type material in close proximity to the sensitizer provides an alternative (faster) route for the electron to leave its excited state, viz. by "injection" into the n-type semiconductor material. This injection results in a charge separation, whereby the n-type semiconductor has gained a net negative charge and the dye a net positive. Since the dye is now charged, it cannot function to absorb a further photon until it is "regenerated" and this occurs by passing the positive charge ("hole") on to the p-type semiconductor material of the junction (the "hole transporter"). In a solid state device, this hole transporter is in direct contact with the dye material, while in the more common electrolytic dye sensitised photocells, a redox couple (typically iodide/triiodide) serves to regenerate the dye and transports the "hole species" (triiodide) to the counter electrode. Once the electron is passed into the n-type 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 DSC, there are certain processes which occur in any practical device in competition with these desired steps and which

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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.

A schematic diagram indicating a typical structure of the solid-state DSC is given in attached Figure 1 and a diagram indicating some of the key steps in electrical power generation from a DSC is given in attached Figure 2.

Through the present invention, the inventors have now established that coated plasmonic nanoparticles may be used to enhance the light conversion efficiency of a solid-state dye sensitized solar cell. As was indicated above, the dynamics of the energy transfer in a solid-state DSC differs significantly from that of an electrolyte-based cell. In particular, the very fast dynamics of the solid-state hole transporter typically result in certain steps of the energy transfer in SDSCs being orders of magnitude faster than can be achieved with a redox couple. It is the present inventors' belief, without wishing to be bound by theory, that without an outer insulating layer, the contact of metal nanoparticles with the other components of the heterojunction, such as the solid hole transporter, introduces widespread sites of charge-recombination, essentially producing an internal short-circuit in the cell. This is believed to be suppressed by the coating of the nanoparticles with a suitable semi-conducting or insulating material.

Although coated metal particles are known in the art and have been used in electrolyte-based DSCs, it has never been suggested that such a coating could increase the efficiency of heterojunctions having such nanoparticles incorporated therein. To date, known uses of coated nanoparticles are solely to separate the particles from the aggressively corrosive environment of the iodide/triiodide electrolyte (see, for example, Standridge *et al.*, *Langmuir* **25**, 2596-2600, 2009 and Standridge *et al.*, *J. Am. Chem. Soc.* **131**, 8407-8409, 2009). These previous uses of coated nanoparticles emphasise the need to reduce coating thickness in order to allow greater contact between the nanoparticles and the dye sensitizer. It is therefore believed that any previous attempts to incorporate metal nanoparticles into solid-state DSCs have been unsuccessful because there is no aggressive environment in such cells and therefore no reason to use coated particles. The present inventors believe, however, that coating to provide electrical isolation allows the use of nanoparticle sensitizers in solid-state heterojunctions and have now

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demonstrated a marked increase in efficiency using such sensitizers (see below). This particularly applies to inorganic coating materials, such as described herein, not least because the steps of formation of a heterojunction often include high temperature steps and the use of inorganic materials for the coating allows the coated nanoparticles to be incorporated without the risk of damage due to high temperature steps. The coating materials are thus preferably not organic materials since these are sensitive to high temperatures.

The first sensitizing agent in any aspect of the present invention may comprise any nanoparticulate metal having at least one surface plasmon mode in the visible to infra-red regions of the electromagnetic spectrum. As used herein, the term "surface plasmon" is intended to have its conventional meaning, namely a coherent oscillation free electrons on the surface of a metal at the interface between the metal and a dielectric material, where the real part of the dielectric function changes sign across metal-dielectric interface. The "mode" of the surface Plasmon refers to the energy at which the optical photon can couple to the surface Plasmon. Nanoparticles having one or more surface plasmon modes between 400 nm and 2000 nm, preferably between 500 nm and 1000 nm, more preferably between 550 nm and 900 nm, are preferred for use in the invention. Suitable plasmonic materials include Ag, Au, Cu, Pt and mixtures thereof, especially Ag and Au, particularly preferably Au.

As used herein, the terms "nanoparticle" and "nanoparticulate" are not intended to impose any limitation on the desired shape of the plasmonic particles. Specifically, these terms are intended to encompass any structure having nanometre dimensions. Such a structure need not be spherical and indeed it is envisaged that other nanostructures may be equally suitable, or even more advantageous for use in the invention. Appropriate dimensions for the plasmonic nanostructures may readily be selected by those skilled in the art. Whilst such structures will typically be substantially spherical in shape, other nanostructures may also be used which are curved or shaped on the sub-wavelength scale and which therefore enable surface plasmon resonance through relatively broad band light incident at any angle. Other suitable nanostructures include, for example, nanorods, nanoprisms, nanostars, nanobars and nanowires. Such materials are known in the art and may be synthesised using methods disclosed in the literature, for example in Pastoriza-Santos, I. and Liz-Marzan, L. M., Synthesis of silver nanoprisms in DMF, *Nano Letters* 2 (8), 903 (2002) and Kumar, P. S. et al., High-yield synthesis and optical response of gold nanostars, *Nanotechnology* 19 (1) (2008)). Spherical nanoparticles may be synthesised using methods described in Example 1 herein.

Depending on the choice of nanoparticle, these may have more than one surface plasmon mode. For example, non-spherical structures such as nanobars will often have more than one surface plasmon resonance; the vis-near IR extinction spectrum of nanobars is characterised by a

transverse plasmon resonance in the visible and a longitudinal resonance in the near-IR region (Nano Lett. Vol. 7, No. 4, 2007).

The energy resulting from excitation of surface plasmon modes by absorption of incident light may be transferred to the second sensitizing agent (dye sensitizer) by near and/or far-field effects. Near-field enhancement of absorption by the dye sensitizer will typically be observed where the plasmonic nanoparticles have at least one dimension in the range 2 to 80 nm, particularly 2 to 20 nm. Far-field enhancement of absorption by the dye sensitizer will typically be observed where the plasmonic nanoparticles have at least one dimension in the range 20 to 200 nm, particularly 80 to 200 nm. Where spherical nanoparticles are employed these will typically have a mean average diameter in the range of from 10 to 100 nm. Nanoparticles of all shapes will typically have at least one dimension falling within one of the indicated ranges (e.g. from 2 to 200 nm) and may fall in these ranges in two or three dimensions. At least two dimensions within the indicated ranges is preferred. For elongated nanowires or nanorods, the direction of the long axis may extend from 10 to 4000 nm, preferably 20 to 1000 nm.

As previously indicated, it is a key aspect of the invention that the metal nanoparticles should be coated in such a way that these are electrically isolated from at least one of the other components of the heterojunction, i.e. isolated either from the n-type material, the p-type organic hole-transporter or both the n-type material and the hole-transporter. In all instances they must be electronically isolated from the second sensitizing component, the dye-sensitizer. Any coating material should be substantially transparent to the optical field but capable of electrically insulating the metal structures to at least some extent from the photogenerated charge within the device. Suitable coating materials include not only insulating, but also semi-conductor, materials. Insulating materials which may be used include those having a band gap of greater than 3 eV, preferably greater than 5 eV, more preferably 5 to 30 eV. Examples of suitable insulating materials include  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{HfO}$ ,  $\text{ZrO}$ ,  $\text{ZnO}$ ,  $\text{HfO}_2$ ,  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{W}_2\text{O}_5$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{NiO}$ . Amongst these,  $\text{SiO}_2$  is particularly preferred. Semi-conducting materials which may be used include oxides of Ti, Sn, W, Nb, Cu, Zn, Mo and mixtures thereof, e.g.  $\text{TiO}_2$  and  $\text{SnO}_2$ . The use of inorganic materials is preferred. The use of organic materials is not preferred.

The thickness of the coating on the nanoparticles will depend on the nature of the coating material, for example, whether this is a semi-conductor or insulator. A typical coating thickness may lie in the range 0.1 to 100 nm, more preferably 0.5 to 10 nm, e.g. 2 to 5 nm.

Techniques for use in coating the nanoparticles are well known in the art and include methods described in Example 1 herein.

The plasmonic sensitizing agent may be incorporated at any location (or locations) within the p-n heterojunction. More specifically, this may be incorporated at one or more of the following sites:

- i) within a mesoporous layer of n-type material;
- ii) at the junction between the n-type material and the hole transporter;
- iii) between a compact layer of n-type material and a mesoporous layer of n-type material;
- iv) within the hole transporter;
- v) between the anode and a compact layer of n-type material; and
- vi) between the hole transporter and the cathode.

These sites are shown schematically in accompanying Figure 3. Typically, the plasmonic sensitizing agent will be incorporated within the mesoporous layer of the n-type semi-conductor material.

Particularly preferred for use in the invention are silica-coated gold nanoparticles, for example those in which the diameter of the gold particles is, for example 5 to 25 nm, preferably about 13 nm and the thickness of the silica coating is 1 to 7 nm, preferably about 3 nm. These nanoparticles are preferably incorporated into the device by coating the dye-sensitized mesoporous n-type material with the silica-coated gold nanoparticles prior to hole-transporter infiltration.

The presence of one or more types of coated nanoparticles in any of the positions i) to vi) in no way precludes the inclusion of the same or different coated nanoparticles at any other site. In one embodiment, at least one type of coated nanoparticles providing at least some near-field enhancement of the second sensitizer is included at one of more of sites i) to vi) (e.g. at site i), at site ii) and/or at site iii)). In an alternative or combined embodiment, at least one type of coated nanoparticles providing at least some far-field enhancement of the second sensitizer is included at one of more of sites i) to vi) (e.g. at site iv), at site v) and/or at site vi)).

In any embodiment, but particularly in the case where the plasmonic nanoparticles are provided at the junction between the n-type material and the hole transporter (i.e. the nanoparticles are distributed at the surface of the n-type material), a coating of a further semi-conductor material may be provided over the surface of the bulk n-type material and over the coated nanoparticles (where present). This additional coating may comprise a semiconductor material which is the same or different to the semiconductor of the bulk of the n-type material. However, this will generally be the same material as that used for the bulk of the n-type material. Semi-conductor materials which may be used to provide this additional coating may be any of those herein

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described in respect of the bulk n-type material, but preferably will be selected from  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{WO}_3$ ,  $\text{NiO}$ ,  $\text{PbO}$ . The coating will generally be of the order of 0.2 to 100 nm in thickness, preferably 1 to 10 nm more preferably 2 to 5 nm.

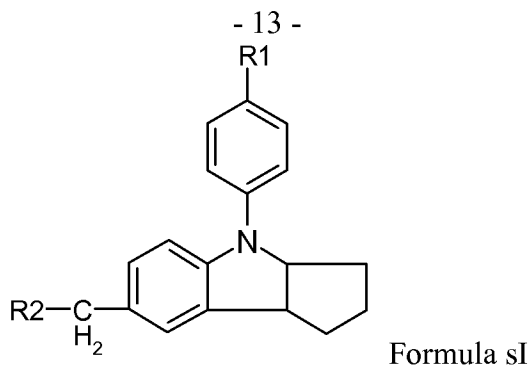
In one optional embodiment of the present invention, the coated metal nanoparticles of the first sensitizing agent are discrete and although they may optionally be fused to the n-type material they are not fused to each other. Similarly, in one optional embodiment, the coated metal nanoparticles are not sintered to form a matrix but rather remain as discrete particles.  $\text{TiO}_2$  may be used as the coating material in some embodiments, however, in a further optional embodiment, the coating of the coated nanoparticles is optionally an insulating or semi-conducting material not comprising  $\text{TiO}_2$ . Alternatively or additionally,  $\text{ZnO}$  may be used as the coating material in some embodiments, however, in a further optional embodiment, the coating of the coated nanoparticles is optionally an insulating or semi-conducting material not comprising  $\text{ZnO}$ . In particular, the metal nanoparticles may optionally not be arranged as a fused matrix of  $\text{TiO}_2$ -coated particles. The metal nanoparticles may further optionally not be arranged as a fused matrix of  $\text{ZnO}$ -coated particles.

In one preferred embodiment, the material forming the coating of the coated metal nanoparticles is not the same material as forms the bulk of the n-type semiconductor material and is preferably not the same as any material comprised in the n-type semiconductor material. In one embodiment the coating material is insulating and the n-type material is semiconducting. Correspondingly, the coating material may have a higher band gap than the n-type material.

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 in addition to the plasmonic sensitizer. Referred to herein as the second sensitizing agent, this material may be a dye or any material which generates an electronic excitation as a result of photon absorption and which is capable of electron injection into the n-type material. 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.

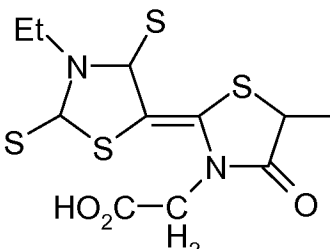
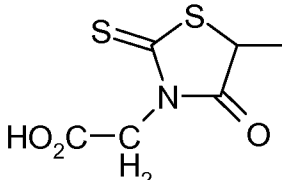
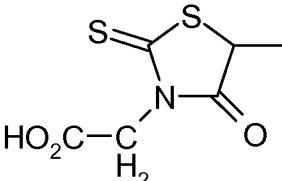
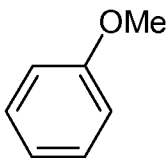
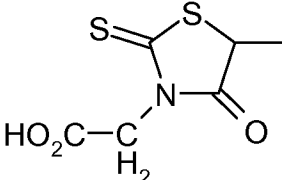
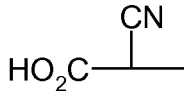
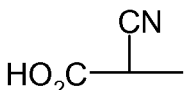
A common category of organic dye sensitizers are indolene based dyes, of which D102, D131 and D149 (shown below) are particular examples.

The general structure of indolene dyes is that of Formula SI below:



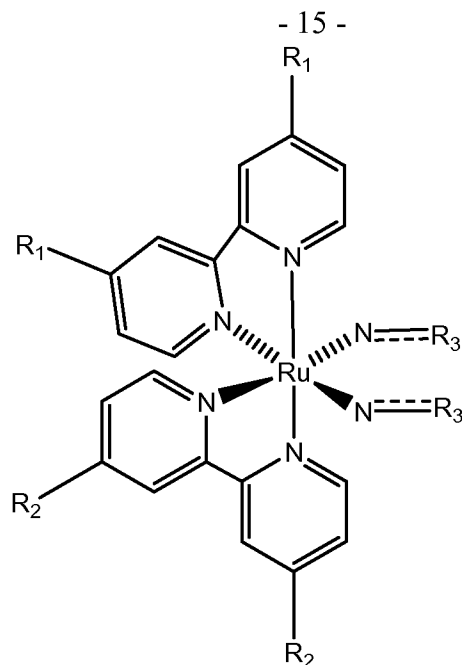
wherein R1 and R2 are independently optionally substituted alkyl, alkenyl, alkoxy, heterocyclic and/or aromatic groups, preferably with molecular weight less than around 360 amu. Most preferably, R1 will comprise aralkyl, alkoxy, alkoxy aryl and/or aralkenyl groups (especially groups of formula  $C_xH_yO_z$  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:

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| Dye Name         | R <sub>1</sub>                                                                      | R <sub>2</sub>                                                                       |
|------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| D <sub>149</sub> | Ph <sub>2</sub> C=CH                                                                |    |
| D <sub>102</sub> | Ph <sub>2</sub> C=CH                                                                |    |
| D <sub>77</sub>  | OMe                                                                                 |   |
| D <sub>103</sub> |  |  |
| D <sub>131</sub> | Ph <sub>2</sub> C=CH                                                                |  |
| D <sub>120</sub> | OMe                                                                                 |  |

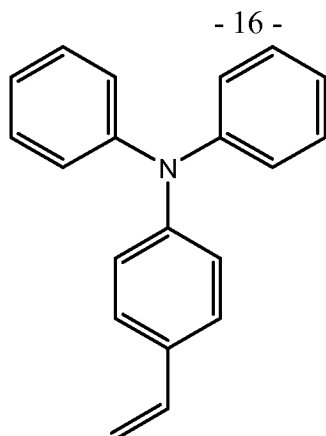
Indolene dyes are discussed, for example, in Horiuchi et al. J Am. Chem. Soc. **126** 12218-12219 (2004), which is hereby incorporated by reference.

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



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 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  $CHa-Z$  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 such a hetero atom or group as appropriate; R3 is preferably  $=C=S$ .

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:

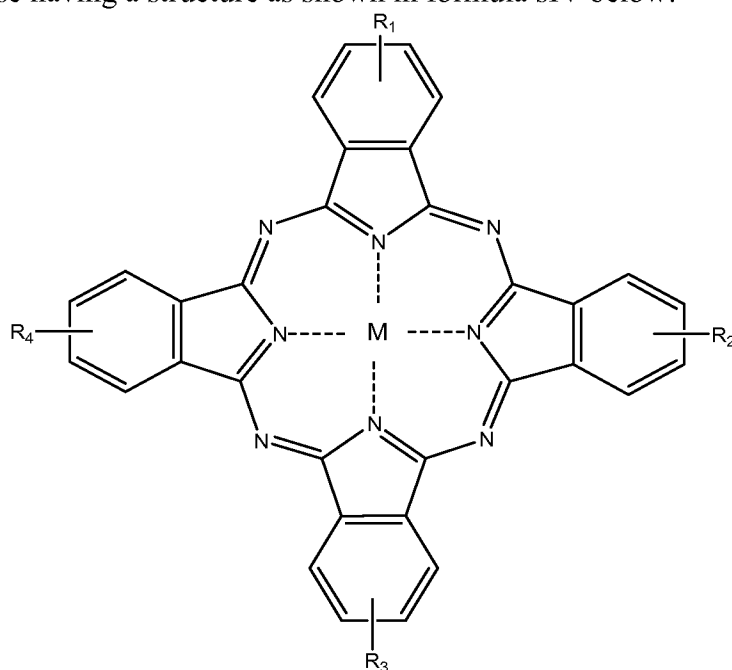


Formula sIII

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 Chimica 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.

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.

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:

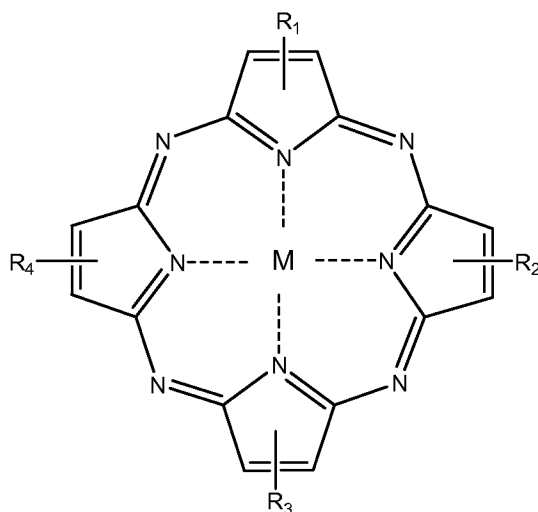


Formula sIV

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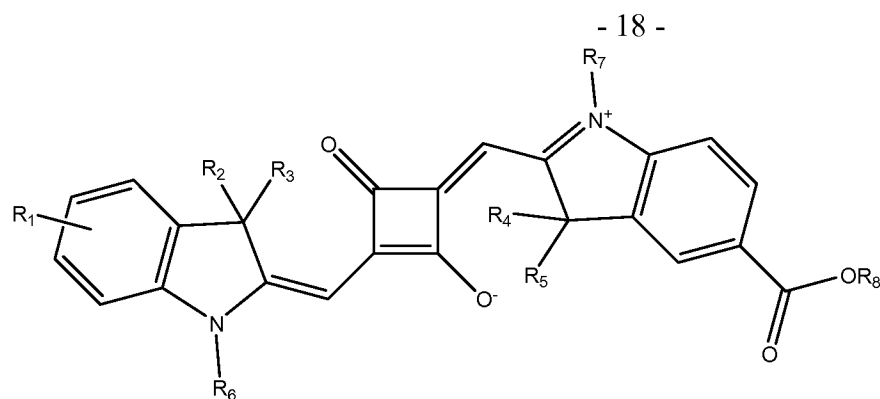
Wherein M is a metal ion, such as a transition metal ion, and may be an ion of Co, Fe, Ru, Zn or a mixture thereof. Zinc ions are preferred. Each of R1 to R4, which may be the same or different is preferably straight or branched chain alkyl, alkoxy, carboxylic acid or ester groups such as  $C_nH_{2n+1}$  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 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  $CO_2H$ .

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 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:



Formula sV

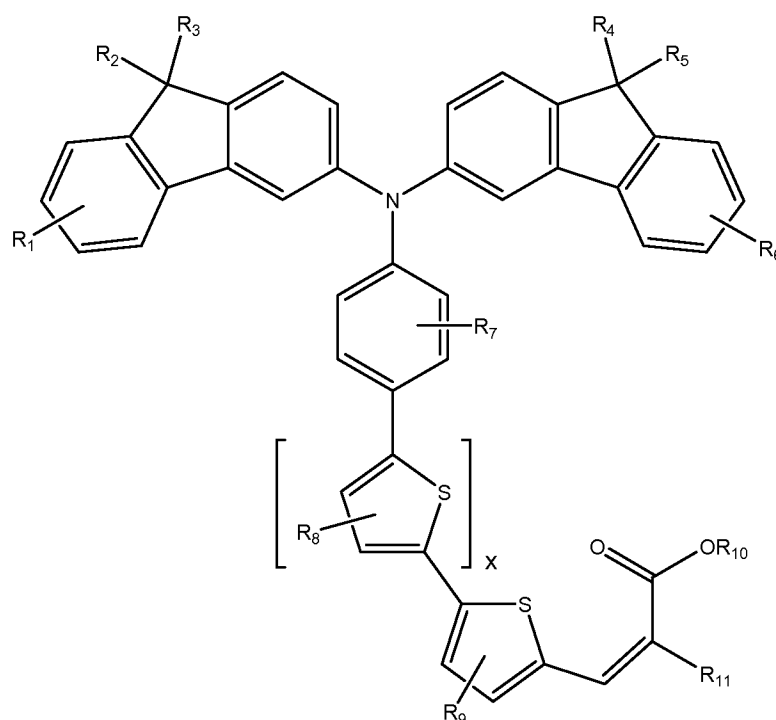
Squaraine dyes form a preferred category of dye for use in the present invention. The above Burke citation provides information on Squaraine dyes, but briefly, these may be, for example, of the following formula sVI



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 will 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 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).

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



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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 each of 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 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.

Although many of the dyes indicated above show broad spectrum absorption in the visible region, one of the key advantages of the present invention is that the 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.

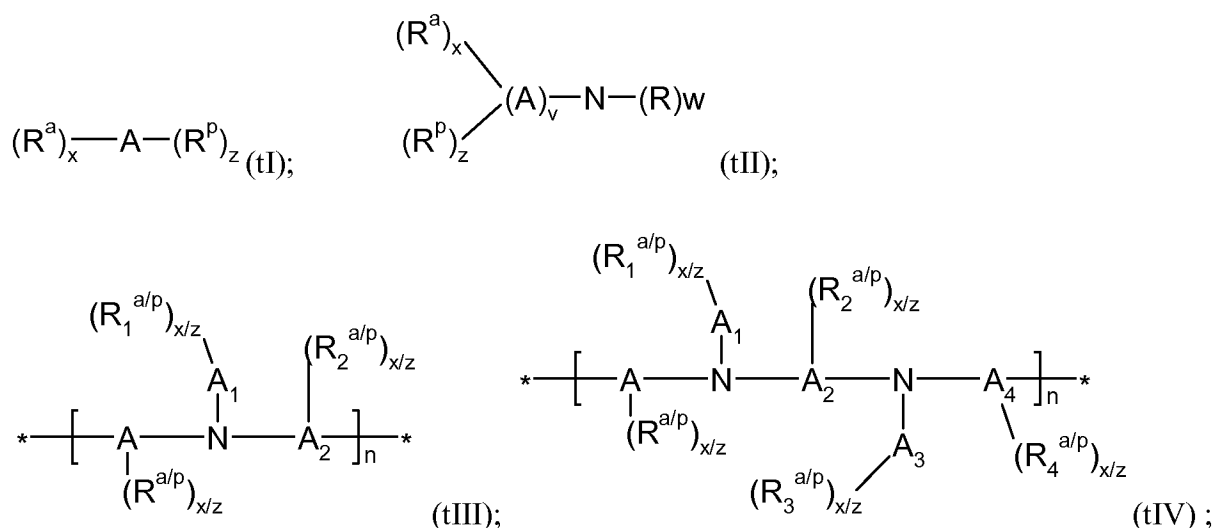
Whilst it is envisaged that in general only a single dye sensitizer will be employed in the p-n heterojunctions herein described, two or more dye sensitizers may nevertheless be used. For example, all aspects of the present invention are suitable for use with co-sensitisation using a plurality of (e.g. at least 2, such as 2, 3, 4 or 5) different 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 from one dye to another of lower energy, from which it is then injected into the n-type material. However, it is preferable 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 complimentary absorption characteristics. Some complimentary pairings include, for example, the near-infra red absorbing zinc phthalocyanine dyes referred to above in combination with indoline or ruthenium-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 light absorbing polyfluorene polymer with a near IR absorbing zinc phthalocyanine or squaraine dye.

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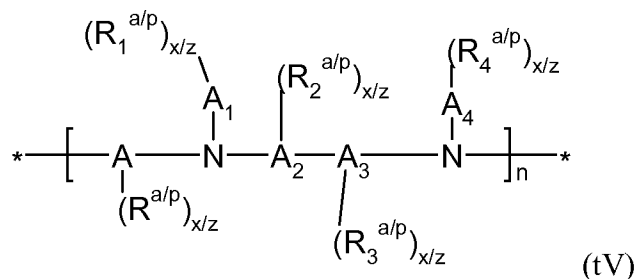
Two or more dye sensitizers may, for example, be used where the plasmonic nanoparticles have two or more surface plasmon modes. Such a situation may arise either where a plurality of different plasmonic nanoparticles are used having different surface plasmon modes or, alternatively, where any given plasmonic nanoparticle may have different surface plasmon modes (for example due to its shape and/or dimensions). In cases such as this, it may be advantageous that each of the different surface plasmon modes overlaps with the absorption spectrum of a different dye sensitizer(s) thereby maximising the number of electrons injected into the n-type material.

In all aspects of the present invention a solid state hole transporter is a key constituent, since this forms the p-type material of the p-n heterojunction. The hole transporter will preferably be a molecular p-type material rather than an inorganic material such as a salt, and more preferably will be an organic molecular material. Suitable materials will typically comprise an extended pi-bonding system through which charge may readily pass. Suitable materials will also preferably be amorphous or substantially amorphous solids rather than being crystalline at the appropriate working temperatures (e.g. around 30-70°C). The organic hole-transporter would preferably have a high energy HOMO to LUMO transition, rendering its predominant function dye-regeneration and hole-transport. However, it may optionally have a narrow HOMO to LUMO transition, with its additional function being to absorb solar light, and subsequently transfer an electron to the n-type material, or its excited state energy to a dye molecule tethered to the n-type material surface. The then excited dye molecule would subsequently transfer an electron to the n-type material and the hole to the hole-transporter, as part of the photovoltaic conversion process.

According to a preferred embodiment, the solid state hole transporter is a material comprising a structure according to any of formulae (tI) , (tII), (tIII), (tIV) and/or (tV) below:



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in which N, if present, is a nitrogen atom;

n, if applicable, is in the range of 1-20;

A is a mono-, or polycyclic system comprising at least one pair of a conjugated double bond (-C=C-C=C-), the cyclic system optionally comprising one or several heteroatoms, and optionally being substituted, whereby in a compound comprising several structures A, each A may be selected independently from another A present in the same structure (tII - tV);

each of A<sub>1</sub>-A<sub>4</sub>, if present, is an A independently selected from the A as defined above;

v in (tII) recites the number of cyclic systems A linked by a single bond to the nitrogen atom and is 1, 2 or 3;

(R)<sub>w</sub> is an optional residue selected from a hydrocarbon residue comprising from 1 to 30 carbon atoms, optionally substituted and optionally comprising 1 or several heteroatoms, with w being 0, 1 or 2 provided that v + w does not exceed 3, and, if w = 2, the respective R<sub>w1</sub> or R<sub>w2</sub> being the same or different;

R<sub>a</sub> represents a residue capable, optionally together with other R<sub>a</sub> present on the same structure (tI-tV), of decreasing the melting point of an organic compound and is selected from a linear, branched or cyclic alkyl or a residue comprising one or several oxygen atoms, wherein the alkyl or the oxygen comprising residue is optionally halogenated;

x is the number of independently selected residues R<sub>a</sub> linked to an A and is selected from 0 to a maximum possible number of substituents of a respective A, independently from the number x of other residues R<sub>a</sub> linked to another A optionally present;

with the proviso that per structure (tI-tV) there is at least one R<sub>a</sub> being an oxygen-containing residue as defined above; and, if several R<sub>a</sub> are present on the same structure (I-V), they are the same or different; and wherein two or more R<sub>a</sub> may form an oxygen-containing ring;

R<sub>p</sub> represents an optional residue enabling a polymerisation reaction with compounds comprising structure (tI - tV) used as monomers, and/or a cross-linking between different compounds comprising structures (tI - tV);

z is the number of residues R<sub>p</sub> linked to an A and is 0, 1, and/or 2, independently from the number z of other residues R<sub>p</sub> linked to another A optionally present;

R<sub>p</sub> may be linked to an N-atom, to an A and/or to a substituent R<sub>p</sub> of other structures according (tI - tV), resulting in repeated, cross-linked and/or polymerised moieties of (tI - tV);

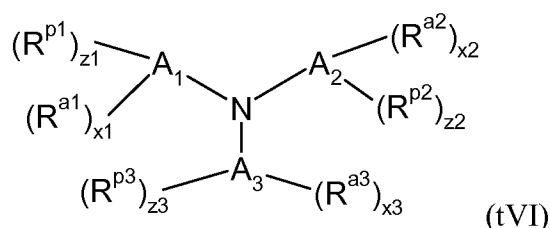
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$(R^{a/p})_{x/z}$  and  $(R_{1-4}^{a/p})_{x/z}$ , if present, represent independently selected residues Ra and Rp as defined above.

Preferably, the charge transporting material comprises compounds having the structures (tI) – (tV).

General reference to the several structures, such as in the references “(tI-tV)”, “(tVII-tXVI)”, or “A<sub>1</sub>-A<sub>4</sub>”, for example, means reference to any one selected amongst (tI), (tII), (tIII), (tIV), or (tV), any one selected amongst (tVII), (tVIII), (tIX), (tX), (tXI), (tXII), (tXIII), (tXIV), (tXV) or (tXVI), or any one selected amongst A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> or A<sub>4</sub>, respectively. In addition, in the charge transporting material for use in the invention, for example, different compounds of structures (tI-tV) may be combined and, if desired cross-linked and/or polymerised. Similarly, in any structure (tI-tV), different structures for A may be selected independently, for example from (tVII-tXVI).

According to a preferred embodiment, the organic charge transporting material of the device of the invention comprises a structure according to formula (tVI):



in which Ra1, Ra2 and Ra3 and x1, x2 and x3 are defined, independently, like Ra and x, respectively, above;

Rp1, Rp2 and Rp3 and z1, z2 and z3 are defined, independently, like Rp and z, respectively, above. Formula (tVI) thus represents a specimen of formula (tII) above, in which v is 3, and in which R(w) is absent.

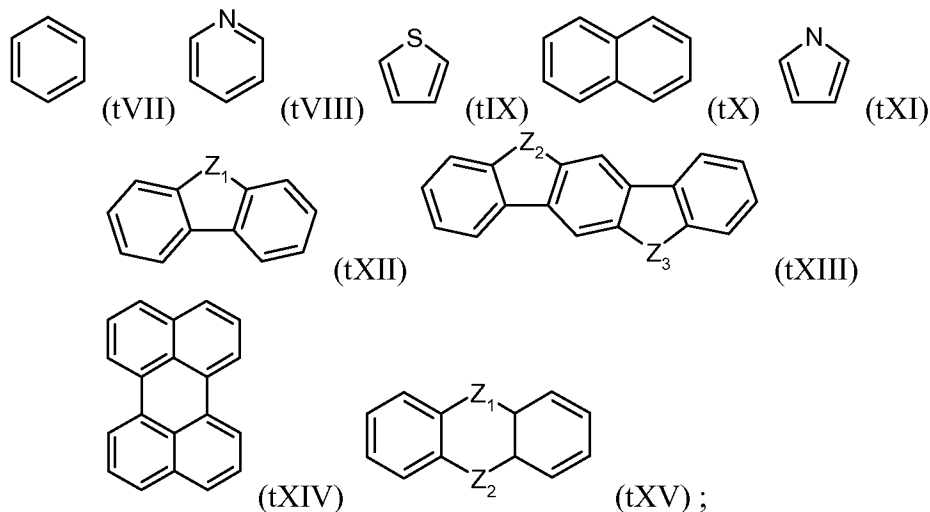
Preferably, A is a mono- or polycyclic, optionally substituted aromatic system, optionally comprising one or several heteroatoms. Preferably, A is mono-, bi- or tricyclic, more preferably mono-, or bicyclic. Preferably, if one or more heteroatoms are present, they are independently selected from O, S, P, and/or N, more preferably from S, P and/or N, most preferably they are N-atoms.

According to a preferred embodiment, A is selected from benzol, naphthalene, indene, fluorene, phenanthrene, anthracene, triphenylene, pyrene, pentalene, perylene, indene, azulene, heptalene, biphenylene, indacene, phenalene, acenaphtene, fluoranthene, and heterocyclic compounds such as pyridine, pyrimidine, pyridazine, quinolizidine, quinoline, isoquinoline, quinoxaline,

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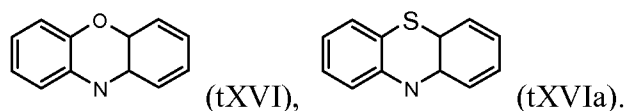
phthalazine, naphthyridine, quinazoline, cinnoline, pteridine, indolizine, indole, isoindole, carbazole, carboline, acridine, phenanthridine, 1,10-phenanthroline, thiophene, thianthrene, oxanthrene, and derivatives thereof, each of which may optionally be substituted.

According to a preferred embodiment, A is selected from structures of formula (tVII-tXIV) given below:



in which each of Z<sup>1</sup>, Z<sup>2</sup> and Z<sup>3</sup> is the same or different and is selected from the group consisting of O, S, SO, SO<sub>2</sub>, NR<sup>1</sup>, N<sup>+</sup>(R<sup>1'</sup>)(R<sup>1''</sup>), C(R<sup>2</sup>)(R<sup>3</sup>), Si(R<sup>2</sup>)(R<sup>3</sup>) and P(O)(OR<sup>4</sup>), wherein R<sup>1</sup>, R<sup>1'</sup> and R<sup>1''</sup> are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups, haloalkyl groups, alkoxy groups, alkoxyalkyl groups, aryl groups, aryloxy groups, and aralkyl groups, which are substituted with at least one group of formula -N<sup>+</sup>(R<sup>5</sup>)<sub>3</sub> wherein each group R<sup>5</sup> is the same or different and is selected from the group consisting of hydrogen atoms, alkyl groups and aryl groups, R<sup>2</sup>, R<sup>3</sup>, R<sup>2'</sup> and R<sup>3'</sup> are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups, haloalkyl groups, alkoxy groups, halogen atoms, nitro groups, cyano groups, alkoxyalkyl groups, aryl groups, aryloxy groups and aralkyl groups or R<sup>2</sup> and R<sup>3</sup> together with the carbon atom to which they are attached represent a carbonyl group, and R<sup>4</sup> is selected from the group consisting of hydrogen atoms, alkyl groups, haloalkyl groups, alkoxyalkyl groups, aryl groups, aryloxy groups and aralkyl groups.

Preferred embodiments of, structure (tXV) for A may be selected from structures (tXVI) and (tXVIa) below:



Preferably, in any structure of (tI-tV) all A are the same, but differently substituted. For example, all A are the same, some of which may be substituted and some of which are not. Preferably, all A are the same and identically substituted.

Any A may be substituted by other substituents than Ra and/or Rp. Other substituents may be selected at the choice of the skilled person and no specific requirements are indicated herein with respect to them. Other substituents may thus correspond to (R)<sub>w</sub> in (tII) defined above. Other substituents and R(w) may generally be selected from linear, branched or cyclic hydrocarbon residues comprising from 1 to 30 carbon atoms, optionally substituted and optionally comprising 1 or several heteroatoms, for example. The hydrocarbon may comprise C-C single, double or triple bonds. For example, it may comprise conjugated double bonds. For example, optional other residues on A may be substituted with halogens, preferably -F and/or -Cl, with -CN or -NO<sub>2</sub>, for example.

One or more carbon atoms of other substituents of A may or may not be replaced by any heteroatom and/or group selected from the group of -O-, -C(O)-, -C(O)O-, -S-, -S(O)-, SO<sub>2</sub>-, -S(O)<sub>2</sub>O-, -N=, -P=, -NR'-, -PR'-, -P(O)(OR')-, -P(O)(OR')O-, -P(O)(NR'R')-, -P(O)(NR'R')O-, P(O)(NR'R')NR'-, -S(O)NR'-, and -S(O)<sub>2</sub>NR', with R' being H, a C1-C6 alkyl, optionally partially halogenated.

According to a preferred embodiment, any A may optionally be substituted with one or several substituents independently selected from nitro, cyano, amino groups, and/or substituents selected from alkyl, alkenyl, alkynyl, haloalkyl, alkoxy, and alkoxyalkyl groups, including substituted substituents. Alkyl, alkenyl, alkynyl, haloalkyl, alkoxy and alkoxyalkyl are as defined below.

Preferably, further residues optionally present on A, such as R(w) in (tII), for example, are selected from C4-C30 alkenes comprising two or more conjugated double bonds.

Ra may be used as a residue capable of controlling the melting point of an organic, charge-transporting compound. The reference with respect to the ability to control the melting point is the same charge transporting material devoid of the at least one residue Ra. In particular, the function of Ra is to provide a charge transporting material that adopts the desired phase at the temperatures indicated herein. The adjustment of the melting point to obtain the desired characteristics in the temperature ranges indicated above may be brought about by a single residue Ra or a combination of identical or different residues Ra, present in any of the structures (tI)-(tV).

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At least one linear, branched or cyclic residue containing one or several oxygen atoms may be used for lowering the melting point, and thus the absence of such residues or alternative residues may be used to correspondingly raise melting points, thus obtaining the desired characteristics. Other residues, include for example alkyls as defined below, may assist in the adjustment of the melting point and/or phase characteristics.

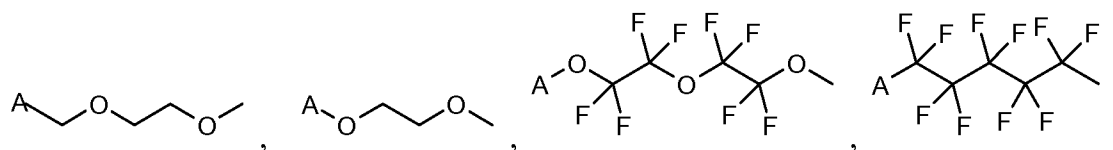
Ra may be halogenated and/or perhalogenated in that one, several or all H of the residue Ra may be replaced with halogens. Preferably, the halogen is fluorine.

If Ra is oxygen containing compound, it is preferably a linear, branched, or cyclic saturated C1-C30 hydrocarbon comprising 1 – 15 oxygen atoms, with the proviso that the number of oxygen atoms does preferably not exceed the number of carbons. Preferably, Ra comprises at least 1.1 to 2 as much carbon as oxygen atoms. Preferably, Ra is a C2 – C20, saturated hydrocarbon comprising 2-10 oxygen atoms, more preferably a C3-C10 saturated hydrocarbon comprising 3-6 oxygen atoms.

Preferably, Ra is linear or branched. More preferably Ra is linear.

Preferably, Ra is selected from a C1-C30, preferably C2-C15 and most preferably a C3-C8 alkoxy, alkoxyalkyl, alkoxyalkoxy, alkylalkoxy group as defined below.

Examples of residues Ra may independently be selected from the following structures:



with A indicating any A in formula (tI-V) above.

Any Ra present may be linked to a carbon atom or a heteroatom optionally present in A. If Ra is linked to a heteroatom, it is preferably linked to a N-atom. Preferably, however, any Ra is linked to a carbon atom. Within the same structure (tI-tV), any Ra may be linked to a C or a heteroatom independently of another Ra present on the same A or in the same structure.

Preferably, every structure A, such as A, A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and A<sub>4</sub>, if present in formulae (tI-tV) above comprises at least one residue Ra. For example, in the compound according to structure (tI-tV), at least one structure A comprises an oxygen containing residues Ra as defined above, whereas one or more other and/or the same A of the same compound comprise an aliphatic residue Ra, for

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example an alkyl group as defined below, preferably a C2-C20, more preferably C3-C15 alkyl, preferably linear.

The following definitions of residues are given with respect to all reference, to the respective residue, in addition to preferred definitions optionally given elsewhere. These apply specifically to the formulae relating to hole transporters (tN formulae) but may optionally also be applied to all other formulae herein where this does not conflict with other definitions provided.

An alkoxyalkoxy group above is an alkoxy group as defined below, which is substituted with one or several alkoxy groups as defined below, whereby any substituting alkoxy groups may be substituted with one or more alkoxy groups, provided that the total number of 30 carbons is not exceeded.

An alkoxy group is a linear, branched or cyclic alkoxy group having from 1 to 30, preferably 2 to 20, more preferably 3-10 carbon atoms.

An alkoxyalkyl group is an alkyl group as defined below substituted with an alkoxy group as defined above.

An alkyl group is a linear, branched and/or cyclic having from 1-30, preferably 2-20, more preferably 3-10, most preferably 4-8 carbon atoms. An alkenyl groups is linear or branched C2-C30, preferably C2-C20, more preferably C3-C10 alkenyl group. An alkynyl group is a linear or branched C2-C30, preferably C2-C20, more preferably C3-C10 linear or branched alkynyl group. In the case that the unsaturated residue, alkenyl or alkynyl has only 2 carbons, it is not branched.

A haloalkyl groups above is an alkyl groups as defined above which is substituted with at least one halogen atom.

An alkylalkoxy group is an alkoxy group as defined above substituted with at least one alkyl group as defined above, provided that the total number of 30 carbons is not exceeded.

The aryl group above and the aryl moiety of the aralkyl groups (which have from 1 to 20 carbon atoms in the alkyl moiety) and the aryloxy groups above is an aromatic hydrocarbon group having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above and alkoxy groups as defined above.

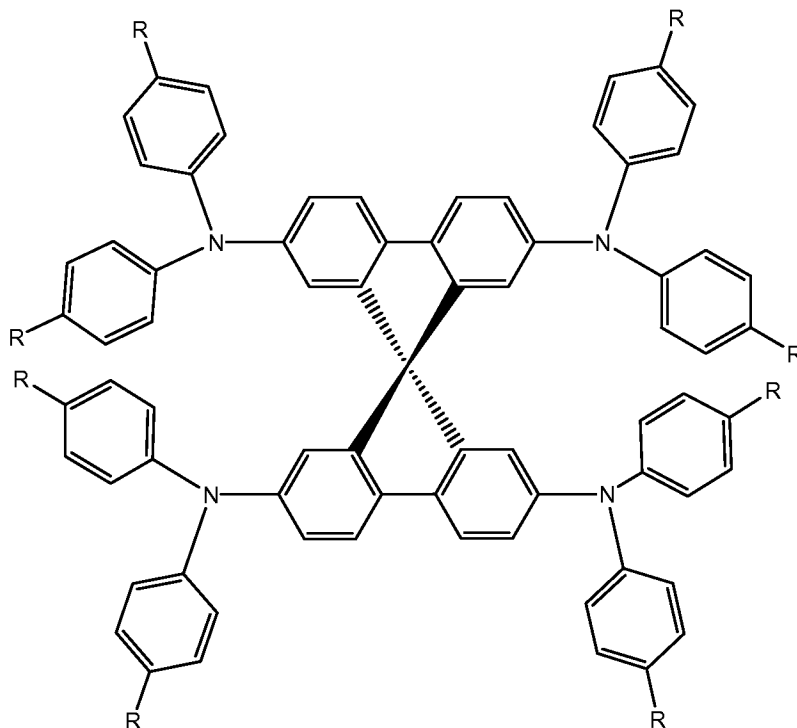
The organic charge transporting material may comprise a residue  $R_p$  linked to an A. According to a preferred embodiment,  $R_p$  is selected from vinyl, allyl, ethinyl, independently from any other  $R_p$  optionally present on the A to which it is linked or optionally present on a different A within the structures (tI) and/or (tII).

The charge transporting material comprised in the device of the invention may be selected from compounds corresponding to the structures of formulae (tI-tV) as such. In this case,  $n$ , if applicable, is 1 and the charge transporting material comprises individual compounds of formulae (tI-tV), or mixtures comprising two or more different compounds according formulae (tI-tV).

The compounds of structures (tI-tV) may also be coupled (e.g. dimerised), oligomerised, polymerized and/or cross-linked. This may, for example, be mediated by the residue  $R_p$  optionally present on any of the structures (tI-tV). As a result, oligomers and/or polymers of a given compound selected from (tI-tV) or mixtures of different compounds selected from structures (tI-tV) may be obtained to form a charge transporting material. Small  $n$  is preferably in the range of 2-10.

A particularly preferred organic molecular hole transporter contains a spiro group to retard crystallisation. A most preferred organic hole transporter is a compound of formula tXVII below, and is described in detail in Snaith et al. Applied Physics Letters **89** 262114 (2006), which is herein incorporated by reference.

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Formula tXVII

wherein R is alkyl or O-alkyl, where the alkyl group is preferably methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or tert-butyl, preferably methyl.

In particular, the present invention relates to SDSCs, which is to say solid-state dye sensitized solar cells. Thus it is preferable that the heterojunctions, devices and solar cells of the present invention do not contain a liquid electrolyte. Rather the SDSCs of the invention should preferably contain an organic hole transporter such as a molecular hole transporter. An iodine/iodide redox couple electrolyte is particularly preferably not present. This is due to the corrosive nature of the electrolyte and the difficulties in liquid handling, storage etc. and long term stability.

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.  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  are common examples, as are MgO and  $\text{SnO}_2$ . The n-type material is used in the form of a layer and will typically be mesoporous providing a relatively thick layer of around 0.05 - 100  $\mu\text{m}$  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  $\text{SnO}_2$ . This can greatly reduce the fast recombination from the n-type

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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.  $\text{SnO}_2$ ) 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, teluride, and/or multicomponent semiconductor, any of which may be coated as described above. Suitable materials include single metal oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{W}_2\text{O}_5$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{MoO}_3$ ,  $\text{PbO}$ ,  $\text{CdO}$  and/or  $\text{MnO}$ ; compound metal oxides such as  $\text{Zn}_x\text{Ti}_y\text{O}_z$ ,  $\text{ZrTiO}_4$ ,  $\text{ZrW}_2\text{O}_8$ ,  $\text{SiAlO}_{3.5}$ ,  $\text{Si}_2\text{AlO}_{5.5}$ ,  $\text{SiTiO}_4$  and/or  $\text{AlTiO}_5$ ; 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  $\text{Cs}_2\text{C}_5$ ; sulphides such as  $\text{PbS}$ ,  $\text{CdS}$ ,  $\text{CuS}$ ; selenides such as  $\text{PbSe}$ ,  $\text{CdSe}$ ; telurides such as  $\text{CdTe}$ ; nitrides such as  $\text{TiN}$ ; and/or multicomponent semiconductors such as  $\text{CIGaS}_2$ .

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. In one optional embodiment the particles sintered to form a porous layer of n-type material are not surface coated.

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 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

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planar film may also or alternatively have a thickness of 0.005 to 5  $\mu\text{m}$ , preferably 0.025 to 0.2  $\mu\text{m}$ , and more preferably 0.05 to 0.1  $\mu\text{m}$ .

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 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 or -4.7 to -1 eV, such as -4.7 to -2.5 eV, or -4.5 to -3 eV

Suitable coating materials, where present, include single metal oxides such as MgO,  $\text{Al}_2\text{O}_3$ , ZrO, ZnO,  $\text{HfO}_2$ ,  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{W}_2\text{O}_5$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , NiO,  $\text{MoO}_3$ , PbO, CdO and/or MnO; compound metal oxides such as  $\text{Zn}_x\text{Ti}_y\text{O}_z$ ,  $\text{ZrTiO}_4$ ,  $\text{ZrW}_2\text{O}_8$ ,  $\text{SiAlO}_{3.5}$ ,  $\text{Si}_2\text{AlO}_{5.5}$ ,  $\text{SiTiO}_4$  and/or  $\text{AlTiO}_5$ ; 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; carbonates such as  $\text{Cs}_2\text{C}_5$ ; 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  $\text{CIGaS}_2$ . Some suitable materials are discussed in Grätzel (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 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.

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 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 impurities, or may alternatively be doped in order to optimise the function of the p-n-heterojunction device, for

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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  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$  and  $\text{WO}_3$  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).

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 where context allows, unless indicated otherwise.

In one preferred aspect of the present invention, the n-type semiconductor material is in the form of a nanostructured porous layer. In a further preferred embodiment, that layer does not surround the coated metal nanoparticles. In one preferred embodiment, the coated metal nanoparticles are substantially not encapsulated by the n-type semiconductor material.

The method of the present invention provides for the production of a solid state p-n heterojunction by incorporation of a plasmonic sensitizing agent. More particularly, the invention provides a method for the manufacture of a solid-state p-n heterojunction incorporating a first sensitizing agent which comprises coated nanoparticles of at least one metal and a second sensitizing agent which comprises at least one molecular or polymeric sensitizing agent, said method comprising:

- a) coating a cathode with a compact layer of an n-type semiconductor material;
- b) optionally forming a porous layer of an n-type semiconductor material on said compact layer;
- c) surface sensitizing said compact layer or, where present, said porous layer with said second sensitizing agent (if applicable);

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- d) forming a layer of a solid-state p-type semiconductor material in contact with said compact layer or, where present, said porous layer of an n-type semiconductor material; and
- e) forming an anode on said p-type semiconductor material;

wherein said first sensitizing agent is incorporated before step a), before step b), during step b), before step c), during step c), before step d), during step d), and/or before step e).

In one embodiment of the invention, a further layer of an n-type semiconductor may be formed over the bulk structure of the n-type semi-conductor. In this aspect, step b) may comprise the following steps:

- b1) forming a porous layer of an n-type semiconductor material from particles of an n-type semiconductor material and optionally from particles of said first sensitizing agent;
- b2) optionally surface sensitizing said porous layer of an n-type semiconductor material with particles of said first sensitizing agent; and
- b3) optionally depositing a layer of n-type semiconductor material on the surface of said porous layer of an n-type semiconductor material.

The invention is illustrated further in the following non-limiting examples and in the attached Figures, in which:

- Figure 1 - represents an organic solid state dye sensitised solar cell formed with a mesoporous  $\text{TiO}_2$  n-type semiconductor material.
- Figure 2 - shows a schematic representation of charge transfers taking place in DSC operation.  $h\nu$  indicates light absorption,  $e^- \text{inj}$  = electron injection,  $\text{rec}$  = recombination between electrons in the n-type and holes in the p-type material,  $h^+ \text{inj}$  = hole-transfer (dye regeneration), CB = conduction band.
- Figure 3 - represents organic solid-state dye sensitised solar cells in accordance with the invention which incorporate plasmonic particles a) within the mesoporous  $\text{TiO}_2$  phase, b) between the dye-coated  $\text{TiO}_2$  and the hole-transporter, c) between the compact  $\text{TiO}_2$  layer and the mesoporous  $\text{TiO}_2$  layer, d) between the FTO and the compact  $\text{TiO}_2$  layer, e) within the hole-transporter phase and f) between the hole-transporter and the top metallic electrode.

Figure 4 - shows Incident Photon-to-electron Conversion Efficiency (IPCE) for a plasmonic DSC incorporating SiO<sub>2</sub>-gold nanoparticles and for a standard solid-state DSC. The plasmonic DSC incorporated 13nm diameter Au nanoparticles coated with 3nm thick SiO<sub>2</sub> shells. The nanoparticles were incorporated into the film after dye-sensitization, but prior to hole-transporter infiltration, similar to the structure illustrated in Figure 3b. The mesoporous metal oxide was TiO<sub>2</sub> the dye sensitizer is termed Z907, and the hole-transporter is termed spiro-OMeTAD, familiar to those skilled in the art and as described in reference, [Schmidt-Mende et al, Appl. Phys. Lett. 86, 013504 (2005)]

Figures 5a, b - show solar cell performance characteristics of a plasmonic DSC, measured under simulated sunlight of 100 mWcm<sup>-2</sup>, with varying concentrations of the plasmonic metal (Au). 5a) shows short-circuit current and 5b) shows power conversion efficiency. The concentration of the Au refers to an arbitrary concentration of the nanoparticles in ethanol from which they are cast. Note that in each figure zero concentration refers to the standard solar cell.

Figure 7: provides TEM images showing,

a) ~15 nm diameter bare gold nanoparticles, and

b) Au-SiO<sub>2</sub> core-shell nanoparticles with ~15 nm Au cores encapsulated by ~ 3 nm silica shells.

c) The absorption spectra of thin films (~ 1 μm) processed with conventional mesoporous TiO<sub>2</sub> paste at different stages in the fabrication process; directly after doctor blade coating (open-symbols, “pre-sinter”), after two thermal sintering stages at 500 °C and a chemical TiCl<sub>4</sub> treatment (open-symbols with cross-through, “post-sinter”), and with final dye-sensitization with Z907 ruthenium complex (solid-symbols). These are for TiO<sub>2</sub> paste incorporating bare Au nanoparticles (blue circles) and Au-SiO<sub>2</sub> core shell nanoparticles (red squares). Also shown is the absorption spectra of a standard mesoporous TiO<sub>2</sub> film sensitized with Z907 (solid-line).

d) Transmission and reflection spectra for mesoporous TiO<sub>2</sub> films incorporation core-shell nanoparticles of similar concentration to those shown in (c).

Figure 8: a) shows current-voltage characteristic for N719 sensitized liquid electrolyte based DSSCs of 1.1 μm thickness with dye only (open-circles) and with the incorporation of the Au-SiO<sub>2</sub> core (15nm)-shell (3nm) nanoparticles into the paste (squares). Dye only devices showed an average efficiency of  $1.08 \pm 10\%$ , while those incorporating Au-SiO<sub>2</sub> nanoparticles produced an average efficiency of  $1.65 \pm 0.32\%$ .

b) Normalized absorption (as  $1 - \text{transmission} - \text{reflection}$ ) and spectral response of liquid electrolyte based DSSCs sensitized with the Black Dye with and without the incorporation of Au-SiO<sub>2</sub> nanoparticles. The spectral response and absorption (not absorbance) are normalized to aid comparison.

Figure 9. shows electronic characterization of solid-state DSSCs sensitized with Z907-only and also incorporating Au-SiO<sub>2</sub> nanoparticles with Z907 sensitization;

a) Incident photon-to-electron conversion efficiency (IPCE) spectra for a typical Z907 dye-only (circles) and with the additional coating of Au-SiO<sub>2</sub> nanoparticles after dye-sensitization (squares), but prior to hole-transporter coating. The curves for both a typical and the best device are shown for both systems.

b) Current density voltage curves measured under simulated AM1.5 sun light at  $100 \text{ mWcm}^{-2}$  for devices with Z907 dye-only (circles) and both Au-SiO<sub>2</sub> and Z907 sensitization (squares).

c-f). Histograms showing the number of devices versus the electrical performance parameters ((c)  $J_{sc}$ , (d)  $V_{oc}$ , (e) FF, and (f)  $\eta$ ) extracted from JV curves measured under AM1.5 simulated sun light of  $100 \text{ mWcm}^{-2}$  for a series of around 60 devices for both dye-only (solid bars) and Au-SiO<sub>2</sub> nanoparticles (hatched bars). The histograms are fitted with normal distribution curves for the purposes of

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interpretation. The optical density of the Au-SiO<sub>2</sub> nanoparticles within the solid-state DSSCs was around 0.24 and the optical density due to Z907 sensitization was around 0.18, with an average film thickness of 1.2µm. All numerical errors quoted are standard deviation of the mean.

Figure 10: shows the spectroscopic characterization of the Z907-only device and the device incorporating the Au-SiO<sub>2</sub> nanoparticles.

a) in-phase quasi-cw photoinduced absorption (PIA) spectra from the dye-only device (circles) and the device including Au nanoparticles (squares). Excitation at 560nm, power intensity 40mW/cm<sup>2</sup>. The increase in the negative signal for the device incorporating the Au-SiO<sub>2</sub> nanoparticles indicated increased photo induced charge density.

b) Fractional change in transmission from the dye-only device (circles) and the device including the Au np (squares) taken 400 fs (solid) and 10ps (open) after excitation (we note that the 50ps response is near indistinguishable from 10ps)

c) Transient absorption kinetics at 520 nm. We note that the transient absorption signals at 660nm, where only photo induced absorption bands are observed, showed identical trends to the signals at 520 nm. Excitation was at 555nm. Again the increase in the signal strength in c, with the presence of the Au-SiO<sub>2</sub> metal nanoparticles indicate increased photo induced charge generation.

#### Example 1 - Colloidal gold synthesis and gold-silica nanoparticle synthesis

Colloidal gold nanoparticles and silica coated colloidal gold nanoparticles were synthesised as described in Enustun, B. V. and Turkevich, J., Coagulation of colloidal gold, Journal of the American Chemical Society: 85 (21), 3317 (1963); and in Malikova, N. et al., Layer-by-layer assembled mixed spherical and planar gold nanoparticles: Control of interparticle interactions, Langmuir 18 (9), 3694 (2002). Silica shell thicknesses were varied from 2 to 20 nm and Au nanoparticle sizes were varied from 10 to 70 nm, as determined by transmission electron

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microscopy (TEM). The resulting Au-core silica-shell nanoparticles are referred to herein using the terminology Au@Si.

Example 2 - Preparation of titania paste incorporating Au@Si plasmonic

Titanium dioxide nanoparticle pastes were prepared as described by Barbe, C. J. et al., Nanocrystalline titanium oxide electrodes for photovoltaic applications, Journal of the American Ceramic Society 80 (12), 3157 (1997). Silica coated Au nanoparticles were incorporated into the titania pastes in the following manner:

Following synthesis the colloidal nanoparticles were cleaned by centrifugation and re-suspension in water. They were subsequently precipitated in a centrifuge and re-dispersed in ethanol and precipitated and re-dispersed in ethanol once more to fully clean and remove the majority of water. The highly concentrated Au@Si colloid in ethanol was then mixed with a TiO<sub>2</sub> paste at a predetermined volume ratio. The TiO<sub>2</sub>-paste Au@Si colloid dispersion was shaken for 2 hrs and then probed with an ultrasonic probe for 2 minutes (2 seconds on, 2 seconds off) to ensure complete mixing of the materials.

Example 3 - Electrode preparation for TiO<sub>2</sub> based DSCs

Dye-sensitized solar cells of the present invention may be fabricated using known methods, including techniques such as described in Kavan, L. and Gratzel, M. *Electrochim. Acta* **40**, 643 (1995) and Snaith, H. J. and Gratzel, M., *Adv. Mater.* **18**, 1910 (2006).

**3.1 - Cleaning and etching of the electrodes:**

The dye-sensitized solar cells used and presented in these examples were fabricated as follows: Fluorine doped tin oxide (FTO) coated glass sheets (15  $\Omega$ /square, Pilkington USA) were etched with zinc powder and HCl (4N) to give the required electrode pattern. The sheets were subsequently cleaned with soap (2% helmanex in water), distilled water, acetone, ethanol and finally treated under oxygen plasma for 10 minutes to remove any organic residues.

**3.2 - Deposition of the compact TiO<sub>2</sub> layer:**

The FTO sheets were then coated with a compact layer of TiO<sub>2</sub> (100 nm) by aerosol spray pyrolysis deposition of a Ti-ACAC ethanol solution (1:10 Ti-ACAC to ethanol volume ratio) at 450°C using air as the carrier gas (see Kavan, L. and Gratzel, M., Highly efficient

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semiconducting TiO<sub>2</sub> photoelectrodes prepared by aerosol pyrolysis, *Electrochim. Acta* 40, 643 (1995); Snaith, H. J. and Gratzel, M., The Role of a "Schottky Barrier" at an Electron-Collection Electrode in Solid-State Dye-Sensitized Solar Cells. *Adv. Mater.* 18, 1910 (2006).

### **3.3 - Preparing the mesoporous TiO<sub>2</sub> electrodes:**

A standard TiO<sub>2</sub> nanoparticle paste was doctor-bladed onto the compact TiO<sub>2</sub> to give a dry film thickness between 1 and 3 μm, governed by the height of the doctor blade. These sheets were then slowly heated to 500°C (ramped over 30 minutes) and baked at this temperature for 30 minutes under an oxygen flow. After cooling, the sheets were cut into slides of the required size and stored in the dark until further use.

Prior to fabrication of each set of devices, the nanoporous films were soaked in a 0.02 M aqueous solution of TiCl<sub>4</sub> for 1 hours at 70°C. This procedure was applied to grow a thin shell of TiO<sub>2</sub> upon both the TiO<sub>2</sub> and the Au@Si nanoparticles. Following the TiCl<sub>4</sub> treatment the films were rinsed with deionised water, dried in air, and baked once more at 500°C for 45 minutes under oxygen flow. Once cooled to 70°C they were placed in a dye solution overnight.

The ruthenium-based dye used for sensitization was "Z907", an NCS bipyridyl complex (see Schmidt-Mende, L., Zakeeruddin, S. M., and Gratzel, M., Efficiency improvement in solid-state dye-sensitized photovoltaics with an amphiphilic ruthenium-dye, *Applied Physics Letters* 86 (1), 013504 (2005)). The dye solution comprised 0.5 mM of Z907 in acetonitrile and tert-butyl alcohol (volume ratio: 1:1).

### **3.4 - Incorporating Au@Si nanoparticles into the paste (scheme a):**

The procedure as described in 3.1 was repeated except that a standard TiO<sub>2</sub> nanoparticle paste was replaced with a TiO<sub>2</sub>-Au@Si nanoparticle paste prepared as described in Example 2.

### **3.5 - Incorporating Au@Si nanoparticles between the dye and the hole-transporter (scheme b):**

Following dying, the dyed electrodes were rinsed in acetonitrile, dried in air and placed on a spin-coater. A Au@Si colloid in an ethanol solution (prepared as described in Example 1) was then dispensed on top of the dyed electrode, and spin-coated at 2000 rpm for 25 seconds to coat the film with Au@Si nanoparticles.

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**3.6. - Incorporating Au@Si nanoparticles between the compact TiO<sub>2</sub> and the mesoporous TiO<sub>2</sub> layers (scheme c):**

After deposition of the TiO<sub>2</sub> compact layer (procedure 3.2), Au@Si nanoparticles were deposited upon this film via spin-coating from an ethanol dispersion at 2000 rpm for 25 seconds. The subsequent mesoporous TiO<sub>2</sub> film and the device assembly remained as standard.

**3.7 - Incorporating Au@Si nanoparticles between the FTO electrode and the compact TiO<sub>2</sub> layer (scheme d):**

After cleaning of the FTO sheets, Au@Si nanoparticles were deposited upon this film via spin-coating from an ethanol dispersion at 2000 rpm for 25 seconds. The subsequent compact layer deposition, mesoporous TiO<sub>2</sub> film and the device assembly remained as standard.

**Example 4 - Hole-transporter deposition and device assembly**

The hole transporting material used was spiro-OMeTAD, which was dissolved in chlorobenzene at a typical concentration of 180 mg/ml. After fully dissolving the spiro-OMeTAD at 100°C for 30 minutes the solution was cooled and tertbutyl pyridine (*t*BP) was added directly to the solution with a volume to mass ratio of 1:26 µl/mg *t*BP:spiro-MeOTAD. Lithium bis(trifluoromethylsulfonyl)amine salt (Li-TFSI) ionic dopant was pre-dissolved in acetonitrile at 170 mg/ml, then added to the hole-transporter solution at 1:12 µl/mg of Li-TFSI solution:spiro-MeOTAD. The dye coated mesoporous films (with and without Au@Si nanoparticles) were briefly rinsed in acetonitrile and dried in air for one minute. A small quantity (20 to 70 µl) of the spiro-OMeTAD solution was dispensed onto each dye coated substrate and left for 20 s before spin-coating at 2000 rpm for 25 s in air. The films were then placed in a thermal evaporator where 150 nm thick silver electrodes were deposited through a shadow mask under high vacuum (10<sup>-6</sup> mBar).

**4.1 - Incorporating Au@Si nanoparticles into the hole-transporter phase (scheme e):**

Colloidal Au@Si nanoparticles in ethanol (prepared as in Example 1) were precipitated in a centrifuge and the ethanol removed. A few tens of microlitres of hexylamine was added to the precipitated nanoparticles with further addition of 1 ml of chlorobenzene. The Au@Si nanoparticles were re-dispersed in this solution via shaking and ultrasonification. The Au@Si in chlorobenzene was then added at various concentrations to the spiro-OMeTAD, *t*BP, Li-TFSI

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solution. The subsequent hole-transporter coating and electrode deposition was performed on standard electrodes in the standard manner with the spiro-OMeTAD-Au@Si solution.

**4.2 - Incorporating Au@Si nanoparticles between the hole-transporter and the metallic hole-collecting electrode (scheme f):**

Following spin-coating of the hole-transporter on standard electrodes, a Au@Si nanoparticle ethanol solution (prepared as in Example 1) was dispensed upon the top of the spiro-OMeTAD film and spin-coated at 2000 rpm for 25 seconds. The device was then placed in the thermal evaporator and silver electrodes were deposited through a shadow mask as standard.

Example 5 - Preparation of SDSCs incorporating Ag-core silica-shell nanoparticles.

Methods analogous to those described above were used to incorporate Ag-core silica-shell nanoparticles (termed Ag@Si) into solid-state DSCs in the following locations:

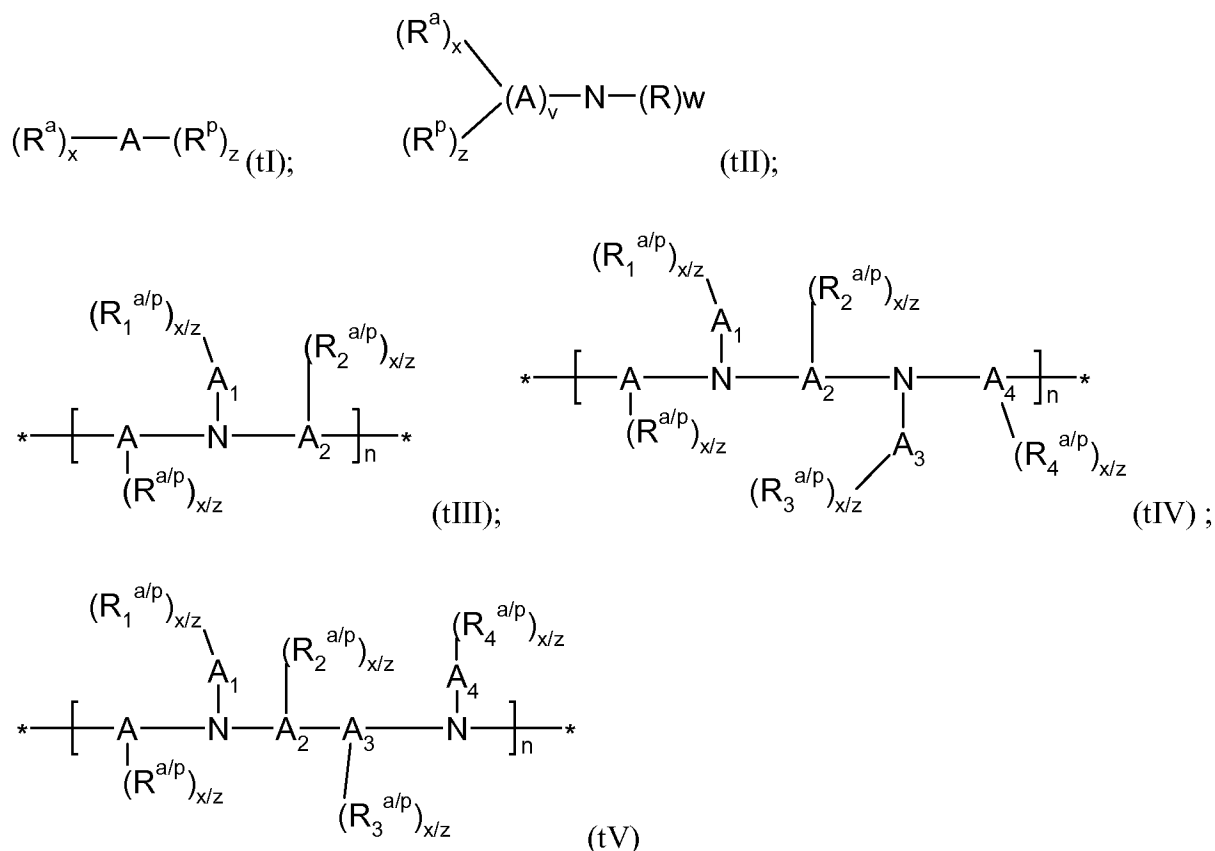
- a. Within the mesoporous TiO<sub>2</sub> phase
- b. Between the dye-coated TiO<sub>2</sub> and the hole-transporter
- c. Between the compact TiO<sub>2</sub> layer and the mesoporous TiO<sub>2</sub> layer
- d. Between the FTO and the compact TiO<sub>2</sub> layer
- e. Within the hole-transporter phase
- f. Between the hole-transporter and the top metallic electrode.

Claims:

- 1) A solid-state p-n heterojunction comprising an organic p-type material in contact with an n-type material wherein said heterojunction is sensitised by at least one sensitizing agent, wherein said sensitizing agent comprises nanoparticles of at least one metal, and wherein the nanoparticles are coated and have at least one surface plasmon mode in the visible to infra-red regions of the electromagnetic spectrum.
- 2) A solid-state p-n heterojunction as claimed in claim 1 comprising an organic p-type material in contact with an n-type material wherein said heterojunction is sensitised by at least two sensitizing agents comprising a first sensitizing agent and a second sensitizing agent, wherein said first sensitizing agent comprises coated nanoparticles of at least one metal and said second sensitizing agent comprises at least one molecular or polymeric sensitizing agent, and wherein the coated metal nanoparticles have at least one surface plasmon mode in the visible to infra-red regions of the electromagnetic spectrum.
- 3) A solid-state p-n heterojunction as claimed in claim 1 or claim 2 wherein said sensitizing or said first sensitizing agent comprises coated nanoparticles of at least one of copper, silver, gold and mixtures thereof.
- 4) A solid-state p-n heterojunction as claimed in any preceding claim wherein the coating of said first sensitizing agent comprises an insulating material having a band gap of greater than 3eV, preferably greater than 5eV, for example 5 to 30 eV.
- 5) A solid-state p-n heterojunction as claimed in any preceding claim wherein the coating of said first sensitizing agent comprises an insulating inorganic material, preferably a wide band gap metal oxide.
- 6) A solid-state p-n heterojunction as claimed in any preceding claim wherein the coating of said first sensitizing agent is selected from SiO<sub>2</sub>, MgO, Y<sub>2</sub>O<sub>5</sub>, NbO, ZrO, HfO, Al<sub>2</sub>O<sub>3</sub> and combinations thereof.
- 7) A solid-state p-n heterojunction as claimed in any preceding claim wherein the coating of said first sensitizing agent is 1 to 100 nm.
- 8) A solid-state p-n heterojunction as claimed in any preceding claim wherein said first sensitizing agent comprises at least one metal nanoparticle that provides near-field enhancement of light absorption by at least one molecular or polymeric sensitizing agent of said second sensitizing agent.

- 9) A solid-state p-n heterojunction as claimed in any preceding claim wherein said first sensitizing agent comprises at least one metal nanoparticle that provides near-field enhancement of light absorption by at least one of the p-type or n-type semiconducting materials.
- 10) A solid-state p-n heterojunction as claimed in claim 8 or claim 9 wherein said first sensitizing agent comprises coated metal nanoparticles having at least one dimension in the range 2 to 100 nm, particularly 2 to 20 nm.
- 11) A solid-state p-n heterojunction as claimed in any preceding claim wherein said first sensitizing agent comprises at least one metal nanoparticle that provides far-field enhancement of light absorption by at least one molecular or polymeric sensitizing agent of said second sensitizing agent and/or by at least one of the p-type or n-type semiconducting materials.
- 12) A solid-state p-n heterojunction as claimed in claim 11 wherein said first sensitizing agent comprises coated metal nanoparticles having at least one dimension in the range 20 to 200 nm, particularly 50 to 100 nm.
- 13) A solid state p-n heterojunction as claimed in any preceding claim wherein said first sensitizing agent is incorporated at one or more of the following sites:
- i) within a mesoporous layer of n-type material;
  - ii) at the junction between the n-type material and the p-type hole transporter;
  - iii) between a compact layer of n-type material and a mesoporous layer of n-type material;
  - iv) within the hole transporter; and
  - v) between the anode and a compact layer of n-type material
  - vi) between the hole transporter and the cathode.
- 14) A solid state p-n heterojunction as claimed in any preceding claim wherein said second sensitizing agent comprises at least one dye selected from a ruthenium complex dye, a metal-phthalocyanine complex dye, a metal-porphyrin complex dye, a squaraine dye, a thiophene based dye, a fluorine based dye, a polymer dye, and mixtures thereof.
- 15) A solid state p-n heterojunction as claimed in any preceding claim wherein said second sensitizing agent comprises said p-type semiconductor material and/or said n-type semiconductor material.
- 16) A solid state p-n heterojunction as claimed in any preceding claim wherein said p-type material is an organic hole-transporter, preferably a substantially amorphous organic hole transporter.

17) A solid state p-n heterojunction as claimed in claim 16 wherein said organic hole-transporter is at least one optionally oligomerised, polymerized and/or cross-linked compound of formula (tI), (tII), (tIII), (tIV) and/or (tV) below,



in which N, if present, is a nitrogen atom;

n, if applicable, is in the range of 1-20;

A is a mono-, or polycyclic system comprising at least one pair of a conjugated double bond (-C=C-C=C-), the cyclic system optionally comprising one or several heteroatoms, and optionally being substituted, whereby in a compound comprising several structures A, each A may be selected independently from another A present in the same structure (tI-tV);

each of A<sub>1</sub>-A<sub>4</sub>, if present, is an A independently selected from the A as defined above;

v in (tII) recites the number of cyclic systems A linked by a single bond to the nitrogen atom and is 1, 2 or 3;

(R)<sub>w</sub> is an optional residue selected from a hydrocarbon residue comprising from 1 to 30 carbon atoms, optionally substituted and optionally comprising 1 or several heteroatoms, with w being 0, 1 or 2 provided that v + w does not exceed 3, and, if w = 2, the respective R<sub>w1</sub> or R<sub>w2</sub> being the same or different;

R<sub>a</sub> represents a residue capable, optionally together with other R<sub>a</sub> present on the same structure (tI-tV), of decreasing the melting point of an organic compound and is selected from a

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linear, branched or cyclic alkyl or a residue comprising one or several oxygen atoms, wherein the alkyl and/or the oxygen comprising residue is optionally halogenated;

x is the number of independently selected residues Ra linked to an A and is selected from 0 to a maximum possible number of substituents of a respective A, independently from the number x of other residues Ra linked to another A optionally present;

with the proviso that per structure (I-V) there is at least one Ra being an oxygen containing residue as defined above; and, if several Ra are present on the same structure (tI-tV), they are the same or different; and wherein two or more Ra may form an oxygen-containing ring;

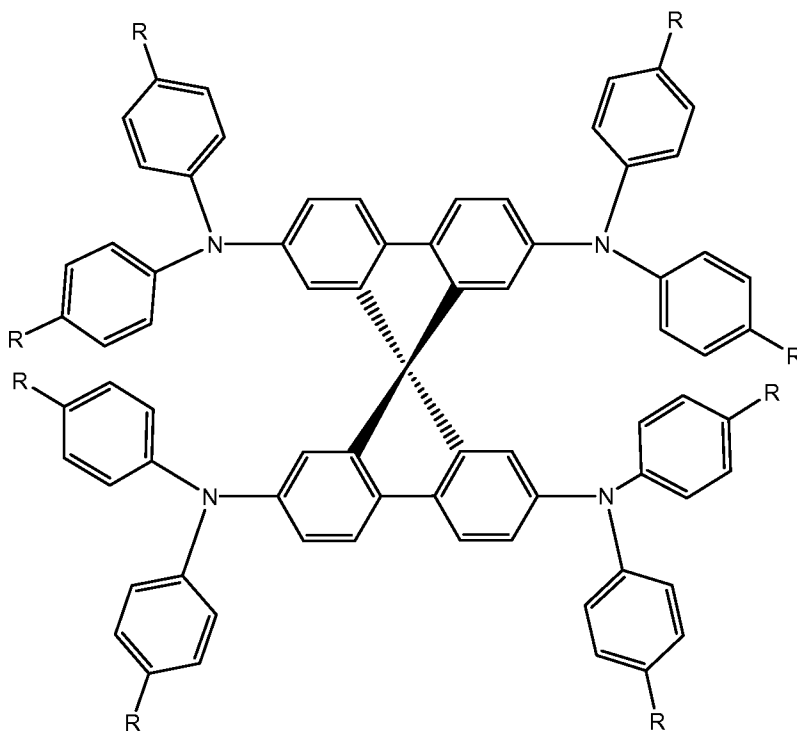
Rp represents an optional residue enabling a polymerisation reaction with compounds comprising structure (tI - tV) used as monomers, and/or a cross-linking between different compounds comprising structures (tI - tV);

z is the number of residues Rp linked to an A and is 0, 1, and/or 2, independently from the number z of other residues Rp linked to another A optionally present;

Rp may be linked to an N-atom, to an A and/or to a substituent Rp of other structures according (tI - tV), resulting in repeated, cross-linked and/or polymerised moieties of (tI - tV);

$(R^{a/p})_{x/z}$  and  $(R_{1-4}^{a/p})_{x/z}$ , if present, represent independently selected residues Ra and Rp as defined above;

18) A solid state p-n heterojunction as claimed in claim 16 or claim 17 wherein said organic hole-transporter is a compound of formula tXVII below:



Formula tXVII

wherein R is C1-C6 alkyl or C1-C6 O-alkyl.

19) A solid state p-n heterojunction as claimed in any 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  $\text{TiO}_2$ .

20) A solid state p-n heterojunction as claimed in any preceding claim wherein said n-type material is porous, preferably having a surface area of  $1\text{--}1000\text{ m}^2\text{g}^{-1}$  and preferably in the form of an electrically continuous layer, most preferably of thickness 0.1 to 20  $\mu\text{m}$ .

21) A solid-state p-n heterojunction as claimed in any 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.

22) A solid state p-n heterojunction as claimed in any preceding claim wherein said n-type semiconductor material is essentially pure material or is doped throughout with at least one dopant material of greater valency than the bulk material (n-type doping) and/or is doped with at least one dopant material of lower valency than the bulk (p-type doping), and wherein said n-type material is optionally surface coated.

23) A solid-state p-n heterojunction as claimed in any preceding claim wherein said first sensitizing agent is distributed primarily at the surface of the n-type semiconductor material.

24) A solid-state p-n heterojunction as claimed in claim 23, having a coating of a further semiconductor material over the surface of the bulk n-type material and over the coated nanoparticles distributed at the surface of the n-type semiconductor material.

25) A solid-state p-n heterojunction as claimed in claim 24 wherein said coating is 0.2 to 5 nm in thickness.

26) A solid-state p-n heterojunction as claimed in claim 19 or claim 20 wherein said coating is formed from an n-type semiconductor, preferably the same n-type semiconductor as the bulk of the n-type material.

27) An optoelectronic device comprising at least one solid state p-n heterojunction as claimed in any preceding claim.

- 28) An optoelectronic device as claimed in claim 27 wherein said device is a solar cell or photo-detector.
- 29) Use of a first and second sensitizing agents in a solid-state p-n heterojunction wherein said first sensitizing agent comprises coated nanoparticles of at least one metal and said second sensitizing agent comprises at least one molecular or polymeric sensitizing agent, and wherein the coated metal nanoparticles have at least one surface plasmon mode in the visible to infra-red regions of the electromagnetic spectrum.
- 30) Use as claimed in claim 29 wherein said heterojunction is an organic solid state p-n heterojunction as claimed in any of claims 1 to 26.
- 31) Use as claimed in claim 29 or claim 30 to generate increased light conversion efficiency in the solid-state p-n heterojunction in comparison with the second sensitizing agent used as sole sensitizer in an equivalent heterojunction.
- 32) Use as claimed in claim 31 wherein said increased light conversion efficiency occurs at least partially by plasmonic enhancement of the absorption of the second sensitizer due to near-field effects of the surface plasmon modes in said first sensitizer.
- 33) Use as claimed in claim 31 or claim 32 wherein said increased light conversion efficiency occurs at least partially by enhancement of the absorption of the second sensitizer due to far-field scattering effects of the surface plasmon modes in said first sensitizer.
- 34) Use as claimed in any of claims 29 to 33 in a solar cell.
- 35) A method for the manufacture of a solid-state p-n heterojunction incorporating a first sensitizing agent which comprises coated nanoparticles of at least one metal and a second sensitizing agent which comprises at least one molecular or polymeric sensitizing agent, said method comprising:
- a) coating a cathode with a compact layer of an n-type semiconductor material;
  - b) optionally forming a porous layer of an n-type semiconductor material on said compact layer,

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- c) surface sensitizing said compact layer or, where present, said porous layer with said second sensitizing agent;
- d) forming a layer of a solid-state p-type semiconductor material in contact with said compact layer or, where present, said porous layer of an n-type semiconductor material; and
- e) forming an anode on said p-type semiconductor material;

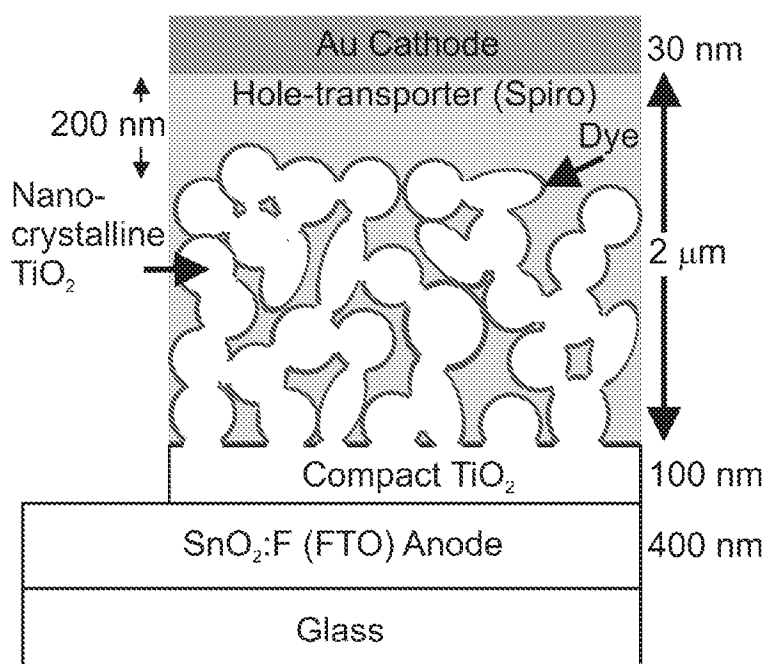
wherein said first sensitizing agent is incorporated before step a), before step b), during step b), before step c), during step c), before step d), during step d), and/or before step e).

36) A method as claimed in claim 35, wherein step b) comprises:

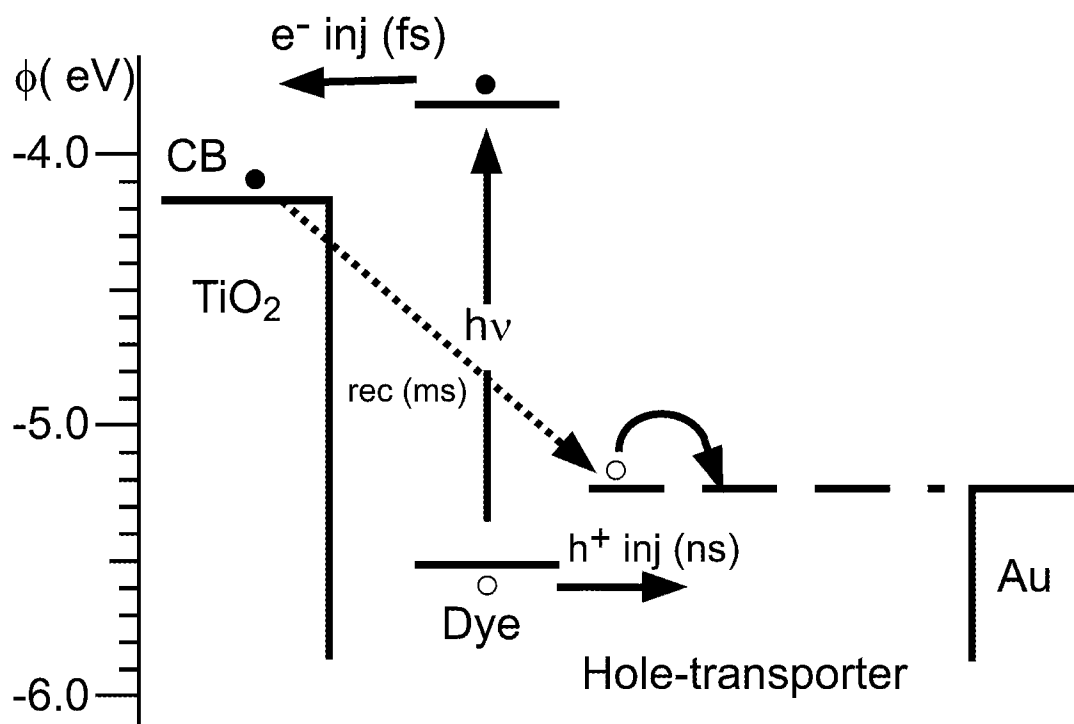
- b1) forming a porous layer of an n-type semiconductor material from particles of an n-type semiconductor material and optionally from particles of said first sensitizing agent;
- b2) optionally surface sensitizing said porous layer of an n-type semiconductor material with particles of said first sensitizing agent; and
- b3) optionally depositing a layer of n-type semiconductor material on the surface of said porous layer of an n-type semiconductor material.

37) 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 claims 35 or 36.

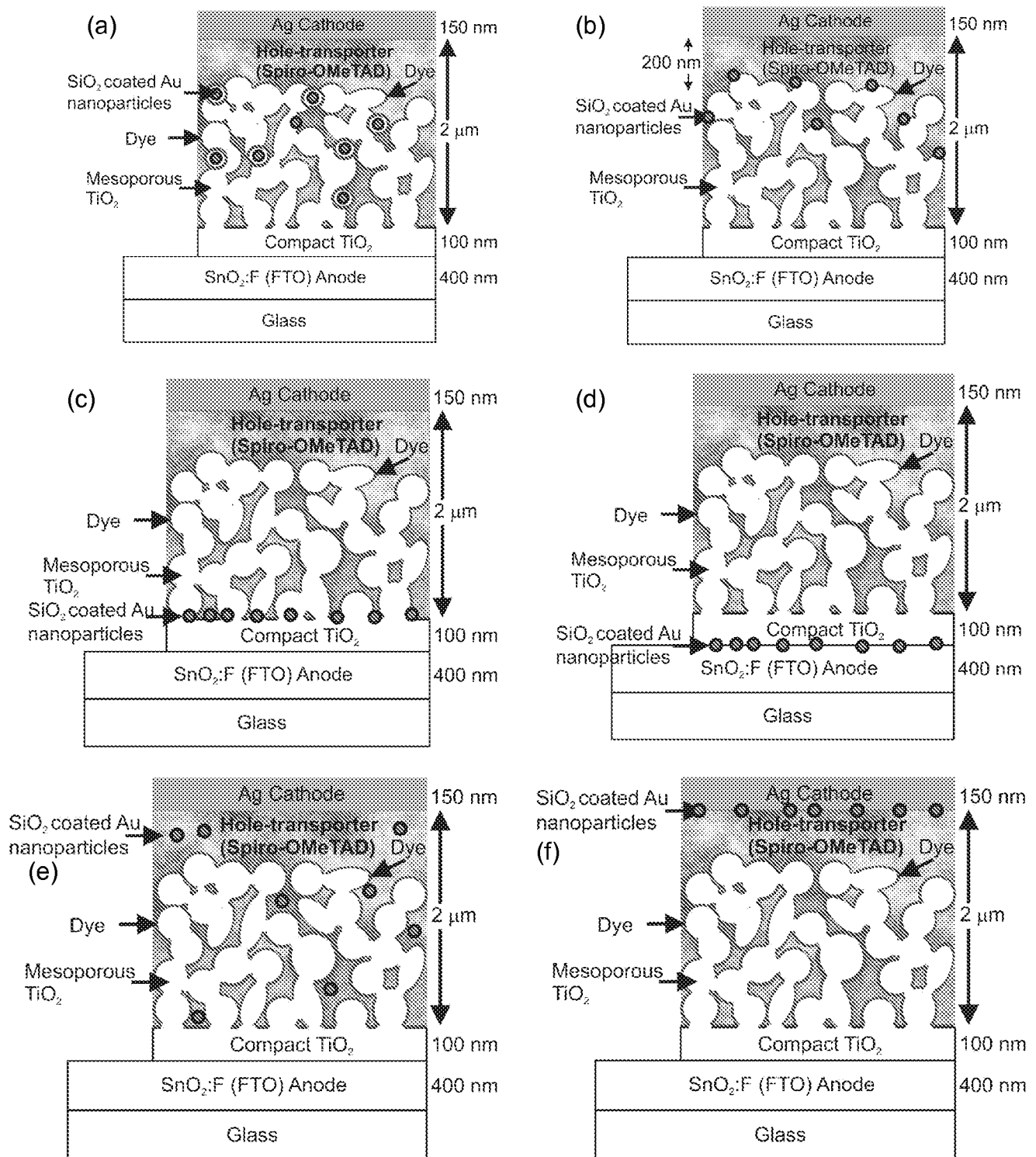
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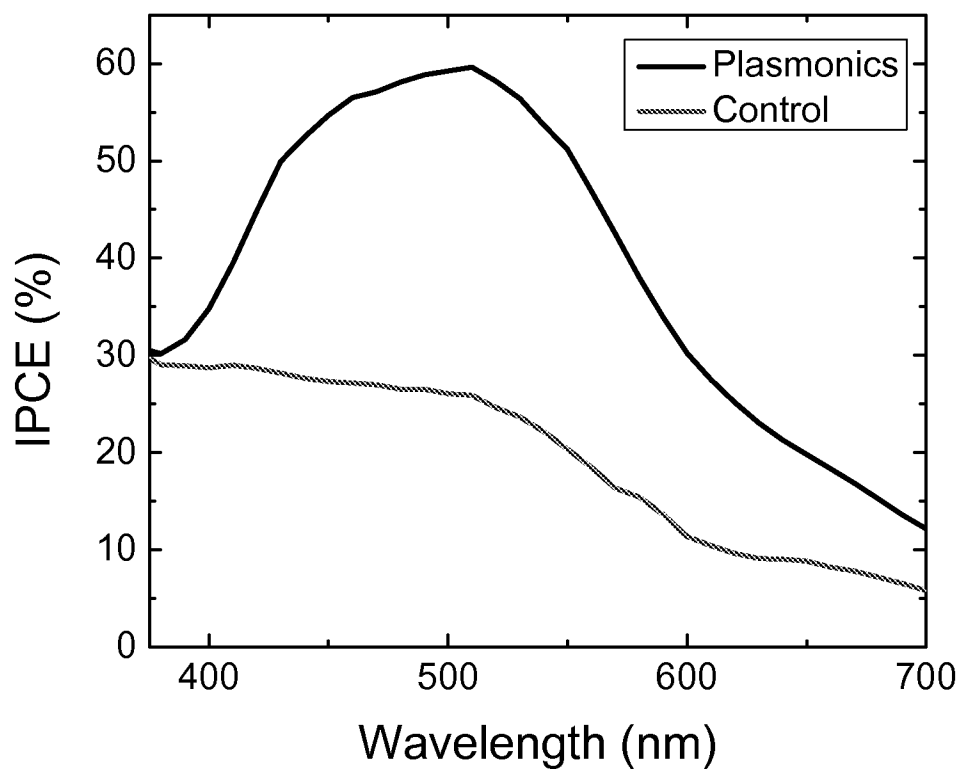
**Figure 1** - Schematic diagram of a solid state dye sensitised solar cell formed with a mesoporous TiO<sub>2</sub> n-type semiconductor material.



**Figure 2** - Schematic representation of charge transfers taking place in DSC operation. e<sup>-</sup>inj = electron injection into the TiO<sub>2</sub>, CB = conduction band, rec = electron-hole recombination, h<sup>+</sup>inj = hole-transfer to the hole-transporter, hν = light absorption.



**Figure 3:** Illustration of solid-state DSCs incorporating plasmonic particles, a) within the mesoporous TiO<sub>2</sub> phase, b) between the dye-coated TiO<sub>2</sub> and the hole-transporter, c) between the compact TiO<sub>2</sub> layer and the mesoporous TiO<sub>2</sub> layer, d) between the FTO and the compact TiO<sub>2</sub> layer, e) within the hole-transporter phase and f) between the hole-transporter and the top metallic electrode.



**Fig. 4** - Incident Photon-to-electron Conversion Efficiency (IPCE) for a plasmonic DSC incorporating SiO<sub>2</sub>-coated gold nanoparticles and for a standard solid-state DSC

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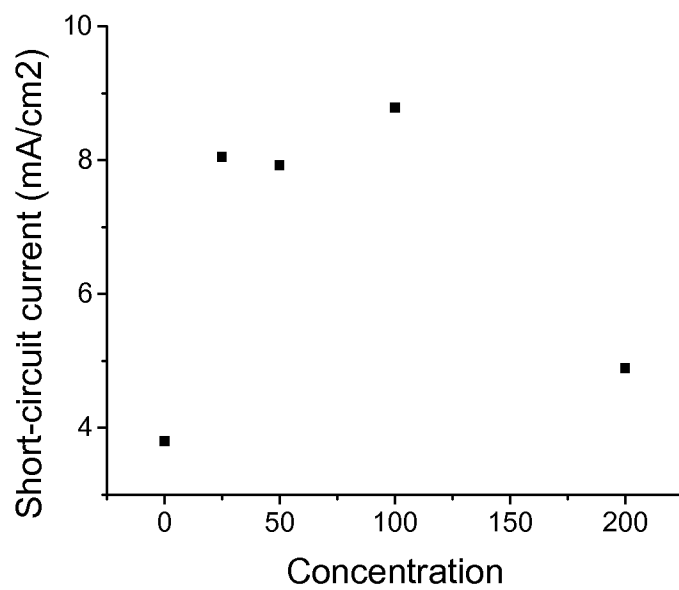


Fig. 5

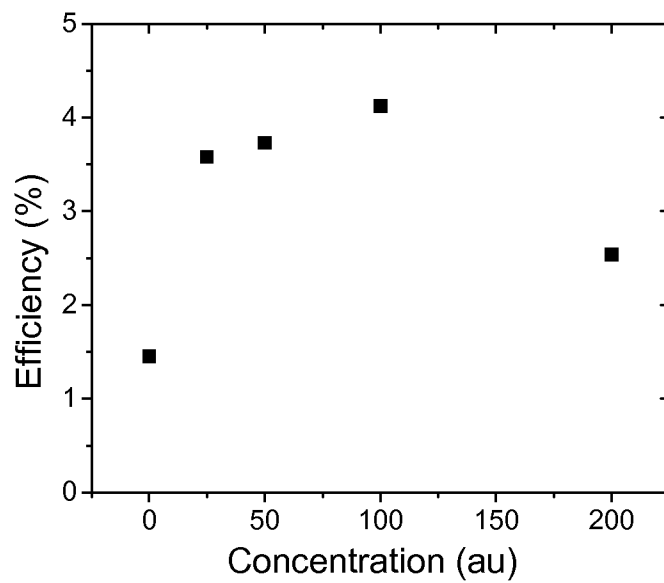
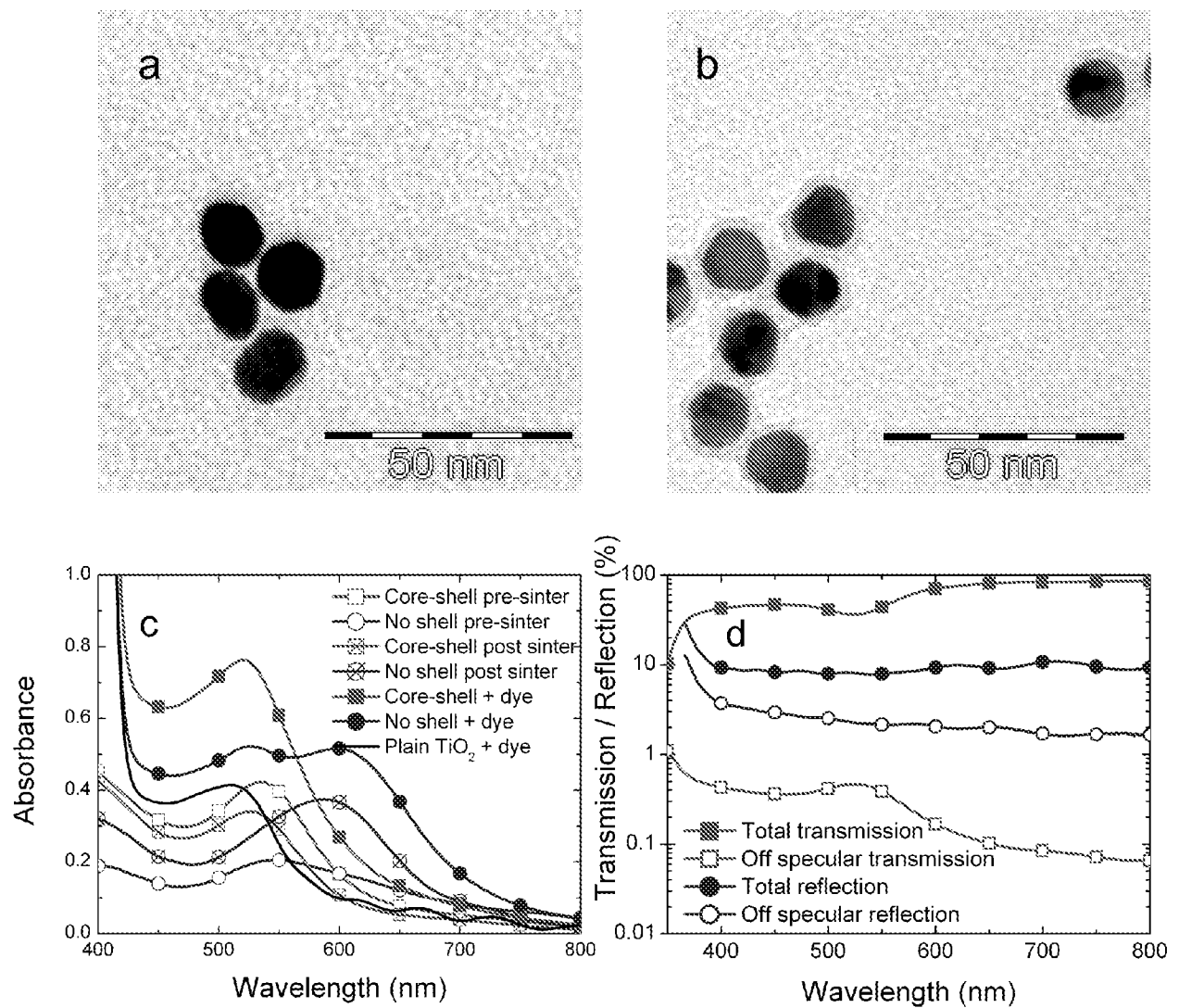


Fig. 6



**Figure 7:** TEM images showing, a)  $\sim 15$  nm diameter bare gold nanoparticles, and b) Au-SiO<sub>2</sub> core-shell nanoparticles with  $\sim 15$  nm Au cores encapsulated by  $\sim 3$  nm silica shells. c) The absorption spectra of thin films ( $\sim 1$   $\mu\text{m}$ ) processed with conventional mesoporous TiO<sub>2</sub> paste at different stages in the fabrication process and d) Transmission and reflection spectra for mesoporous TiO<sub>2</sub> films incorporating core-shell nanoparticles of similar concentration to those shown in (c).

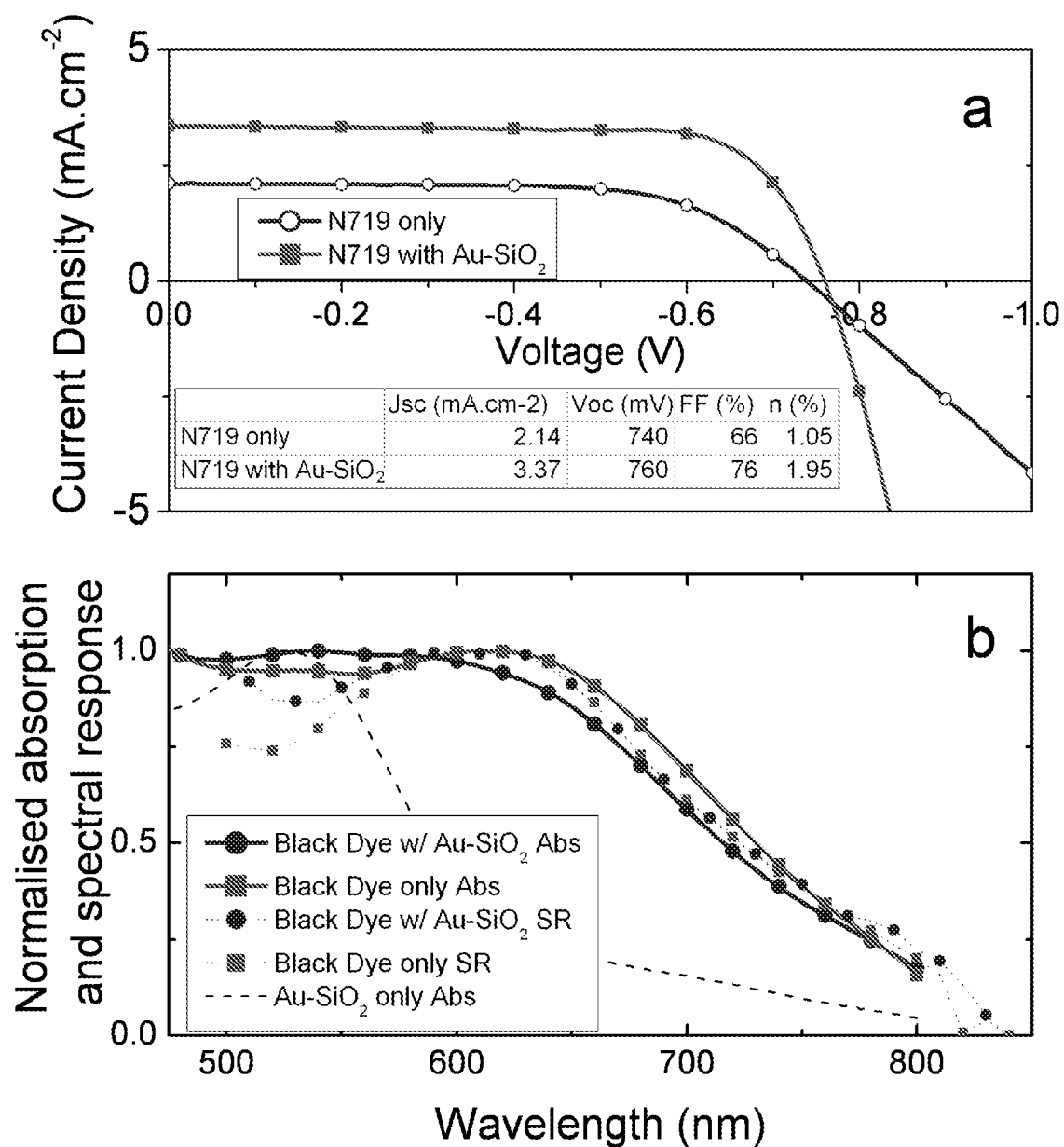


Figure 8: a) Current-voltage characteristic and b) normalised absorption and spectral response liquid electrolyte based DSSCs.

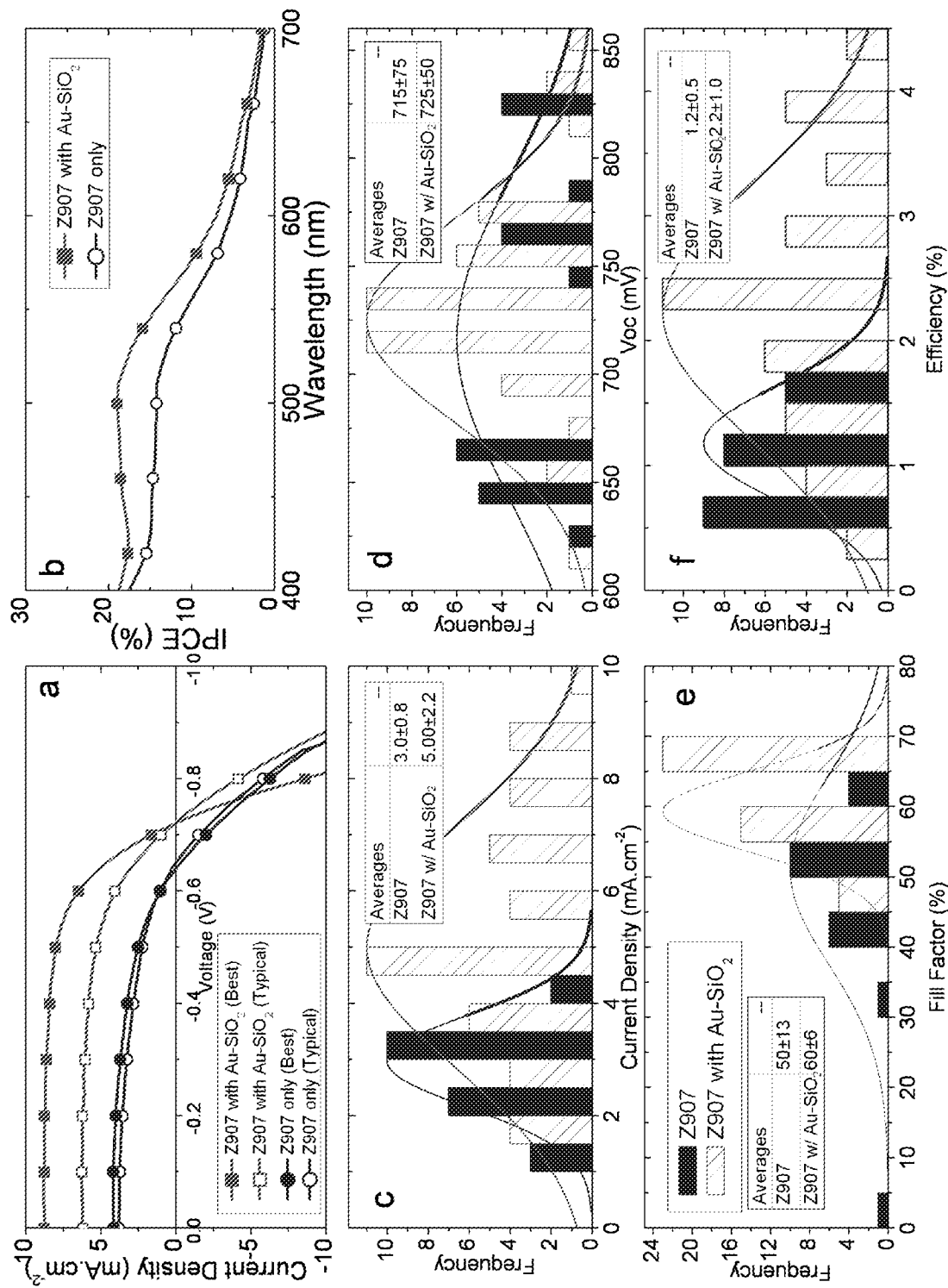


Figure 9. Electronic characterization of solid-state DSSCs sensitized with Z907-only and also with Au-SiO<sub>2</sub> nanoparticles with Z907 sensitization.

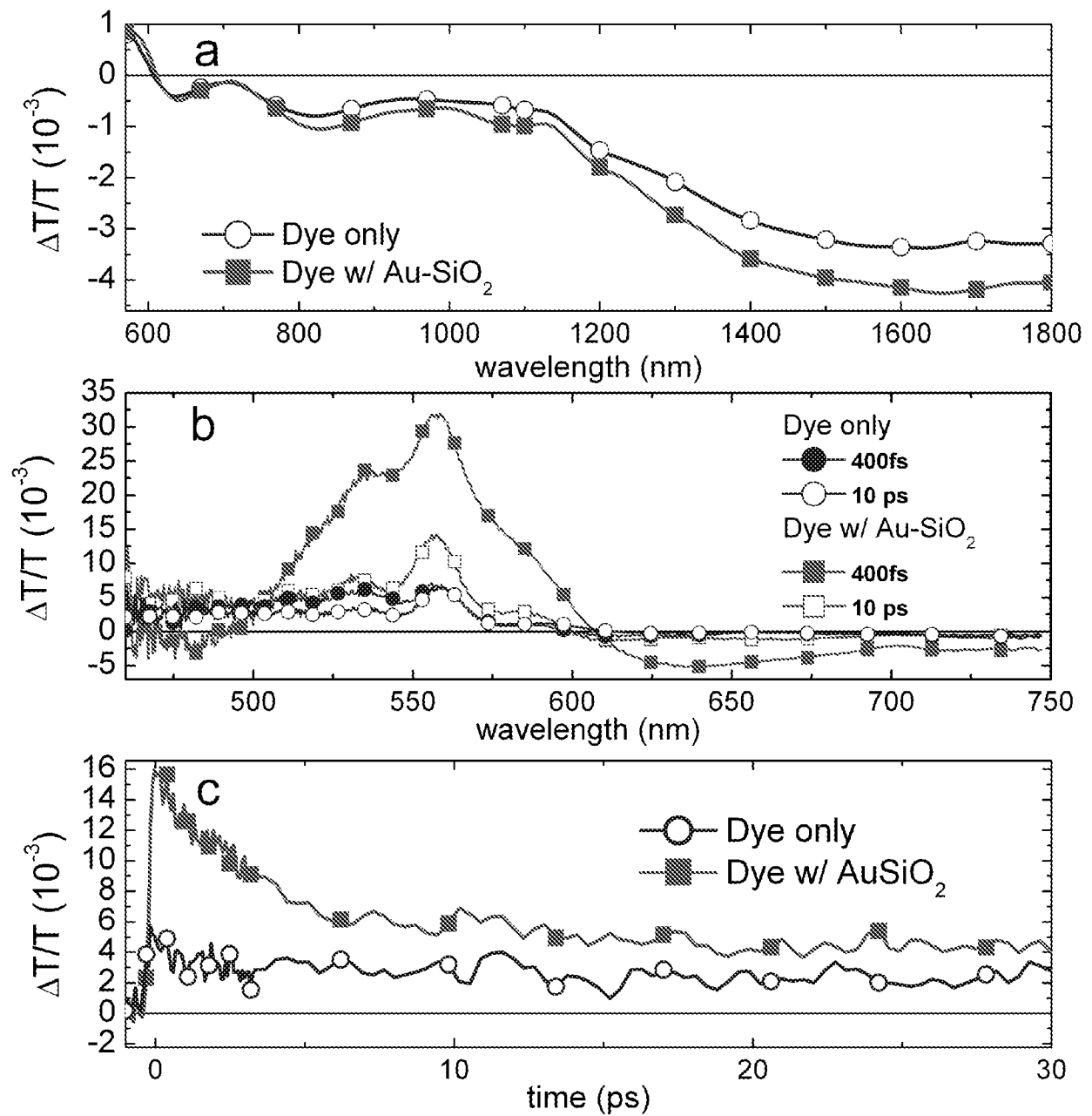


Figure 10: Spectroscopic characterization of the Z907-only device and the device incorporating the Au-SiO<sub>2</sub> nanoparticles.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/GB2010/051986

**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 practical, search terms used)  
EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                | Relevant to claim No. |
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| X         | US 2006/032529 A1 (RAND BARRY P [US] ET<br>AL) 16 February 2006 (2006-02-16)<br>paragraphs [0071], [0073], [0080],<br>[0093]<br><br>-----<br>-/-- | 1-37                  |

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

19 January 2011

Date of mailing of the international search report

26/01/2011

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2010/051986

## C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                                                                                                 | Relevant to claim No.     |
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| A         | STANDRIDGE S D ET AL: "Toward plasmonic solar cells: Protection of silver nanoparticles via atomic layer deposition of TiO <sub>2</sub> ",<br>LANGMUIR 20090303 AMERICAN CHEMICAL SOCIETY USA,<br>vol. 25, no. 5, 3 March 2009 (2009-03-03),<br>pages 2596-2600, XP7916739,<br>DOI: DOI:10.1021/LA900113E<br>cited in the application<br>the whole document                                                                                                        | 1                         |
| A         | KRÜGER JESSICA ET AL: "Improvement of the photovoltaic performance of solid-state dye-sensitized device by silver complexation of the sensitizer cis-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato) ruthenium(II)",<br>APPLIED PHYSICS LETTERS, AIP, AMERICAN INSTITUTE OF PHYSICS, MELVILLE, NY, US,<br>vol. 81, no. 2, 8 July 2002 (2002-07-08),<br>pages 367-369, XP012032480,<br>ISSN: 0003-6951, DOI:<br>DOI:10.1063/1.1490394<br>the whole document | 1                         |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No  
PCT/GB2010/051986

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| US 2005236033                             | A1                  | 27-10-2005                 | NONE                |
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|                                           |                     | CA 2577147                 | A1 09-03-2006       |
|                                           |                     | CN 101023540               | A 22-08-2007        |
|                                           |                     | CN 101728486               | A 09-06-2010        |
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