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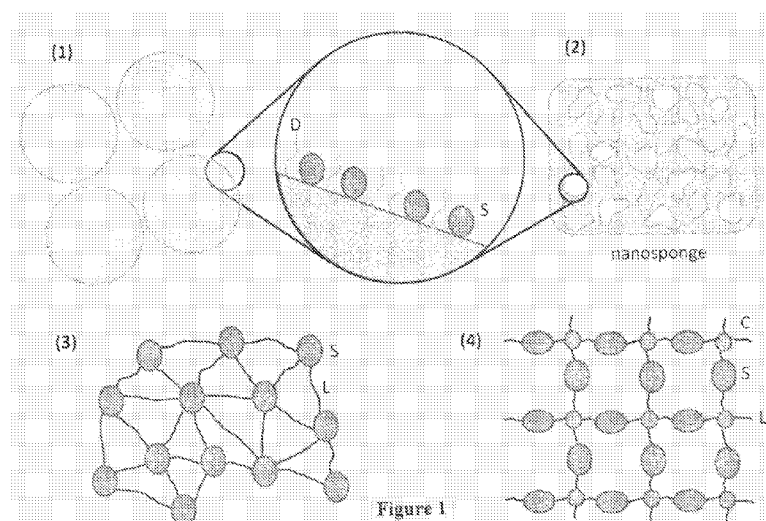


Figure 1

(57) **Abstract:** The invention relates to a system for upconversion of photons, comprising a solid sensitizer medium comprising a sensitizer, said sensitizer medium being disposed in an emitter medium comprising an emitter which is capable of absorbing energy from an excited state of the sensitizer.

PHOTON UPCONVERTER

Field

[0001] The invention relates to a system for photon upconversion.

Background

[0002] Single threshold solar cells fail to make use of light whose energy is below the absorption threshold of the material (bandgap). This limits the efficiency of such devices to 33% under one sun. If sub-bandgap light can be harvested, then the efficiency limit is increased to 43%, and the optimal threshold is increased from 1.34 eV to about 1.7 eV. Although there exists a number of photovoltaic devices with bandgaps in this favourable energy range (such as amorphous silicon-, organic bulk heterojunction- or dye-sensitized solar cells), there is currently no solution for the efficient harvest of sub-bandgap photons, i.e. to significantly augment photocurrent in such devices. However, the process of upconversion by triplet-triplet annihilation up-conversion (TTA-UC) is encouraging, but requires nano-engineering of the material to enable both high efficacy and feasible device integration schemes.

Summary of Invention

[0003] In a first aspect of the invention there is provided a system for upconversion of photons, comprising a solid sensitizer medium comprising a sensitizer, said sensitizer medium being disposed in an emitter medium comprising an emitter which is capable of accepting energy from an excited state of the sensitizer so as to upconvert said energy. The energy upconversion may produce upconverted luminescence, e.g. fluorescence.

[0004] The following options may be used with the first aspect, either individually or in any suitable combination.

[0005] The sensitizer may be capable of absorbing photons having energy of less than about 2eV. In doing so, it may generate the excited state of the sensitizer, energy from which can be transferred to the emitter. It may be capable of absorbing photons of wavelength of about 600 to about 750nm. It may for example be a metalloporphyrin, such as a palladium tris- or tetrakis-quinoxalinoporphyrin.

[0006] The emitter may be a polycyclic aromatic compound, for example diphenylanthracene or rubrene. The polycyclic aromatic compound may be purely carbocyclic (i.e. benzenoid) or may comprise one or more heteroaromatic rings such as pyridine rings. The rings of the polycyclic aromatic compound may be fused rings or may be discrete linked rings or there may be a mixture of these.

[0007] The sensitizer medium may comprise molecules of the sensitizer coupled (e.g. chemically bonded) to surfaces of nanoparticles; or molecules of the sensitizer coupled (e.g. chemically bonded) to surfaces of a nanoporous substrate; or a crosslinked polymer wherein molecules of the sensitizer are monomer units of the polymer; or a metal-organic framework in which metal atoms or clusters are joined by linker groups comprising molecules of the sensitizer, or a covalent network wherein molecules of the sensitizer are integrated. In the metal-organic framework, the linker groups may be coupled to the metal atoms or clusters by ionic bonds to polyvalent metal ions or may be coupled thereto by complexation of functional groups on the linker groups with the metal atoms or clusters. More generally, the sensitizer medium may comprise a molecular framework (which may be for example a metal-organic framework, a polymeric framework or some other type of molecular framework) in which the sensitizer molecules are structural elements.

[0008] In some embodiments the sensitizer medium comprises molecules of the sensitizer coupled to surfaces either of nanoparticles or of a nanoporous substrate. The coupling may be by means of a linker group. The process of making the sensitizer medium may comprise either coupling molecules of the sensitizer to a nanoporous substrate having linker groups thereon, or coupling molecules of the sensitizer having linker groups thereon to a nanoporous substrate.

[0009] In some embodiments the sensitizer medium comprises molecules of the sensitizer coupled to surfaces either of nanoparticles or of a nanoporous substrate and the surfaces of the nanoparticles or of the nanoporous substrate have spacer molecules coupled thereto. The spacer molecules may be incapable of absorbing photons at a wavelength which is absorbed by the sensitizer. The molar ratio of spacer molecules to sensitizer molecules may be between about 1:1 to about 100:1. In other embodiments, no spacer molecules are present.

[0010] The sensitizer medium may comprise molecules of the sensitizer coupled to surfaces of nanoparticles. The nanoparticles may be, or may contain, metallic nanoparticles. The metallic

nanoparticles may exhibit plasmon resonance at a wavelength at which the sensitizer absorbs photons. This may serve to enhance light absorption by the sensitizer. The system may additionally comprise spacer nanoparticles having no molecules of the sensitizer coupled thereto. The ratio of the metallic nanoparticles to the spacer nanoparticles and the size of the spacer nanoparticles may be such that the mean distance between the metallic nanoparticles results in approximate tessellation of, or at least partial overlap of, the absorption cross-section of the metallic nanoparticles at the wavelength of the plasmon resonance, i.e. at the wavelength at which the sensitizer absorbs photons. Thus the ratio and size may be such that the mean distance between the metallic nanoparticles is approximately the same as, or within about 20% of the diameter of the absorption cross-section. In some embodiments, the metallic nanoparticles and the spacer nanoparticles have approximately the same diameter. The ratio of the metallic nanoparticles to the spacer nanoparticles may be such that the mean distance between the metallic nanoparticles results in non-overlapping metallic nanoparticle absorption cross-sections, or such that the mean distance is greater than the absorption cross-section of the metallic nanoparticles. A suitable ratio may be from about 1:1 to about 1000:1.

[0011] The metallic nanoparticles may be coated by a dielectric layer. This may serve to avoid or restrict direct contact between the sensitizer molecules and the surface of the metal nanoparticles. A suitable thickness of that coating may be between 1 and 5 nm. The dielectric layer may for example comprise silica, another metal oxide (e.g. alumina, zirconia, titania, tin oxide, a mixed metal oxide, a mixture of metal oxides), or an organic polymer.

[0012] The spacer nanoparticles may have a refractive index approximately the same as that of the emitter medium, e.g. within about 10% thereof, or within about 5 or 2% thereof.

[0013] The sensitizer medium may comprise a crosslinked polymer. In this case the molecules of the sensitizer may be monomer units of the polymer. They may be crosslinking monomer units of the polymer, whereby the sensitizer molecules are joined by linker monomer units, or they may be coupled to crosslinking monomer units of the polymer by linker groups (or the crosslinking monomer units may comprise linker groups).

[0014] The emitter medium may comprise a solution of the emitter in a solvent. It may additionally or alternatively comprise an emitter polymer comprising molecules of the emitter, and/or nanocrystals of an emitter substance, and/or an amorphous solid consisting of or

comprising the emitter. The emitter polymer may comprise chromophoric units of a conjugated polymer that function effectively as emitter molecules. Alternatively, or additionally, the emitter polymer may have conjugated sections that assemble in various conformations to form chromophores, i.e. the moieties that interact with and emit light. These moieties may not be discrete sections of the polymer such as, for example, a fluorescent molecule attached as a pendant group, but rather the chromophores may be formed through aggregation, e.g. self-aggregation, of the relevant portions of the molecular backbone and/or other portions of the molecular structure of the polymer. One example here is MEH-PPV (poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]).

[0015] In the event that the emitter medium comprises an emitter polymer, the sensitizer medium may comprise:

- molecules of the sensitizer coupled to surfaces of nanoparticles, said nanoparticles being dispersed substantially homogeneously throughout the emitter polymer; or
- molecules of the sensitizer coupled to surfaces of a nanoporous substrate, the emitter polymer being disposed in pores of said nanoporous substrate; or
- a crosslinked polymer wherein molecules of the sensitizer are monomer units of the polymer, wherein said crosslinked polymer and the emitter polymer form an interpenetrating polymer network.

In this case the system may be a solid state system. It may be a particulate solid state system or may be a monolithic solid state system.

[0016] In the event that the emitter medium comprises an emitter amorphous solid, the sensitizer medium may comprise:

- molecules of the sensitizer coupled to surfaces of nanoparticles, said nanoparticles being dispersed substantially homogeneously throughout the emitter amorphous solid; or
- molecules of the sensitizer coupled to surfaces of a nanoporous substrate, the emitter amorphous solid being disposed in pores of said nanoporous substrate.

[0017] In the event that the emitter medium comprises emitter nanocrystals, the sensitizer medium may comprise:

- molecules of the sensitizer coupled to surfaces of nanoparticles, said nanoparticles being mixed with the emitter nanocrystals to form a medium that is homogeneous on the mesoscopic scale; or

- a crosslinked polymer wherein molecules of the sensitizer are monomer units of the polymer, or a metal-organic framework, or covalent network, wherein said emitter nanocrystals are embedded in a homogeneous distribution.

The mesoscopic scale may be considered to be a scale on the order of hundreds of nanometers. Thus “homogeneous on the mesoscopic scale” may be taken to indicate that any inhomogeneities are less than about 200nm, or less than about 150, 100 or 50nm in diameter or size.

[0018] The system may additionally comprise one or more solar cells optically coupled to the emitter medium. In this instance, when the system is exposed to light having a range of wavelengths, that portion of the light which has energy below the threshold energy for the solar cell(s) will be absorbed by the sensitizer and upconverted to above said threshold, and will be converted to electricity by the solar cell(s). That portion of the light which has energy above the threshold energy for the solar cell(s) may be converted directly to electricity by the solar cell(s). The system may be configured so that incident light passes through the solar cell(s) prior to impinging on the sensitizer medium, so that only light that is below the threshold for the solar cell(s) impinges on the sensitizer medium, so as to be upconverted thereby.

[0019] In the event that the system comprises solar cell(s), the optical coupling between the emitter medium and the solar cell(s) may be gasless, e.g. airless. It may have no gaseous component (other than dissolved gases). In one example, the system comprises a solar cell, disposed on a glass substrate and being optically coupled to the emitter medium by means of an oil layer.

[0020] In a second aspect of the invention there is provided a process for making a system according to the first aspect, comprising combining the solid sensitizer medium and the emitter medium.

[0021] The process may comprise coupling the sensitizer to a solid, e.g. to surfaces of nanoparticles or to a nanoporous substrate, so as to prepare the solid sensitizer medium. The coupling may comprise either: coupling a linker species to the solid, e.g. to surfaces either of the nanoparticles or of the nanoporous substrate, and then coupling the sensitizer to the linker species; or coupling the linker species to the sensitizer and then coupling the linker species having the sensitizer coupled thereto to the solid, e.g. to surfaces either of the nanoparticles or of

the nanoporous substrate; or coupling the sensitiser directly to nanoparticles or a nanoporous substrate using a sensitiser with the linker incorporated into the native sensitiser structure through some chemical functionality e.g. one or several aminopropyltriethoxysilane moieties.

[0022] The step of combining the solid sensitizer medium and the emitter medium may comprise immersing the solid sensitizer medium into the emitter medium which is in the form of a solution or it may comprise depositing the emitter medium, optionally in the form of a polymer containing the emitter, onto the solid sensitizer medium. In the event that the emitter medium comprises emitter nanocrystals, it may comprise dispersing the emitter nanocrystals within the solid sensitizer medium or mixing the emitter nanocrystals with the solid sensitizer medium.

[0023] In a third aspect of the invention there is provided a method for upconversion of photons comprising exposing a system according to the first aspect, or a system made by the process of the second aspect, to light of a wavelength capable of exciting the sensitizer. This may result in emission of upconverted light from the emitter medium.

[0024] The system may additionally comprise a photosensitive species having an absorption maximum at higher energy than the absorption maximum of the sensitizer. The photosensitive species may be capable of absorbing the upconverted light emitted by the emitter medium. It may have an absorption maximum approximately equal to the wavelength of the upconverted light emitted by the emitter medium. In this case, exposure of the system to light below the threshold leads to upconversion of said light to above said threshold so as to excite the photosensitive species. In an embodiment, the photosensitive species is a photovoltaic substance. In this case the method may result in generation of an electrical potential and optionally an electric current.

[0025] In a fourth aspect of the invention there is provided use of a system according to the first aspect, or a system made by the process of the second aspect, in an application selected from the group consisting of conversion of solar energy to electricity or solar fuel (e.g. hydrogen gas), biological imaging, drug activation, high-resolution optical and/or fluorescence microscopy, optical data storage and oxygen sensing. For example, photocatalysis may be used to drive a chemical reaction through the use of a catalyst, resulting in a solar fuel (which is a chemical substance generated with the assistance of solar energy). The presently described upconverting

material may be used to enhance the efficiency of the photocatalytic process, thus generating a solar fuel.

Brief Description of Drawings

[0026] Figure 1 is a diagram illustrating approaches for nanostructured sensitization of TTA-UC.

[0027] Figure 2 is a diagram illustrating a scheme for enhancing sensitizer absorption by plasmonic nano-antennae.

[0028] Figure 3 shows graphs of calculated squared electric field amplitude (E^2) enhancement around a gold nanoparticle in real space (top) and its dependence on wavelength and nanoparticle diameter (bottom).

[0029] Figure 4 is a graph showing calculated absorption enhancement at point P of Figure 3 for a given porphyrin and Au nanoparticle.

[0030] Figure 5 is a graph showing integrated E^2 enhancement for a given distance of the sensitizer molecules from the nanoparticle surface (100 nm particle, 668 nm wavelength).

[0031] Figure 6 shows (upper panel) a graph illustrating enhancement of a Si:H solar cell EQE (external quantum efficiency) by application of nanostructured upconverter and (lower panel) an absorption spectrum of the unfunctionalized sensitizer dye in solution.

[0032] Figure 7 shows normalised phosphorescence transients for silica-tethered dye and untethered dye at equal concentrations in Example 2. Note the logarithmic scale of the x axis. The lines are a guide to the eye.

[0033] Figure 8 shows graphs of fitting transients with the mixed-kinetics model used to extract triplet lifetime. The vertical (y) axes of these graphs represent phosphorescence intensity.

Description of Embodiments

[0034] The present invention provides a system for upconversion of photons so as to enable utilisation of low energy photons, for example for electricity generation. An important aspect of the invention is the use of a sensitizer which is immobilised on and/or in a solid substrate. Thus the sensitizer medium of the present invention comprises sensitizer molecules coupled to, or incorporated in, a solid substrate. This enables a high concentration of sensitizer molecules to be used without a risk of exceeding the solubility threshold of the sensitizer. It also enables precise control of the positioning of the sensitizer molecules on and/or in the substrate so as to reduce or minimise the self-quenching of the excited state of the sensitizer molecules by separating sensitizer molecules on a molecular level. In the present specification, the term “comprise” and related terms (e.g. “comprising”) should be taken to indicate the presence of the designated integer(s) and the possibility of other undesignated integers. It should not be taken to denote or imply any particular proportion of the designated integer(s). The term “solid” should be construed as meaning non-fluid, i.e. non-gaseous and non-liquid. The solid may be a crystalline solid or a non-crystalline solid or a partially crystalline solid. A suitable definition of “solid” from the McGraw-Hill Dictionary of Scientific and Technical Terms (4th Edition, ed. Sybil. P. Parker, McGraw-Hill Book Company, New York 1980, page 1769) is “a substance that has a definite volume and shape and resists forces that tend to alter its volume or shape”. The solid may be monolithic or may be particulate. If particulate, it may be nanoparticulate (i.e. having particles in the range of 1 to 1000nm mean diameter), or microparticulate (i.e. having particles in the range of 1 to 1000 microns mean diameter) or may be macroparticulate (i.e. having particles of greater than about 1mm mean diameter) or may be a mixture of such particles.

[0035] In conjunction with the sensitizer medium, having the immobilised sensitizer molecules, the present invention requires an emitter to which energy can be transferred from an excited state of the sensitizer. It will be understood that the present invention lies not entirely in the nature of the sensitizer and emitter but rather in the use of an immobilised sensitizer in combination with an emitter that is matched with the sensitizer in that sense that energy can be transferred to the emitter from a triplet state (commonly the first excited triplet state) of the sensitizer. Many such sensitizer/emitter combinations are known and may be used in the present invention.

[0036] A limitation on the nature of the sensitizer is that it should be capable of maintaining its energy absorption capability once immobilised. Typically the sensitizer (and hence also the solid sensitizer medium which incorporates the sensitizer), is capable of absorbing energy of less than

about 2eV, or less than about 1.5, 1 or 0.5eV, in order to excite to a triplet state. The exciting energy may be for example of energy about 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9 or 2eV. It should be noted that the absorbance of the sensitizer may be broad, so that it may absorb at a range of energies. The above energies may represent a midpoint of the absorption band, or may represent an energy of maximum absorbance. The exciting energy may have a wavelength of about 600 to about 2500nm, or about 600 to 1500, 600 to 1000, 600 to 800, 600 to 750nm, 700 to 2500, 1000 to 2500, 700 to 1000, or 700 to 800nm, e.g. about 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2300, 2400 or 2500nm. Again these wavelengths may represent a midpoint of the absorption band, or may represent a wavelength at maximum absorbance. The sensitizer may be present in the system in greater concentration than the saturation concentration in the emitter medium. It may be present in concentration over 5% greater than the saturation concentration, or over 10, 15, 20 or 25%, or in concentration about 5 to about 100% greater than the saturation concentration, or 10 to 100, 20 to 100, 50 to 100, 5 to 50, 5 to 20 or 10 to 50% greater than the saturation concentration. An advantage of the present invention lies in the immobilisation of sensitizer molecules. Immobilisation can restrict energy loss-causing quenching among sensitizer molecules, which otherwise can severely reduce the efficiency of an upconverter using high concentration sensitizer. This therefore enables a high concentration of sensitizer molecules to be used without introducing the severe losses that would otherwise result.

[0037] The emitter may be any suitable compound to which energy can be transferred from the excited triplet state of the sensitizer. The emitter may be such that two molecules of the emitter to which energy has been transferred from the sensitizer can cooperate to generate upconverted photons. Thus the excited states of the emitter brought about by energy transfer from the sensitizer should be sufficiently mobile in the system that they can collide in order to generate the upconverted photons. In order to achieve this, the emitter molecules themselves may be mobile, or the chemical structure of the emitter medium may be such that it permits the excited states to migrate within the emitter medium. The upconverted photons have an energy greater than the energy of the photons initially absorbed by the sensitizer, and may have an energy of up to double that of the incident photons. Thus they may have an energy of about 1 to about 4eV, or about 1 to 3, 1 to 2, 2 to 4, 3 to 4 or 2 to 3eV, e.g. about 1, 1.5, 2, 2.5, 3, 3.5 or 4 eV. They may have a wavelength of about 300 to about 1200nm, or about 300 to 600, 300 to 500, 300 to 400,

400 to 1200, 600 to 1200 400 to 60, 400 to 500 or 500 to 600nm, e.g. about 300, 350, 400, 450, 500, 550, 600, 700, 800, 900, 1000, 1100 or 1200nm.

[0038] The inventors envisage four different types of solid sensitizer medium: nanoparticles, nanoporous solids, polymeric/covalent networks and metal-organic frameworks.

[0039] *Nanoparticles*: these may be any suitable nanoparticle capable of binding to the sensitizer, and either incapable of quenching electronic energy from, e.g. a triplet state of, the sensitizer, or capable of doing so only at sufficiently slow rate so as to not inhibit the upconversion process. Effectively this simply means that they should have a functional or functionalisable surface. They may for example comprise metal or semiconductor oxide nanoparticles. Suitable metal or semiconductor oxides include silica, germania, titania, alumina, zirconia, mixed metal or semiconductor oxides etc. Alternatively the nanoparticles may be metal nanoparticles, or nanoparticles made of conductive oxides. These may have the benefit of exhibiting plasmon resonance in order to concentrate the energy of the incident radiation in a small spatial region so as to raise the efficiency of the system. The plasmon resonance may be at a wavelength at which the sensitizer absorbs photons, optionally at a wavelength near the maximum absorption wavelength of the sensitizer. Suitable metals include gold, silver, aluminium, copper, nickel, chromium, titanium and platinum. The metal may be a noble metal. Suitable conductive oxides include indium-doped tin oxide, fluorine-doped tin oxide, aluminium-doped zinc oxide, iridium oxide and ruthenium oxide. The nanoparticles may be spherical, or substantially spherical or oblate spherical or irregular or ovoid or some other shape. The diameter of the nanoparticles may be from about 10 to about 1000nm, or about 10 to 500, 10 to 200, 10 to 100, 10 to 50, 20 to 1000, 50 to 1000, 100 to 1000, 200 to 1000, 500 to 1000, 20 to 200, 20 to 100, 50 to 500, 50 to 200 or 50 to 500nm, e.g. about 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900 or 1000nm. This may be a mean or median diameter. It may be a hydrodynamic diameter. The particles may be polydispersed or may be substantially monodispersed. In the event that the particles comprise a metal or a conductive oxide, the particles may be coated with a dielectric layer. Suitable dielectric layers include, but are not limited to, a silica, alumina, zirconia, titania or germania layer or a layer of organic polymer. The thickness of the dielectric layer, if present, may be about 1 to about 20 nm, or about 1 to 10, 1 to 5, 1 to 2, 2 to 20, 5 to 20, 10 to 20, 2 to 10, 2 to 5 or 5 to 10nm, e.g. about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15 or 20nm. The sensitizer may be coupled to the nanoparticles directly or by means of a linker group. The linker

group may comprise a hydrocarbon chain, a polyether chain or some other chain. It may be incapable of absorbing radiation at a wavelength that is capable of exciting the sensitizer. It may also be incapable of absorbing radiation at the upconverted wavelength. It may, if present, be from about 2 to about 50 main chain atoms in length or longer, or about 2 to 20, 2 to 10, 2 to 5, 5 to 50, 10 to 50, 20 to 50, 5 to 20, 5 to 10 or 10 to 20 main chain atoms in length, e.g. about 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45 or 50 main chain atoms in length. Suitable linker chemistries (independently at either end) include siloxane coupling, ester coupling, amide coupling, triazole coupling, ether coupling, metal-thiol coupling or some other coupling chemistry. In a particular example, sensitizers may be coupled to noble metal nanoparticles by means of a thiol terminated linker group attached to the sensitizer molecule, wherein the thiol group binds to the metal nanoparticle surface. The nanoparticles may be in the form of a bed, e.g. a close packed bed, or they may be in suspension in the emitter medium, or they may be in the form of a slurry or paste in the emitter medium.

[0040] *Nanoporous solids*: these may be in the form of nanoporous particles or nanoporous monoliths. In some instances they are formed by sintering nanoparticles, i.e. they may comprise sintered nanoporous particles. They may therefore have the same range of chemistries as described above for the nanoparticles, and may utilise the same range of attachment chemistries for attaching the sensitizer molecules. The pore size of the nanoporous solid may be from about 1 to about 100nm, or about 1 to 50, 1 to 20, 1 to 10, 10 to 100, 20 to 100, 50 to 100, 10 to 50, 10 to 20 or 10 to 50nm, e.g. about 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90 or 100nm. This may be a mean pore size. The pores may be substantially monodispersed or may be polydispersed. In some instances the pore structure of the nanoporous solid may be bimodal, having a population of relatively large and another population of relatively small pores. Other forms of nanoporous solids may be those made by well known sol-gel processes, templating processes etc. These processes commonly result in metal oxide solids as described above for the nanoparticles. The nanoporous solids may be inorganic or may be organically modified, e.g. they may be polyorganosilsesquioxanes or aluminium, germanium, zirconium, titanium or mixed metal analogues. Another alternative for the nanoporous solid is a nanoporous polymeric structure, e.g. a nanoporous resin such as a solid phase peptide synthesis resin. The polymer may be a crosslinked polymer, e.g. a nanoporous poly(styrene-co-divinylbenzene) or poly(methylmethacrylate-co-ethyleneglycol dimethacrylate) or other suitable nanoporous polymeric system. The nanoporous solids may be in the form of monoliths or may be in the form of particles, optionally nanoparticles as described above.

[0041] *Polymeric networks*: the sensitizer molecules may be incorporated into a crosslinked polymer network. They may be incorporated as, or coupled to, crosslink points or may be between crosslinks. It will be apparent that for the former it is necessary that they have, or be coupled to a group having, at least 3 functional groups which can participate in polymerisation whereas in the latter they should have 2 functional groups which can participate in polymerisation. There is a wide variety of polymer chemistries that may be employed, for example polyurethanes, polysiloxanes, polyacrylates, polyolefins, polyamides, polycarbonates etc. and correspondingly the sensitizer molecule used to make the polymer may have a similarly wide range of chemistries. In the context of the present specification, where reference is made to a polymer, or solid, or other material containing, or incorporating, molecules of the sensitizer (or sensitizer molecules), this may, depending on the specific context, refer to physical incorporation of the sensitizer molecules or may refer to chemical incorporation thereof. Thus for example where reference is made to a sensitizer molecule being a monomer of a crosslinked polymer, this may refer to the polymer containing monomer units derived from, or derivable from, the sensitizer molecules and does not necessarily imply the presence of free molecules of the sensitizer.

[0042] An example of the case where the sensitizer molecules represent crosslink points is a polymeric network in which triaminofunctional sensitizer molecules have been copolymerised with a dicarboxylic acid linker species. The dicarboxylic acid may be tailored so as to achieve a desired distance between sensitizer moieties in the resulting polymer. The linker species may be rigid or may be flexible. In this context, a rigid linker species is one in which the distance between the two carboxylic acid groups is fixed. Examples include biphenyl-1,1'-dicarboxylic acid, naphthalene-1,8-dicarboxylic acid, adamantane-1,3-dicarboxylic acid. A flexible linker species in this context is one that is not rigid, i.e. in which the distance between the two carboxylic acids is not fixed. Examples include alkane-1,n-dicarboxylic acids in which n is an integer greater than 1 (e.g. 2, 3, 4, 5, 6, 7, 8, 9 or 10). In particular cases the linker species may be designed so that the polymeric network comprises nanopores in which the emitter medium may be located.

[0043] An example of the case where the sensitizer molecules are located between crosslinks in the polymeric network is a polymeric network in which diaminofunctional sensitizer molecules have been copolymerised with tricarboxylic acid crosslinking species. In this case the tricarboxylic acid may be tailored so as to achieve a desired distance between sensitizer moieties

in the resulting polymer. The crosslinking species may be rigid or may be flexible or may be semiflexible. In this context, a rigid crosslinking species is one in which the distance between the three carboxylic acid groups is fixed. Examples include biphenyl-1,1'-dicarboxylic acid, naphthalene-1,5-dicarboxylic acid and adamantane-1,3-dicarboxylic acid etc. A flexible linker species in this context is one that is not rigid, i.e. in which the distance between all three carboxylic acids is not fixed. Examples include alkane-1,n-dicarboxylic acids in which n is an integer greater than 1 (e.g. 2, 3, 4, 5, 6, 7, 8, 9 or 10). A semiflexible crosslinking species in this context is one in which the distance between two of the three carboxylic acid groups is fixed and the distance between each of those two and the third carboxylic acid group is not fixed. Examples include 3-(3-carboxypropyl)biphenyl-1,1'-dicarboxylic acid, 3-(3-carboxypropyl)naphthalene-1,5-dicarboxylic acid, 5-(3-carboxypropyl)adamantane-1,3-dicarboxylic acid etc. In particular cases the linker species may be designed so that the polymeric network comprises nanopores in which the emitter may be located. In any of the above structural types, the linker may be about 1 to about 50nm in length, or about 1 to 25, 1 to 10, 1 to 5, 5 to 50, 10 to 50, 20 to 50, 5 to 20, 5 to 10, 10 to 20 or 20 to 40nm, e.g. about 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45 or 50nm.

[0044] In some instances the crosslinked polymer network may comprise sensitizer molecules as crosslink monomer units and sensitizer molecules as non-crosslink monomer units. In this case, the two different classes of sensitizer molecules in the polymer network may be separated by linker groups.

[0045] *Metal-organic frameworks*: the sensitizer molecules may be incorporated into a metal-organic framework. They may be incorporated as, or integrated into, or coupled to the linker groups between the metal centers. The linker groups may be rigid linker groups. In this context, the term "rigid" indicates that there is a fixed distance between the functional groups of the linker group. In the case where the sensitizer molecules are coupled to the linker groups, they may have one functional group to attach to the organic linker group. In the case where the sensitizer molecules are incorporated as or integrated into the linker groups, they may have two functional groups to either connect to two metal centers, or to two organic chains which then connect to metal centers, or may have more than two such functional groups. The total length of the linker groups may be chosen such that the pore size of the metal-organic framework is be from about 1 to about 100nm, or about 1 to 50, 1 to 20, 1 to 10, 10 to 100, 20 to 100, 50 to 100, 10 to 50, 10 to 20 or 10 to 50nm, e.g. about 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60,

70, 80, 90 or 100nm. Suitable functional groups for coupling to the metal centres include carboxylic acid group or other acidic groups, which can form ionic bonds to the metals, and amine and phosphine groups which can complex to the metal centres. The metal of the metal-organic framework may be any metal capable of coupling to more than one organic linker group. It may be a transition metal. It may be a metal of valency greater than 1, e.g. 2, 3, 4, 5 or 6. It may be a metal capable of forming organometallic bonds to a linker group.

[0046] In the event that the solid sensitizer medium comprises nanoparticles or a nanoporous solid, there may be spacer molecules coupled to the nanoparticles or nanoporous solid as well as sensitizer molecules. The purpose of these is to separate the sensitizer molecules on the surface of the nanoparticles or nanoporous solid so as to inhibit or prevent self-quenching of triplet states of the sensitizer molecules. The spacer molecules may therefore be molecules that are incapable of absorbing energy from the triplet state of the sensitizer, i.e. that do not quench the excited sensitizer. They may also be incapable of absorbing energy at a wavelength absorbed by the sensitizer. They may be incapable of absorbing energy at the upconverted wavelength. They may comprise alkyl chains, or polyether chains, or some other suitable chain, together with a coupling group suitable for coupling them to the surface of the nanoparticles or nanoporous solid. The nature of the coupling group will depend on the chemical nature of the surface of the nanoparticles or nanoporous solid. Conveniently, although not essentially, the coupling group will be the same as the group on the sensitizer molecules through which the sensitizer molecules couple to the surface of the nanoparticles or nanoporous solid. The length of the chains of the spacer molecules should be sufficient to prevent or inhibit interaction between the sensitizer molecules. A suitable length will therefore depend on the nature of the sensitizer molecules and the presence or absence and size of linker groups present between the sensitizer molecules and the surface of the nanoparticles or nanoporous solid. It will be understood that there should be a sufficiently high proportion of spacer molecules as to effectively inhibit or prevent self-quenching of triplet states of the sensitizer molecules. The molar ratio of spacer molecules to sensitizer molecules on the surface of the nanoparticles or nanoporous solid may be about 1 to about 100 (i.e. about 1:1 to about 100:1) or about 1 to 50, 1 to 20, 1 to 10, 1 to 5, 1 to 2, 2 to 100, 10 to 100, 20 to 100, 50 to 100, 5 to 50, 5 to 20, 20 to 50, 30 to 70 or 10 to 20, e.g. about 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90 or 100 or more.

[0047] In the event that the solid sensitizer medium comprises metallic nanoparticles which exhibit plasmon resonance, the sensitizer medium may additionally comprise spacer

nanoparticles. This may serve to ensure that the spacing between nanoparticles is greater than the absorption cross section of the sensitizer-bound nanoparticles, since the physical cross section of the nanoparticles may be significantly smaller than the absorption cross-section. The spacer nanoparticles therefore should have no significant absorption at the wavelength at which the sensitizer absorbs. They may also have no significant absorption at the upconverted wavelength. They may comprise the same material as the nanoparticles having bound sensitizer (with the exception of the sensitizer itself) or may be a different material. They may be for example metal nanoparticles or metal oxide nanoparticles or semiconductor oxide or organic (e.g. polymeric) nanoparticles or may be some other type of nanoparticle. They may have substantially the same diameter as the nanoparticles having bound sensitizer or may have a different diameter (either smaller or larger). The spacer nanoparticles may be approximately index matched with the emitter medium in which the solid sensitizer medium is located. They may have a refractive index of within about 10% of the emitter medium, or within about 5 or 2% thereof. This may serve to reduce scattering of light within the system so as to reduce energy losses. The ratio of the metallic nanoparticles to the spacer nanoparticles may be from about 1:1 to about 1000:1, or about 1:1 to 100:1, 1:1 to 10:1, 1:1 to 5:1, 1:1 to 2:1, 2:1 to 10:1, 10:1 to 100:1, 100:1 to 1000:1, 10:1 to 1000:1, 100:1 to 1000:1 or 5:1 to 500:1, e.g. 1:1, 3:2, 2:1, 3:1, 4:1, 5:1, 10:1, 20:1, 50:1, 100:1, 200:1, 300:1, 400:1, 500:1, 600:1, 700:1, 800:1, 900:1 or 1000:1 or even greater.

[0048] The sensitizer medium is disposed in the emitter medium. The term “disposed in” should be construed widely. Thus the sensitizer medium may be dispersed or distributed through the emitter medium or may be interspersed through the emitter medium or may be intermixed with the emitter medium or may be dispersed in the emitter medium in some other way. For example, if the emitter medium comprises nanocrystals and the sensitizer medium is a microporous solid, the nanocrystals of the emitter medium may be dispersed through the sensitizer medium, which is thereby “disposed in” the emitter medium in the sense that portions of the sensitizer medium are present between portions of the emitter medium. In another example, the sensitizer medium may comprise nanoparticles and the emitter medium may comprise nanocrystals. In this case the two may be mixed, for example to form a substantially homogeneous mixture of the two. Again, in this instance, the sensitizer medium may be viewed as being “disposed in” the emitter medium in the sense that portions of the sensitizer medium are present between portions of the emitter medium. Thus the invention may be viewed as a system for upconversion of photons, comprising (a) a solid sensitizer medium comprising a sensitizer, and (b) an emitter medium

comprising an emitter which is capable of accepting energy from an excited state of the sensitizer so as to upconvert said energy, wherein the sensitizer medium and the emitter medium are intimately mixed.

[0049] The emitter may be dissolved in the emitter medium. The concentration of the emitter may be sufficient to ensure that excited state emitter molecules encounter each other so as to generate upconverted photon emissions sufficiently frequently that the excited state does not decay before they do so. A typical triplet state lifetime of the emitter molecules is about 10 microseconds or less and hence the concentration should be sufficient to ensure that successful collisions between excited triplet states of the emitter molecules occur on average more than once per 10 microseconds, or more than once per 9, 8, 7, 6, 5, 4, 3, 2 or 1 microsecond. Suitable concentrations of emitter are greater than about 5mM, or greater than about 10, 15, 20 or 25mM, or about 5 to about 50mM, or about 5 to 20, 5 to 10, 10 to 50, 20 to 50 or 20 to 30mM, e.g. about 5, 10, 15, 20, 25, 30, 35, 40, 45 or 50mM, or in some instances greater than 50mM. The emitter medium should be capable of dissolving this concentration of emitter. Commonly the emitter medium comprises an organic solvent. The nature of the emitter medium will depend on the nature of the emitter. Suitable solvents include benzene, toluene, xylene, pyridine, chlorobenzene, chloroform, dichloromethane, diethyl ether, tetrahydrofuran etc. The solvent should not absorb significantly at the wavelength of either the incident radiation or emitted (upconverted) radiation.

[0050] In some embodiments the emitter medium comprises an emitter polymer, which may be a conjugated polymer (i.e. a polymer comprising conjugated unsaturation or one or more repeated unsaturated moieties), or a polymer with molecules of the emitter coupled thereto. The coupling should be such that the emitter maintains its ability to accept the transfer of triplet state energy from the sensitizer and upconvert to generate higher energy photons. In these embodiments the emitter polymer may have nanoparticles of the solid sensitizer medium (as described above) embedded therein, preferably substantially homogeneously distributed therein, or it may be dispersed within the pores of a nanoporous solid sensitizer medium (as described above), or it may form an interpenetrating network with the polymer network solid sensitizer medium (as described above) or a metal-organic framework (as described above) or a covalent framework (as described above). In any of these options, the emitter polymer may be disposed such that emitters are in sufficiently close proximity to sensitizer molecules on the solid sensitizer medium as to be capable of accepting energy being transferred from the triplet state of

the sensitizer molecules and in sufficient proximity to other emitters to allow collision between excited triplet states of the emitters within the triplet state lifetime of the emitters, so as to allow upconversion to form higher energy photons. Alternatively or additionally, the emitter polymer may facilitate the migration of excited states of emitters, e.g. along a suitable conjugated polymer backbone, thus relaxing the requirement of proximity between the emitters formed by or attached to the polymer.

[0051] The emitter polymer may have chemical groups suitable for attachment of the emitter molecules. As with the crosslinked sensitizer polymer, there are numerous suitable chemistries for the emitter polymer. There is no requirement for the emitter polymer to be crosslinked, although it may be crosslinked. The emitter polymer may for example be a polyurethane, polysiloxane, polyacrylate, polyolefin, polyamide, polycarbonate, polyphenylene, polythiophene, polypyrrole or other suitable polymer, optionally crosslinked. Commonly the emitter polymer will have a glass transition point below the operating temperature of the upconversion system. It may have a glass transition temperature less than about 20°C, or less than about 15, 10, 5 or 0°C. This may serve to allow the emitter molecule sufficient mobility to facilitate the upconversion process as described above. The emitter polymer may be non-crystalline, or have low crystallinity (e.g. less than about 20, 10, 5, 2 or 1% crystallinity), at the operating temperature of the upconversion system.

[0052] The process for making the upconversion system of the present invention may comprise combining a solid sensitizer medium with an emitter medium. In the event that the solid sensitizer medium is nanoparticulate and the emitter medium is liquid, this may comprise dispersing the solid sensitizer medium in the emitter medium. If the solid sensitizer medium is nanoporous and the emitter medium is liquid, it may comprise infusing the emitter medium into the pores of the solid sensitizer medium. In the event that the solid sensitizer medium is nanoporous and the emitter medium is a polymer, whereby the two form an interpenetrating polymer network or a bicontinuous microemulsion or some other form of bicontinuous system, the process may comprise infusing a liquid emitter monomer into the solid sensitizer medium and polymerising the liquid emitter monomer so as to form the polymeric emitter medium, or infusing a solution of the emitter polymer in a solvent into the solid sensitizer medium and subsequently evaporating the solvent or blending the molten emitter polymer with the sensitizer medium (optionally also in molten form) and allowing the combination to cool and solidify. The liquid emitter monomer may comprise a polymerisable moiety coupled to an emitter. The

polymerisable moiety may be polymerisable thermally or photochemically or by gamma radiation or by some other means.

[0053] Nanoparticulate solid sensitizer media may be made using any suitable nanoparticle substrate. These may be made by well known methods. In the event that the nanoparticle substrate is an oxide, e.g. silica, a convenient means to couple the sensitizer to the substrate is by means of a silane coupling reaction. In one form, this involves reacting the substrate with a functionalised organoalkoxysilane, e.g. an aminoalkyltrialkoxysilane (for example an aminopropyltrimethoxy- or triethoxy-silane). Many suitable silanes are well known coupling agents, e.g. aminopropyltriethoxysilane. The functional group introduced thereby onto the surface of the substrate may be reacted with a suitable functional group on the sensitizer, e.g. a carboxylic acid, an acyl halide group or some other suitably reactive group. This results in an amide linkage between the linker chain and the sensitizer, and a siloxane linkage between the linker chain and the substrate. Alternatively the functionalised organoalkoxysilane may first be reacted with the sensitizer to attach a linker chain to the sensitizer, and subsequently reacted, via the distal end of the linker chain to the substrate so as to form a similar structure as described above. The sensitizer molecule may be designed and synthesised with the linker moiety already incorporated, in which case the sensitizer may be combined directly with the substrate to facilitate linking thereto. The same chemistry as described above may be used in order to couple a nanoporous oxide substrate to the sensitizer to form a nanoporous solid sensitizer medium. It will be recognised that other means to couple the sensitizer to the linker may be used, depending on the functionality of the sensitizer. For example sensitizers having alcohol groups may couple via ether or ester formation, alkynes or azides may be coupled to a suitable linker via copper (I) catalysed cycloaddition reactions ("click chemistry") etc.

[0054] In the event that the nanoparticles comprise elemental metals, e.g. Pt, Au, Ag etc., a suitable coupling may be through a metal-sulfur coupling. In this event, the linker molecule may be a thiol containing a coupling group, e.g. a carboxylic acid or acyl halide group. As discussed above, there are a variety of other ways to couple to such a linker which are well known to those skilled in the art. Thus suitable linker compounds include ω -functional alkane-1-thiols. The length of the alkyl chain (corresponding to the length of the linker group in the solid sensitizer medium) may be about 2 to about 20 carbon atoms, or about 2 to 16, 2 to 12, 2 to 8, 6 to 20, 12 to 20 or 6 to 16, e.g. 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20. Suitable

functional groups as described above will depend on the nature of the sensitizer and its functionality.

[0055] It will be understood that the coupling reactions used in the process may require catalysts and/or heat and/or irradiation in order to proceed efficiently. The conditions of these reactions will depend on the specifics of those reactions and will be well known to skilled workers.

[0056] The upconversion system of the present invention may be integrated into a solar energy conversion system. Thus optically coupling the upconversion system with a solar energy converter (e.g. a silicon solar cell such as an amorphous silicon solar cell) may provide a system in which a wide range of wavelengths may be absorbed and converted to electrical energy. In such a system, wavelengths with sufficient energy to activate the solar energy converter will do so, so as to provide electrical energy. Wavelengths of insufficient energy (i.e. below the threshold for the solar energy converter) will be upconverted by the upconversion system so as to convert them to suitable wavelengths above the threshold. These can then be absorbed by the solar energy converter so as to generate additional electrical energy. In some embodiments, therefore, the sensitizer is substantially incapable of absorbing wavelengths of sufficient energy to activate the solar energy converter. The optical coupling of the upconversion system to the solar energy converter may be by means of a transmission medium. Commonly this is a liquid medium so as to minimise energy losses, for example losses by scattering or reflection of light. A suitable medium is an oil, e.g. a paraffin oil or a silicone oil. Commonly the coupling is free of gases (other than those which may be in solution in the liquid medium).

[0057] The upconversion system of the present invention may also be integrated into a photoelectrochemical device, e.g. for water splitting. Such a system may for example comprise a solar energy converter as described above with electrochemically active electrodes, permitting the device to split water into hydrogen and oxygen, or performing either of the two half reactions. The voltages needed for water splitting require single-threshold photovoltaic absorber materials with thresholds well in the visible range of the solar spectrum. Thus, single-threshold photoelectrochemical devices sacrifice a large part of the solar spectrum, which can be remedied by the application of upconversion as described herein.

[0058] The upconversion system of the present invention may also be used for oxygen sensing. Oxygen provides an efficient quenching mechanism of the sensitizer triplet states of certain

sensitizer species (e.g., of Pd, Pt, Ir, Cu, or Ru-containing metallo-porphyrins) and the upconversion yield can therefore be sensitively dependent on the oxygen partial pressure. By monitoring the quenching of upconversion according to the present invention, an oxygen concentration may be readily determined.

[0059] Other applications for the upconversion system include activation of drug precursors. Thus in some medical applications, a drug precursor may be located in the body of a patient and activated (i.e. converted to the active drug) by means of irradiation. A problem with this is that the higher energy radiation required for the drug activation may be more harmful or have less appropriate penetration characteristics through body tissues. In such cases, the drug precursor may be colocated with an upconversion system as described herein. Lower wavelength radiation may therefore be used to activate the upconversion system within the patient's body. The upconverted light may then be used to activate the drug precursor *in situ*.

[0060] Still other applications are in the field of microscopy and imaging. In these applications, the upconversion system may be used to convert incident radiation to wavelengths which are not subject to interference from naturally occurring sources e.g. autofluorescence.

TTA-upconversion process

[0061] TTA-UC is a process allowing for efficient conversion of low-energy light (mostly in, but not limited to, the red part of the solar spectrum) to light of higher energy (yellow, green or blue light, depending on the envisioned application). It is based on the presence of two types of organic chromophores: a sensitizer species which absorbs the low-energy light, and transfers its energy to a second species, the emitter. Excited triplet states have the important property of storing the energy during the process, and the final emission of the upconverted light proceeds through bimolecular collisions of emitter molecules being in their first excited triplet-state.

[0062] The dynamics of the process can be understood from rate equations, which also give unequivocal hints on how to maximize the efficiency of TTA-UC. The efficiency of the process depends quadratically on the concentration of emitters in the triplet state, denoted [T]. The change in time of this quantity $d[T]/dt$ is described by the equation:

$$d[T]/dt = k_p.[S] - k_1.[T] - k_2.[T]^2$$

in which k_p is the rate constant for optical excitation of the sensitizer (thus describing the illumination conditions of the system), k_1 is the first order rate constant for the loss of emitter triplets by undesired, yet ever present loss mechanisms, and k_2 is the rate constant for TTA (triplet-triplet annihilation), actually leading to the desired upconversion.

[0063] For TTA-UC to proceed efficiently, the quantity $k_2 \cdot [T]$ must exceed k_1 . In the steady-state (which describes the envisioned case of application), the quantity $[T] \sim k_p[S]/k_1$ and so it is necessary that $k_p \cdot k_2[S] > k_1^2$. k_1 and k_2 are fundamental properties of the involved molecules and cannot easily be engineered. Although it might be conceivable to alter the chemical structure of the involved species, the two other quantities involved - k_p , describing the rate of excitation of the sensitizers, and $[S]$, the concentration of sensitizers, are more easily accessed.

[0064] This invention relates to methods for increasing $[S]$ through nanostructured sensitization. Simultaneously, k_p may also be increased through integration of plasmonic nano-antennae.

Nanostructured sensitization

[0065] The TTA-upconversion efficiency depends on the concentration of sensitizer molecules. Using PQ4PdNA (palladium tetrakisquinoxalino-porphyrin with nitro-amine ligands) as sensitizer and rubrene as emitter, dissolved in toluene, the inventors have also observed that the current gain of a solar cell, augmented with this upconverting solution, is increased upon concentrating the molecules. Using numerical modeling, the inventors also showed that a further increase of the concentration by a factor of >100 would boost the upconversion yield into a range where it would be relevant for application in state-of-the-art photovoltaic devices. However, the present system based on molecules dissolved in organic solvents is limited by the finite solubility of the molecular species, and would not allow reaching such concentrations.

[0066] The present invention addresses this problem by binding one or both of the molecular species to either a surface or into a bulk material. In doing so, it is preferable that there is no self-quenching of the sensitizer triplets, i.e. the interactions between two sensitizer molecules should be minimized or even inhibited, that the transfer of triplets from sensitizer to emitter molecules is efficient, i.e. that there are molecular collisions at sufficient rate between the two species or a sufficient electronic coupling by orbital overlap (either direct or mediated through conjugated molecular chains), and that the interaction of two emitter molecules also proceeds at a high rate, again facilitated by either a high collision rate or orbital overlap.

[0067] The invention utilises a general strategy in which sensitizer molecules are bound to a support structure. Suitable support structures include a surface or a porous molecular network. The support structure carrying the sensitizer molecules is surrounded/interspersed by the emitter species, optionally in solution. Thus in certain embodiments, the sensitizer molecules are immobilized, preventing self-quenching, while TET (triplet-energy transfer) and TTA can proceed at high rates as bimolecular collisions between sensitizer and emitter as well as between emitters are facilitated by the latter species being in solution.

[0068] The support structures may be designed such that they:

- i) do not quench the triplets from either sensitizer or emitter molecules,
- ii) have maximum surface area in order to maximize the sensitizer concentration [T], and
- iii) do not have a large refractive index contrast to the solvent medium hosting the emitter species, to avoid optical losses by scattering.

[0069] The following architectures are suitable:

- 1) A colloidal ensemble of metal oxide or silica nanoparticles (NP) coated with sensitizer molecules (S), immersed in emitter solution. Spacer molecules (D) may be used to dilute the surface load of sensitizer molecules to control the level of self-quenching of sensitizer triplets.
- 2) A metal oxide or silica nanosponge (e.g. made by fusing respective nanoparticles) whose cavities are coated with sensitizer molecules, interspersed with emitter solution. Again, spacer molecules (D) may be used to dilute the surface load of sensitizers.
- 3) A cross-linked random polymer network with long linker molecules (L) between functionalized sensitizers in order to form an open network structure, interspersed with emitter solution. Sensitizers with a different number of linkable ligands may be mixed in order to intentionally introduce "topological defects", which would increase the porosity of the network and allow better penetration by the emitter solution. In addition, this may serve to broaden the absorption spectrum of such solid state sensitizer by blending different sensitizer molecular species.
- 4) A cross-linked polymer network with symmetry centre molecules (C), imposing a certain short-range order by their ligand symmetry. These molecules may be connected by linker species (L), containing one (or more) sensitizer molecules (S) on a linear chain. Again, the number (or symmetry) of linkable ligands, in this case of the C species, could be

varied in order to create topological defects. Sketches of these four approaches are provided in Figure 1.

Demonstration of feasibility

[0070] A palladium trisquinoxalino-porphyrin functionalized with a carboxylic acid ligand, was coated onto amine-functionalized silica nanoparticles by means of a peptide linkage reaction. This procedure resulted in brightly green colored colloidal nanoparticles which performed TTA-UC when immersed into a rubrene emitter solution and illuminated with a red laser. Similar experiments with a simpler carboxylic acid functionalized palladium porphyrin (absorbing in the green spectral region), directly coated onto zirconium dioxide nanoparticles also resulted in TTA-UC in combination with a diphenylanthracene emitter solution.

[0071] A Stern-Volmer quenching study of the phosphorescence generated from the deaerated functionalised silica nanoparticles showed that sensitiser triplets were quenched by rubrene emitter with near-unity efficiency at rubrene concentrations greater than about 5mM.

[0072] In separate work, the lifetime of sensitiser phosphorescence was measured in a time-resolved pulse excitation experiment for two materials: metalloporphyrin sensitiser tethered to silica nanoparticles, and the same metalloporphyrin dissolved in solution to give an equal per-volume concentration of sensitiser. The phosphoresce lifetime of the tethered sensitiser was substantially increased compared to the free solution, indicating that unwanted inter-sensitiser quenching of triplet energy was reduced by the use of a nano-scaffold.

[0073] Time-resolved detection of this UC fluorescence after pulsed excitation revealed an almost purely second-order decay of the fluorescence signal, which indicated that the upconversion process is the dominant channel, and parasitic non-radiative decay is negligible in the excitation density range studied.

Plasmonic nano-antennae

[0074] Plasmons are collective excitations of conduction electrons in metals, which in general couple strongly to electromagnetic radiation. They usually exhibit one or more sharply peaked resonances at a well-defined wavelength where the interaction with incident photons is maximized. Noble metal particles in the diameter range about 20 to about 100nm have one

dominant resonance of dipolar character, whose resonance frequency lies in the visible region of the electromagnetic spectrum when embedded in a low-index medium. It should be noted that the refractive index of the host medium may shift the energetic position of the resonance, with higher refractive indices leading to red-shifted resonances. Depending on the particle size, either absorption (small particles) or scattering (larger particles) dominates, while in both cases the respective cross section of the process can be several ten times the actual geometric cross section of the particle. This effect is accompanied by an equally strong enhancement of the electric field amplitude in the vicinity (i.e. within about 0 to about 20nm) of the nanoparticle.

[0075] This effect is capable of enhancing both absorption and emission of photons by/from organic dyes, due to the much enhanced dipolar coupling between molecules and the electromagnetic field in the spatial region of field enhancement. In some embodiments of the present invention, this effect is exploited so as to increase absorption of low-energy light in organic chromophores which are the sensitizer species in a TTA-UC system.

[0076] A suitable device may therefore comprise:

- Sensitizer molecules S, being part of a bimolecular system capable of performing TTA-UC, with a functionalizable ligand;
- Metal nanoparticles (MNPs) of appropriate size, i.e. with a plasmonic resonance in the wavelength region of the sensitizer absorption, taking into account the refractive index of the solvent;
- linker molecules A, having a first end capable of binding to the metal nanoparticles (e.g. by means of a thiol-group), and a second end capable of binding the sensitizer molecule;
- Optionally a second species of spacer molecules B which only bind to the MNPs but not to the sensitizers;
- Optionally a second class of spacer nanoparticles (SNPs) consisting of inert material, index-matched to the solvent (e.g. silica in case of toluene solvent).

[0077] Thus in the device the sensitizers S are bound to the metal nanoparticles MNP by means of linker A, while the length of A is selected such that the distance between S and MNP is i) within the region of enhanced electric field amplitude, and ii) large enough to suppress quenching of the S triplets by the metal surface of the MNPs. Simulations of the field profiles and knowledge of the quenching properties suggest a distance of about 2 to about 3 nm to be optimal.

[0078] Depending on the achievable surface load of S on the MNPs and the rigidity of the linkers A, the sensitizers may suffer self-quenching in the event that they collide at a sufficient rate. In this case, the surface population of S-A- assemblies on the MNPs could be diluted by spacers B, which would increase the average distance between sensitizer moieties so as to control the self-quenching. Also, the absorption cross section of the (B-)MNP-A-S assemblies may be several times the geometric cross section of the assembly, and may also depend on the achievable surface loading. Thus, the effective electric field enhancement seen by the sensitizers may be limited by the available EM field energy density, if the (B-)MNP-A-S assemblies were densely packed, i.e. if several MNPs came to lie within one absorption cross section. To realize the maximum E field enhancement, the (B-)MNP-A-S assemblies may be diluted by spacer nanoparticles to an extent that the average distance between them equals their absorption cross section of light at the wavelength of maximum absorption. An illustration of this situation is depicted in Fig. 2.

Demonstration of feasibility: The example of PQ4PdNA

[0079] The inventors have developed upconversion-augmented solar cells using a palladium tetrakisquinoxalino-porphyrin with nitro-amine ligands (PQ4PdNA) as the sensitizer, and rubrene (5,6,11,12-tetraphenyltetracene) as the emitter, both dissolved in toluene. This combination yields up to 7×10^{-4} mA/cm² current enhancement at 1 sun. In the following, the design of a plasmonic antenna system for this porphyrin is outlined.

[0080] The peak absorption wavelength of PQ4PdNA is 674 nm with the Q absorption band extending approximately from about 650 nm to about 725 nm. The diameter of the nanoparticle should be chosen such that the wavelength-dependent field enhancement, weighted with the porphyrin absorption strength, is maximized. Finite difference time domain calculations were applied to solve Maxwell's equations for a plane wave incident on a nanoparticle in a medium with refractive index 1.5, which is about that of toluene or similar organic solvents. The E^2 enhancement pattern sampled in the XZ-plane (incident wave in the positive Y direction) is plotted in Fig. 3. It can be observed that E^2 peaks at values above 35-fold of the amplitude of the incident wave, close to the nanoparticle on the Z axis. The magnitude of the field enhancement depends on the wavelength of incident light and the size of the nanoparticle. The top panel shows that E^2 peaks at around 575 nm for a 60 nm sized particle, with bigger nanoparticles leading to shallower, broader and red-shifted resonances. Integrating the product of porphyrin

absorption cross-section (dashed in Fig. 3, top panel) with the E^2 enhancement dispersion for different nanoparticle sizes yields the expected absorption enhancement at a specific point in real space. For the point P, coinciding roughly with the maximum E^2 field amplitude, the resulting profile is given in Fig. 4 for PQ4PdNA and the similar compound PQ4Pd (without the nitro-amine ligands, leading to a slightly blueshifted absorption peak).

[0081] It remains to quantify the overall absorption enhancement in case of homogeneously porphyrin-coated nanoparticle surfaces. To this end it is helpful that the size range of particles analyzed here only shows dipolar resonances. Only for $d > 100$ nm the slight onset of a quadrupolar resonance is visible (indicated by the hump appearing in the wavelength dispersion in Fig. 3, top panel, at about 550 nm). However, this resonance is still extremely weak and can be neglected in the spatial distribution in the E^2 enhancement, which thus retains the C_{2v} symmetry of the dipolar resonance. Therefore, it is straightforward to perform a surface integration through the three-dimensional E^2 enhancement “field” on a concentric sphere with a given distance from the surface of the nanoparticle, based on the 2D slices of the E^2 profiles obtained from the finite difference time domain (FDTD) simulations. The respective data is shown in Fig. 5.

[0082] Two conclusions can be drawn here. Firstly, as compared to the absolute maximum of the E^2 enhancement, which was about 40 around point P for the 100nm particle at 668 nm (cf. Fig. 3), the average E^2 is slightly less than half of that value. Secondly, there is a drop of the average E^2 enhancement when moving outward from the NP surface, in this case by about a factor 0.5 within the first 5 nm. Both observations seem realistic when compared to the field distribution shown in Fig. 3 (bottom panel).

[0083] From these results one may conclude that binding the sensitizers closest to the MNPs is preferred, however the presence of metal surfaces can cause triplet quenching. Exciton quenching of C60 near a gold surface obeys roughly a power law behavior with exponent about 3, with the quenching rate being in the ns^{-1} range for the small distances studied. For the porphyrin/rubrene system the rate constant for triplet energy transfer from sensitizer to emitter is around 0.3 to $2 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$. At the maximum emitter concentration, which is about $5 \cdot 10^{-2} \text{ M}$ in toluene, a maximum TET rate of 10^8 s^{-1} , or 0.1 ns^{-1} , may be expected. The quenching rate by the metal surface is preferably below that value to avoid excessive loss of excitons. Based on the data from K. Kuhnke et al., *Phys. Rev. Lett.* 79, 3246 (1997), this would mean that a distance of

about 7 nm would be needed to reach the same values for both rate constants, which would significantly diminish the E^2 enhancement effect.

[0084] However, it was found that the quenching of triplet states by the presence of metals is significantly less efficient, due to the much smaller oscillator strength of the triplet state. There is a factor of about 10 between the required distances from metal surfaces for singlet and triplet excited states. Thus, in the case of sensitizers with very fast intersystem crossing to the triplet state, distances of a few nm to the MNP should be sufficient, which would allow effective average field enhancements of greater than about 15.

[0085] Further potential may exist that could be exploited by tuning the effective permittivity of the nanoparticle coating. The calculations were done assuming the refractive index of the solvent ($n=1.5$), which is true in the limit of a dilute coating. However, if the linker molecules A (and, eventually, B) are closely packed on the surface of the nanoparticle, the effective index might be higher. As a fact, a permittivity of 2.1 is realistic for $(CH_2)_n$ -thiol linker molecules, which could represent a feasible design for the present case as well. For such permittivity, the plasmon resonances would already be considerably red-shifted – by about 100 nm on the wavelength scale – allowing for much sharper resonance peaks in the wavelength region of the sensitizer absorption. Indeed, in this case, the 60 nm diameter nanoparticles having the highest E^2 peak (Fig. 3) would host a resonance at about 670 nm with the potential of an even higher average field enhancement. In practice, the surface loading of the particles and thus the effective permittivity may be controlled precisely in order to target a specific plasmonic resonance.

Candidate materials and mechanisms

Choice of sensitizer species

[0086] The procedures proposed herein may be applied to any organic dye which allows being functionalized with a linkable ligand such as e.g. an amine group. In some cases this may affect the photophysical properties, such as the absorption range, but this effect does not severely limit the wide range of applicable molecules. Suitable organic dyes include for example optionally substituted porphyrins, texaphyrins, sapphyrins, orangerins, phthalocyanins and carbon-bridged pyrrolic systems. These may optionally include a metal, optionally a complexed metal. Suitable metals include for example Li, Mg, Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ru, Pd, Ag, Re, Os,

Ir, Pt, Pb, U. Other suitable dyes include benzopyridines, benzopyrazines, quinolates, hydroxyquinolates and acetylacetonates, all of which may optionally be substituted.

Coating of sensitizers onto metal oxide/silica surfaces

[0087] The linkage between the metal oxide/silica support structures and the sensitizers may for example be established by:

- a) functionalizing the metal oxide/silica surfaces with amine ($-NH_2$) groups, or
- b) functionalizing the sensitizers with a carboxylic acid ($-COOH$) or an acyl chloride ($-COCl$), and then
- c) performing a peptide reaction to achieve the link.

[0088] Alternatively, the linkage may be established by designing and producing a sensitizer that incorporates a linking moiety into its structure, such that linking occurs in a single step when the sensitizer and support are combined under appropriate reaction conditions.

Coating of sensitizers onto metal nanoparticles

[0089] The bonding between sensitizers and the metal nanoparticles envisioned to exploit plasmonic near-field enhancement may be accomplished by means of a linker group (e.g. an alkane chain) with a thiol ligand, which will form a bond to gold or silver. The other end of the linker may be connected to the sensitizer by means of a peptide bond or other suitable bond as described above.

Polymer networks containing sensitizers

[0090] The bonding between sensitizers and linkers/center molecules (cf. Fig. 1) may be facilitated by the peptide reaction described above, but other approaches such as click reactions may also be used. One approach uses an aromatic substitution reaction between pyrrole and aromatic dialdehydes to create a porous porphyrin network with alkane linker groups. Another approach uses self-assembly strategies for perylene bisimide dyes, which also lead to 3D porous supramolecular structures.

[0091] In approach (4) of Fig. 1, the choice of the center molecules determines the short-range structure in approach. A tetrahedral coordination of the center may be achieved by use of a

central carbon atom connected to four phenyl groups which terminate in the linkable amine groups. Achieving cubic symmetry or various other types of coordination may be achieved with metal-organic frameworks, e.g. cubic with terbium dicarboxylate center molecules.

[0092] The inventors have demonstrated that second order decay predominates with a nanostructured sensitizer. However, the exemplified porphyrin sensitizer material absorbs green light, not red light as preferred for application to solar cells. It is however clear that red-absorbing porphyrins may be used as the sensitizer.

[0093] The following applications are envisaged for the present invention:

1. High efficiency third generation solar cells.
2. Biological imaging
3. Low photon energy drug activation
4. High-resolution optical microscopy
5. Optical data storage
6. Oxygen sensing

Examples

Example 1

[0094] This example details the preparation and application of an example system from the present application, comprising a colloidal ensemble of metal oxide or silica nanoparticles (NP) coated with sensitizer molecules (S), immersed in emitter solution.

Preparation of silica-based upconverter

[0095] Silica nanoparticles (20 nm diameter) were treated with 1% v/v (3-aminopropyl)trimethoxysilane in toluene (AR grade, dried with molecular sieves and nitrogen bubbling) for two hours in a plastic vessel with continuous nitrogen bubbling. The nanoparticles were isolated by centrifuging (4000 rpm, 5 min), the supernatant was removed, then the treated silica was washed with toluene, redispersed by mechanical shaking, and centrifuged three further times. The particles were then dried in a vacuum desiccator (10^{-2} mbar pressure) at room temperature for three hours.

[0096] Dye was tethered to the amine-coated silica nanoparticles using solid-phase peptide synthesis techniques. A porphyrin dye, PQ4Pd functionalised with a carboxylic acid moiety, was dissolved in dichloromethane (DCM) to 1.3mM concentration, and the acid group was activated by adding 2-1H-benzotriazol-1-yl-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) coupling reagent ($1.1\times$ molar ratio with respect to the dye) and N,N-diisopropylethylamine ($4\times$ molar ratio). 1ml of the dye solution was added to 50mg treated silica in an agate mortar, and the mixture was ground for 30 seconds, to create an even dispersion of particles within the dye solution. The mixture was transferred to an opaque glass vial, which was sealed, and left for 24 hours with gentle agitation and heating.

[0097] The dye-treated nanoparticles were isolated using the same technique as above, but with washing by dichloromethane. Washing was continued until the supernatant was free of dye. Supernatant was retained for calculation of the dye loading on the particles. The particles were stored in the dark under air when not in use.

[0098] Emitter solution was prepared by dissolving rubrene in AR-grade toluene to 15 mM concentration. An upconverter mixture was prepared by combining, in a darkened room, a small quantity of dye-treated nanoparticles with a volume of emitter solution sufficient to ensure complete immersion of the solid (30mg silica to 1ml emitter solution). The mixture was ground with an agate mortar and pestle, then transferred to the bulb of a vacuum cuvette. The upconverter mixture was degassed by three freeze-pump-thaw cycles at a final pressure of 10^{-5} mbar. The sample vessel was sealed with a tap, and the mixture was transferred to the cuvette section. The solid material was left to settle to the bottom of the cuvette. Upconversion was achieved by illuminating the solid material with a 650nm wavelength light source. The emission of upconverted light from the illuminated area was readily apparent to the eye as yellow light emanating from the sample. This emission was also detected in various experiments using a spectrally resolved intensified CCD camera and using a solar cell. It will be understood that intensity measurement of upconverted light is not easy to quantify, due to the power dependence etc., however the enhancement effect on solar cell performance was quantified.

Example application: Augmentation of thin-film solar cells

[0099] Current solar cells are fundamentally limited by their inability to harvest photons with energies less than the absorber optical threshold. Thin-film solar cells such as a-Si:H or organic

solar cells, usually having band gaps above the optimum single-band gap value of 1.34 eV given by the Shockley-Queisser limit, and a much smaller volume to absorb the light, are particularly prone to this loss mechanism and thus suffer from imperfect usage of the solar spectrum.

Amorphous silicon for example, being a prototypical example of thin-film solar technology, has a band gap of about 1.7eV, thus transmitting red and infrared light unused.

[00100] The inventors have demonstrated that an upconversion system consisting of PQ4Pd and PQ4PdNA porphyrin dyes combined with a rubrene emitter can increase the quantum efficiency, i.e. the photon-to-electronic current conversion efficiency, of a-Si:H solar cells in the absorption range of the sensitizer molecules.

[00101] The application of the upconverter to the solar cell is described below. Employing a semi-transparent solar cell design with two transparent-conductive-oxide (TCO) electrodes, as e.g. ZnO:Al or ITO (indium tin oxide), the solar cell is effectively bifacial, i.e. can be illuminated from both sides. In the simplest realization of an upconversion-augmented solar cell, the glass cuvette containing the UC system described above is optically coupled to the glass substrate of the solar cell by means of a thin layer of immersion oil, which prevents the presence of an air gap between the glass surfaces. The oil facilitates refractive index matching in order to minimize optical losses. The solar cell is then illuminated through the transparent electrode deposited last, which means such that any transmitted light enters the upconverter unit through the glass substrate.

[00102] In principle, the upconverting effect can be detected by measuring the spectral response of the solar cell photocurrent. This is usually done by subjecting the solar cell to illumination of a given wavelength and known photon flux, generated by monochromation of a continuum mimicking the solar spectrum, while detecting the photocurrent. By this procedure, the 'external quantum efficiency' (EQE), i.e. the efficiency of the light-to-current conversion, can be calculated for every wavelength.

[00103] In the present case, a simple EQE measurement is insufficient to characterize a solar cell/UC assembly as the upconversion process is non-linear for low illumination densities. Indeed, even employing a high power white light source, the monochromated EQE probe beam typically has photon fluxes corresponding to much less than 1 sun, and therefore the linear response of the intrinsically quadratic UC process is negligible. To remedy this issue, it is

common practice to apply a 'light bias', resulting in experimental conditions closer to the usual operation scheme of a solar cell. In order to achieve this, the upconverter is illuminated by a continuous laser beam at the peak absorption wavelength of the sensitizer (670 nm) during the lock-in detection of the EQE, in order to create a background triplet concentration and thus increase the yield of upconverted photons. This procedure can be seen as 'light-biasing' the upconverter unit. Note that due to the weak absorption of the solar cells in that spectral range, the photocurrent itself is not significantly biased by the red laser. However, to eliminate any effect of the 670 nm bias on the solar cell response, the laser was not switched off to measure the EQE without UC contribution, but instead the 670nm pump beam was laterally displaced on the active area, thus misaligning it with the EQE probe beam. Thereby, the solar cell still sees the same illumination conditions, but within the area probed by the EQE measurement the UC signal is negligible.

[00104] Employing this procedure, the inventors measured a clear enhancement of solar cell EQE using the nanostructured upconverter as described above, employing a 670 nm light bias corresponding to about 10 suns illumination density. The signal is easily seen in the ratio of EQE curves with active and inactive upconverter, as shown in Figure 6. It can be seen that the EQE improvement roughly reproduces the absorption properties of the dye, as would be expected (to first order). The deviation from the curve stems from the influence of the solar cell transmission characteristics, as well as broadening of the dye absorption bands by binding to the support structure.

Example 2: Phosphorescence lifetime of upconversion sensitisers in solution and tethered to silica nanoparticles

[00105] The triplet lifetime of the sensitizer in triplet-triplet annihilation upconverter systems makes an important contribution to the efficiency of the system. A longer-lived sensitizer triplet state means a greater probability that sensitizer triplets are quenched in high yield by the emitter species, which goes on to upconvert the quenched energy by triplet-triplet annihilation. Because the efficiency of the upconversion process scales quadratically at low (i.e. application-relevant) light intensities, a high concentration of sensitizers is necessary to produce useful upconversion yields. In solution, the tendency of sensitizers to aggregate at appreciable concentrations can lead to shortening of the sensitizer triplet lifetime and thus a drop in

upconversion efficiency. Tethering the sensitiser to nanoparticles to prevent aggregation at high concentrations is one approach to circumventing this problem.

AIM

[00106] This experiment aims to show that tethering sensitisers to silica nanoparticles increases the sensitiser triplet lifetime compared to the same concentration of dye in free solution. Triplet lifetime is inferred from the phosphorescence lifetime of the sensitiser under the conditions of upconverter samples, but in the absence of quencher (i.e. emitter).

EXPERIMENTAL

Particle preparation

[00107] A sensitiser consisting of a palladium-metallated tetraphenyl porphyrin with a statistical mixture of tris- and tetrakis-aminopropyl triethoxysilane ligands was synthesised. A sample of dye-coated silica was prepared by the following method: a known mass of the sensitiser was dissolved in a mixture of dry dichloromethane (DCM) and dry dimethylformamide (DMF). To this solution was added a known quantity of commercially-purchased 20nm diameter silica nanoparticles that had been dried overnight in an oven (110°C). The vessel was sealed and left overnight at room temperature. The vessel was then centrifuged, the supernatant collected, and the solid remnants washed with the same mixture of dry DCM and DMF, and re-dispersed by mechanical shaking. The centrifuge-wash-redisperse process was repeated a further seven times, until a colourless wash was obtained.

[00108] The wash solutions were combined and the absorbance measured; this was used to back-calculate the mass of sensitiser dye left in solution and consequently, the mass of dye absorbed onto the surface, using: $Mass_{absorbed} = Mass_{total} - Mass_{wash}$.

[00109] The dye-coated nanoparticles were dried in the dark in an oven at 120°C then stored in sealed vials in the dark until use.

Sample preparation

[00110] To measure the sensitiser triplet lifetime, we time-resolved the decay of sensitiser phosphorescence under the conditions of an upconverter system but without the emitter added. The highest-concentration dye-coated silica prepared had an effective concentration of approximately 2mM, calculated by considering the quantity of dye contained within a known volume of the silica material. For our first sample (sample 1) a few tens of milligrams of this dye-coated silica was suspended in spectroscopic-grade toluene and transferred to the cuvette portion of a vacuum cuvette (a custom-built apparatus consisting of a standard 1cm quartz cuvette attached to a glass bulb and sealable by a valve). This allows us to deaerate spectroscopic samples by a freeze-pump-thaw process, so that solvent is not removed by pumping). The sample was deaerated so as to remove oxygen by three freeze-pump-thaw cycles with a base pressure of $<(8 \times 10^{-4})$ mbar.

[00111] A second sensitiser sample (sample 2) was also made up. We used a palladium-centered tetra(di-tertiarybutyl phenyl) tetraphenyl porphyrin as the non-bound sensitiser. Note that the di-tertiarybutyl phenyl groups do not participate electronically in the molecule, but are added to increase the solubility of the dye. We added 1.6mg of the dye to 0.7mL of spectroscopic-grade toluene, giving a concentration of 2mM of free (untethered) dye. Dissolution of the dye was rapid. For testing, the sample was transferred to the same (clean) vacuum cuvette and subjected to three freeze-pump-thaw cycles. Solvent evaporation during this process was negligible.

Measurement

[00112] Phosphorescence measurements of degassed samples were carried out using pulsed laser excitation (525nm wavelength, OPO (Euroscan) pumped by the third harmonic of an Nd:YAG (Infinity) at 15Hz repetition rate) at a fixed pulse energy, and time-resolved detection by an electronically-gated intensified CCD camera (Pi-Max) coupled to the output of a spectrograph (Acton). A notch filter over the spectrograph slits attenuated the laser line. The duration of the measurement was adjusted such that all detectable signal had ceased by the end of the collection window. Phosphorescence transients were made by integrating over the wavelengths of the detected phosphorescence band for each time step. This integral was then plotted against time step, and the phosphorescence lifetime was inferred from fitting to the decay of the transient using a standard mixed-kinetics model.

RESULTS

[00113] Phosphorescence transients collected under equivalent excitation conditions can be seen in Figure 7. The lifetime of the tethered dye is significantly increased compared to the free solution. Fitting to the model is by a mixed-kinetics model (see e.g. Cheng et al., *J. Phys. Chem. Letts*, 1, 12, 2010, DOI 10.1021/jz100566u), fits are shown in Figure 8. The fitting term k_1 is the first-order decay rate of the sensitiser triplet state, and is the inverse of the phosphorescence lifetime. From the fits we extract k_1 values of 5200s^{-1} for the silica-tethered 2mM sample, and 381000s^{-1} for the untethered 2mM sample. This corresponds to a triplet lifetime enhancement of approximately 73 times by binding the dye to silica nanoparticles.

CONCLUSION

[00114] In upconversion systems, the sensitiser lifetime must be long enough that quenching by the emitter is with near-unity efficiency. This requirement is in tension with efforts to increase the sensitiser concentration, which can induce undesirable concentration quenching in the sensitiser. Tethering an upconversion sensitiser to silica nanoparticles using aminopropyltriethoxysilane bridging ligands has been shown to dramatically enhance the sensitiser triplet lifetime compared to the same concentration of dye dissolved in free solution, which is a promising result for upconverters using nanostructured sensitisers.

CLAIMS

1. A system for upconversion of photons, comprising a solid sensitizer medium comprising a sensitizer, said sensitizer medium being disposed in an emitter medium comprising an emitter which is capable of accepting energy from an excited state of the sensitizer so as to upconvert said energy.
2. The system of claim 1 wherein the sensitizer is capable of absorbing photons of wavelength of about 600 to about 750nm.
3. The system of claim 1 or claim 2 wherein the sensitizer is a metalloporphyrin.
4. The system of claim 3 wherein the metalloporphyrin is a palladium tris- or tetrakis-quinoxalinoporphyrin.
5. The system of any one of claims 1 to 4 wherein the emitter is a polycyclic aromatic compound.
6. The system of claim 5 wherein the polycyclic aromatic compound is diphenylanthracene or rubrene.
7. The system of any one of claims 1 to 6 wherein the sensitizer medium comprises:
 - molecules of the sensitizer coupled to surfaces of nanoparticles; or
 - molecules of the sensitizer coupled to one or more surfaces of a nanoporous substrate; or
 - a crosslinked polymer wherein molecules of the sensitizer are monomer units of the polymer; or
 - a metal-organic framework wherein metal atoms or clusters are joined by linker groups comprising molecules of the sensitizer.
8. The system of claim 7 wherein the sensitizer medium comprises molecules of the sensitizer coupled to surfaces either of nanoparticles or of a nanoporous substrate and wherein said coupling is by means of a linker group.
9. The system of claim 7 or claim 8 wherein the sensitizer medium comprises molecules of the sensitizer coupled to surfaces either of nanoparticles or of a nanoporous substrate and

wherein the surfaces of the nanoparticles or of the nanoporous substrate have spacer molecules coupled thereto, said spacer molecules being incapable of absorbing photons at a wavelength which is absorbed by the sensitizer.

10. The system of claim 9 wherein the molar ratio of spacer molecules to sensitizer molecules is between about 1:1 and about 100:1.

11. The system of any one of claims 8 to 10 wherein the sensitizer medium comprises molecules of the sensitizer coupled to surfaces of nanoparticles, wherein the nanoparticles are metallic nanoparticles and/or electrically conducting metal oxide nanoparticles, which exhibit plasmon resonance at a wavelength at which the sensitizer absorbs photons.

12. The system of claim 11 additionally comprising spacer nanoparticles having no molecules of the sensitizer coupled thereto, wherein the ratio of the metallic nanoparticles to the spacer nanoparticles and the size of the spacer nanoparticles are such that the mean distance between the metallic nanoparticles is greater than the diameter of the absorption cross-section of the metallic nanoparticles.

13. The system of claim 11 or claim 12 wherein the metallic nanoparticles and/or electrically conducting metal oxide nanoparticles comprise a dielectric coating having the sensitizer coupled thereto.

14. The system of claim 13 wherein the thickness of the dielectric coating is such that the mean distance between the sensitizer molecules and the metal surface is sufficiently large to substantially prevent quenching of an excited state of the sensitizer by the metal.

15. The system of claim 13 or claim 14 wherein the dielectric coating comprises a metal oxide or a semiconductor oxide or a polymer.

16. The system of claim 12 wherein the spacer nanoparticles have a refractive index approximately the same as that of the emitter medium.

17. The system of claim 7 wherein the sensitizer medium comprises a crosslinked polymer wherein molecules of the sensitizer are monomer units of the polymer.

18. The system of claim 17 wherein the molecules of the sensitizer are crosslinking monomer units of the polymer, said molecules being joined by linker monomer units.
19. The system of claim 17 wherein the molecules of the sensitizer are coupled to crosslinking monomer units of the polymer by linker groups.
20. The system of any one of claims 1 to 19 wherein the emitter medium comprises a solution of the emitter in a solvent.
21. The system of any one of claims 1 to 19 wherein the emitter medium is a solid.
22. The system of claim 21 wherein the emitter medium is selected from the group consisting of an emitter polymer comprising molecules of the emitter, a conjugated emitter polymer capable of acting as an emitter, an amorphous solid comprising the emitter molecules, and nanocrystals comprising the emitter molecules.
23. The system of claim 22 wherein the emitter medium is an emitter polymer, and the sensitizer medium comprises:
- molecules of the sensitizer coupled to surfaces of nanoparticles, said nanoparticles being dispersed substantially homogeneously throughout the emitter polymer; or
 - molecules of the sensitizer coupled to surfaces of a nanoporous substrate, the emitter polymer being disposed in pores of said nanoporous substrate; or
 - a crosslinked polymer wherein molecules of the sensitizer are monomer units of said crosslinked polymer, and wherein said crosslinked polymer and the emitter polymer form an interpenetrating polymer network;
- whereby the system is a solid state system.
24. The system of claim 22 wherein the emitter medium comprises an amorphous solid comprising the emitter molecules and the sensitizer medium comprises:
- molecules of the sensitizer coupled to surfaces of nanoparticles, said nanoparticles being dispersed substantially homogeneously throughout the amorphous solid; or
 - molecules of the sensitizer coupled to surfaces of a nanoporous substrate, the amorphous solid being disposed in pores of said nanoporous substrate;
- whereby the system is a solid state system.

25. The system of claim 22 wherein the emitter medium comprises nanocrystals comprising the emitter molecules and the sensitizer medium comprises:
- molecules of the sensitizer coupled to surfaces of nanoparticles, said nanoparticles being mixed with the nanocrystals so as to form a homogeneous medium; or
 - a crosslinked polymer wherein molecules of the sensitizer are monomer units of the polymer, or a metal-organic framework, or covalent network, wherein said nanocrystals are embedded homogeneously through the polymer or framework or network.
26. The system of any one of claims 1 to 25 additionally comprising one or more solar cells optically coupled to the emitter medium.
27. The system of claim 26 wherein the optical coupling is substantially airless.
28. The system of claim 26 or claim 27 comprising two solar cells, each disposed on a glass substrate and each being on an opposite side of the emitter medium and being optically coupled to said medium by means of an oil layer.
29. A process for making a system according to claim 1 comprising combining the solid sensitizer medium and the emitter medium.
30. The process of claim 29 comprising coupling the sensitizer to surfaces of nanoparticles or of a nanoporous substrate so as to prepare the solid sensitizer medium.
31. The process of claim 30 wherein said coupling comprises either:
- coupling a linker species to the surfaces either of the nanoparticles or of the nanoporous substrate and then coupling the sensitizer to the linker species; or
 - coupling the linker species to the sensitizer and then coupling the linker species having the sensitizer coupled thereto to the surfaces either of the nanoparticles or of the nanoporous substrate.
32. The process of claim 30 or claim 31 wherein the nanoparticles are selected from the group consisting of metallic nanoparticles, metallic nanoparticles having a dielectric coating, conductive metal oxide nanoparticles and metal oxide or semiconductor oxide nanoparticles.

33. The process of claim 29 wherein the solid sensitizer medium is either a crosslinked polymer or a metal-organic framework in which the sensitizer molecule is a monomer of said polymer or a linker group of said framework, said process comprising the step of forming the polymer or framework by combining said sensitizer molecule with either a crosslinker or a crosslinking metal ion or cluster, said sensitizer molecule having at least two functional groups capable of coupling with either the crosslinker or the metal ion.
34. A method for upconversion of photons comprising exposing a system according to any one of claims 1 to 28 to light of a wavelength capable of exciting the sensitizer.
35. The method of claim 34 wherein the system additionally comprises a photosensitive species having an excitation threshold above the energy of the absorption maximum of the sensitizer, whereby exposure of the system to said light leads to upconversion of said light to above said excitation threshold so as to excite the photosensitive species.
36. The method of claim 35 wherein the photosensitive species is a photovoltaic substance whereby the method results in generation of an electrical potential.
37. Use of a system according to any one of claims 1 to 28 in an application selected from the group consisting of conversion of solar energy to electricity or solar fuels, biological imaging, drug activation, high-resolution optical and/or fluorescence microscopy, optical data storage and oxygen sensing.
38. Use of a solid sensitizer medium and an emitter medium for upconversion of photons, said sensitizer medium comprising a sensitizer and said emitter medium comprising an emitter which is capable of accepting energy from an excited state of the sensitizer so as to upconvert said energy, said sensitizer medium being disposed in the emitter medium.
39. Use of a solid sensitizer medium and an emitter medium for making a system for upconversion of photons, said sensitizer medium comprising a sensitizer and said emitter medium comprising an emitter which is capable of accepting energy from an excited state of the sensitizer so as to upconvert said energy.

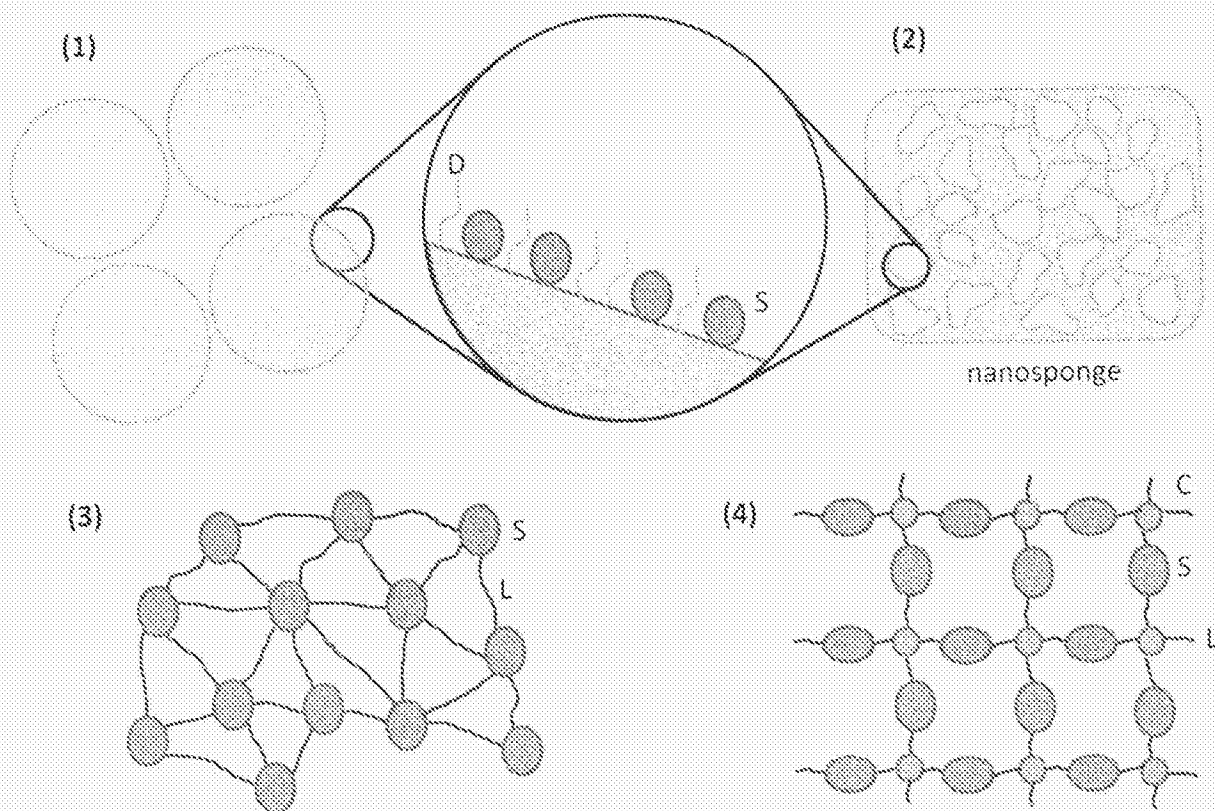


Figure 1

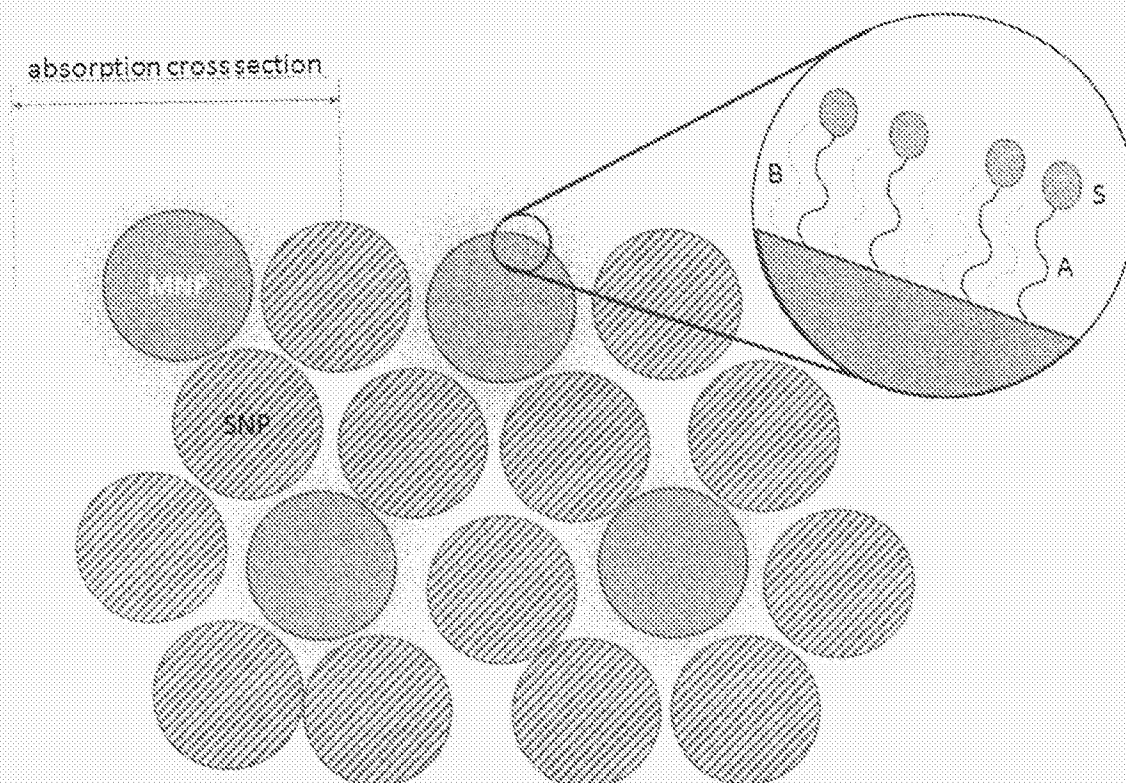


Figure 2

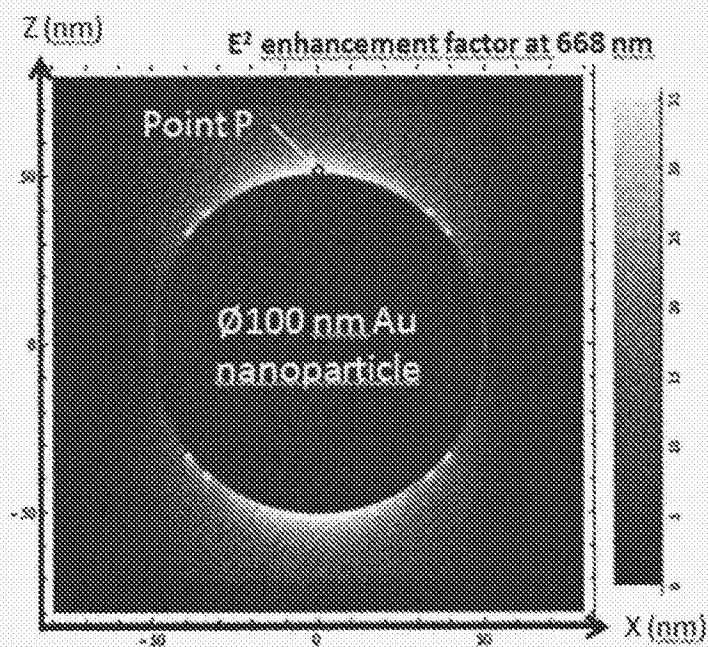
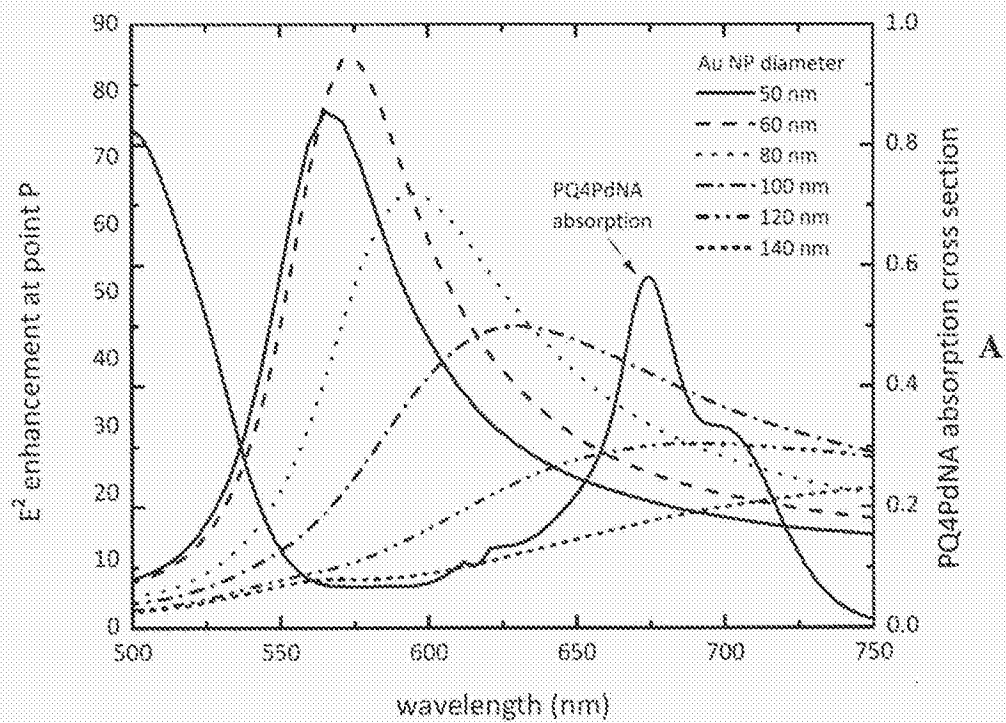


Figure 3

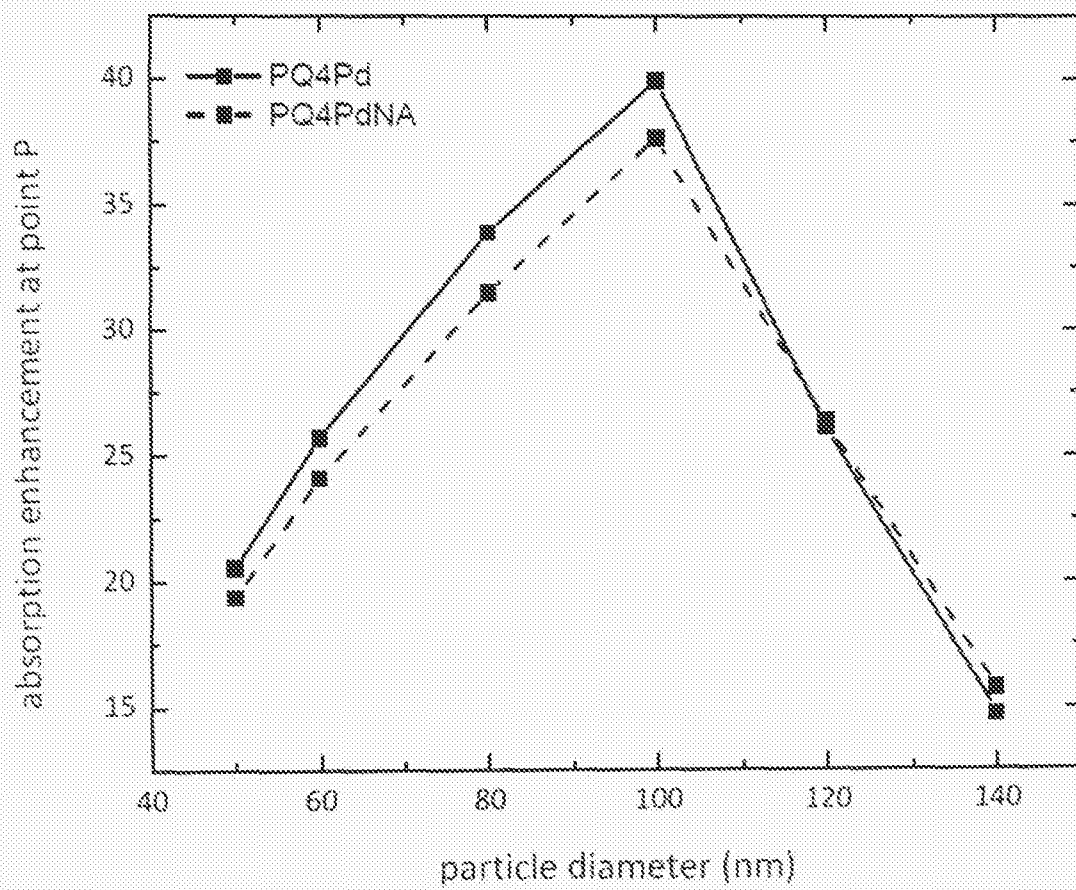


Figure 4

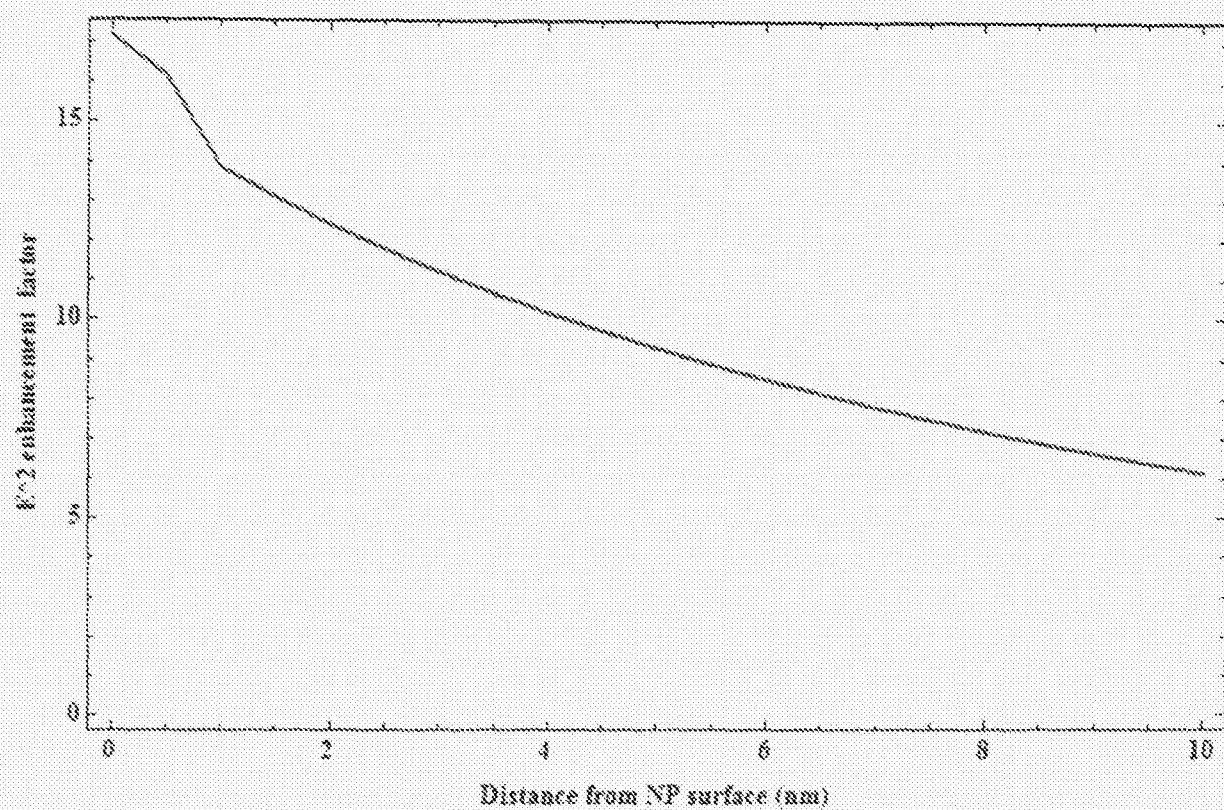


Figure 5

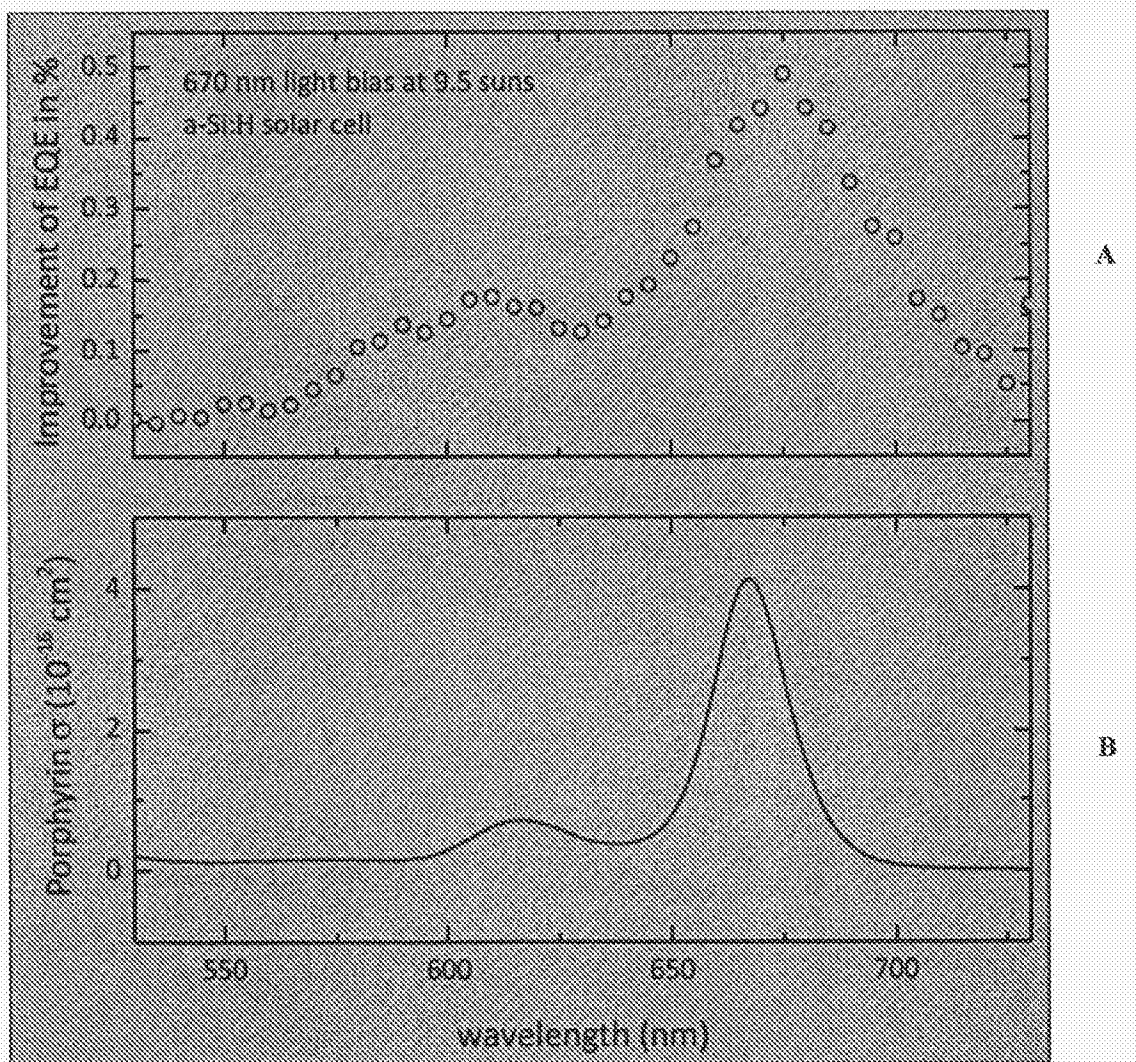


Figure 6

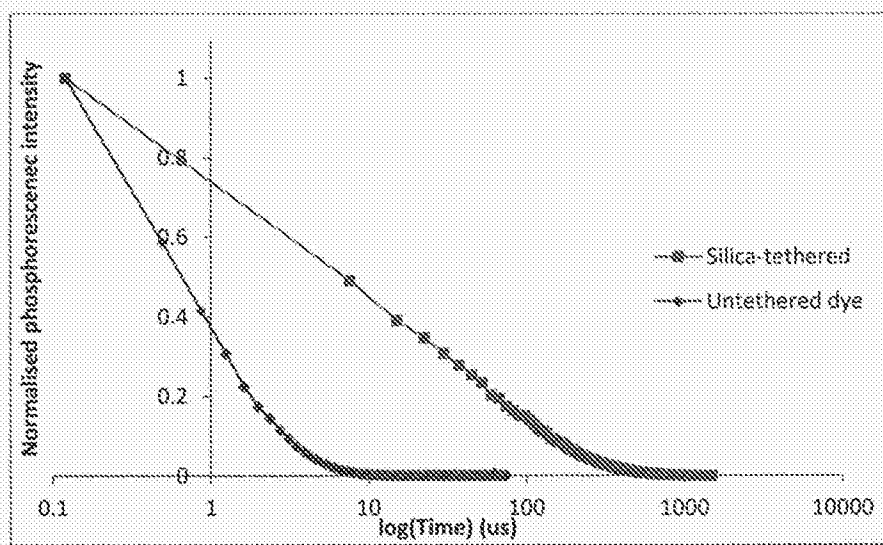


Figure 7

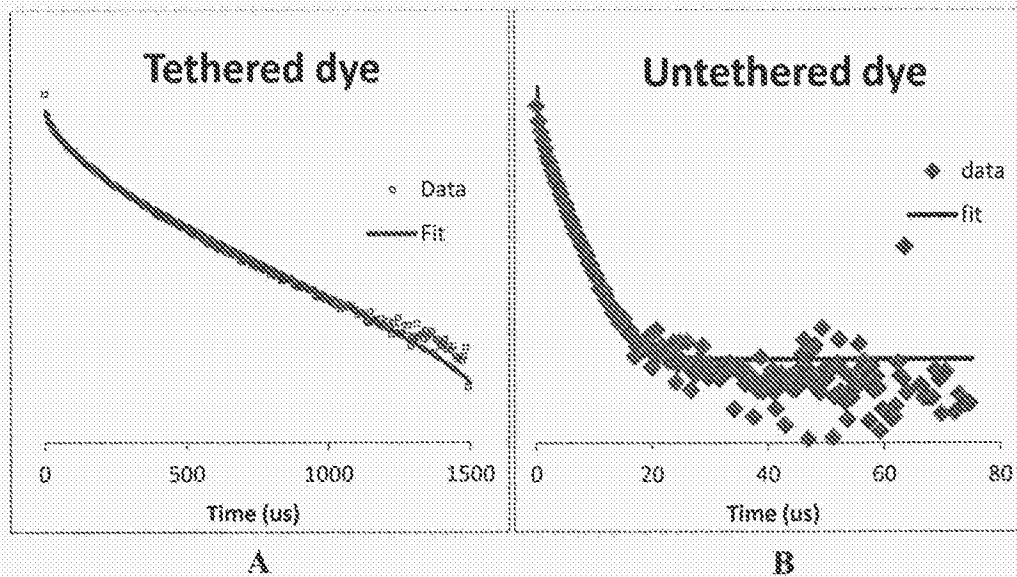


Figure 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2014/000039

A. CLASSIFICATION OF SUBJECT MATTER

G02F 1/361 (2006.01) H01S 3/16 (2006.01) C09K 11/06 (2006.01)

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)

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

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

EPODOC, DWPI, GOOGLE: (OR (UP_CONVERS+ W PHOTON+), (UP_CONERT+ W PHOTON+), Y02B20/CC, (ANTI_STOKE? W SPECT+), UP_CONVERT+, (CONVERS+ W LAYER?)); (OR SENSIT+, METALLOPORPHYRIN?, PALLADIUM+, PD, PT, PLATINUM, IR, IRIIDIUM, CU, COPPER, RU, RUTHENIUM, METALLO_PORPHYRIN?, PQ4PDNA, DYE); (OR EMITTER?, (POLYCYCLIC W AROMATIC?), DI_PHENYLANTHRACENE?, RUBRENE?, POLYMER+, ORGANIC, POLYURETHANE?, POLYSILOXANE?, POLYACRYLATE?, POLYOLEFIN?, POLYAMIDE?, POLYCARBONATE?); and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:	
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Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation).		PCT/AU2014/000039
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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/0013263 A1 (MITEVA et al.) 20 January 2011 Refer to the whole document and in particular to para [0011], [0058], [0064], [0091]-[0092], [0143], [0151], [0168], [0170], [0193], [0198], Figs. 1, 4, 5A, & 18, claims 1, 47	1-3, 5-7, 21-26, 29, 34-39
Y	As above	4, 8-19, 23-25, 27-28, 30-32
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Information on patent family members			
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
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