A photovoltaic apparatus

Field of the invention

The present invention provides a nano-structured material. The nano-structured material may be comprised in a sheet. The sheet may be comprised in an apparatus, particularly a photovoltaic apparatus. In particular, the present invention provides a photovoltaic apparatus with an improved conversion efficiency of light energy to electricity, in particular, solar power to electric power.

Background of the invention

Electricity is mostly produced by the combustion of fossil fuel. The earth's oil reserve is predicted to run out within this century (e.g. petroleum runs out by 2040). As the energy consumption is likely to double within the next 50 years, a major energy shortage will occur. Further, combustion of fossil fuel also leads to adverse effects such as global warming and emissions of carbon dioxide. A clean and renewable source of energy is therefore needed to cope with the problems.

The energy from the sunlight alone is able to produce an average of 1,700 kWh of power annually on each square meter of land. The total amount of solar energy incident upon the earth's surface is sufficient to provide the annual global energy consumption over 10,000 times. Solar energy, with few resource limitations and minimal adverse environmental impact, will become one of the critical renewable sources of energy. Solar cells, also known as photovoltaic (PV) cells, are semiconductor devices that are able to convert sunlight into electric power.

Most commonly used solar cells are silicon based solar cells. Other common materials are amorphous silicon, cadmium telluride (CdTe), or copper indium diselenide (CIS). The selected materials are ideally strong light absorbers,

resulting in a smaller thickness (~1 micron thick). However, the efficiency of existing solar cells is low, with an average conversion efficiency of about 11-16%.

The low conversion efficiency of the solar cells is due to the discrete band structure of semiconductors. The solar spectrum broadly spans from the ultraviolet (UV) to the near infrared (NIR) (280 nm – 2500 nm). Only photons with energies equal to or grater than the band gap energy (Eg) will be absorbed and may contribute to an electrical output of a PV device.

Photons of higher energy (with energy exceeding the band gap of a semiconductor), although absorbed, rapidly thermalize to the conduction band edge. High-energy photons from the solar irradiation will create hot electrons, which are at an effective temperature much greater than that of the lattice. Through electron-phonon scattering events, these hot electrons will cool until reaching thermal equilibrium with the lattice. This contributes to thermalization loss, and is a major limiting factor in photovoltaic solar energy conversion. The excess photon energy is therefore lost as heat within the lattice of the semiconductor. All single-junction solar cells used to date suffer substantial losses due to thermalization of charge carriers within the crystal lattice.

Photons with energy lower than the band gap energy, however, are transmitted through the solar cell and do not contribute to the electrical output. As a result, a compromise between thermalization and sub-band-gap losses exist when selecting semiconductor materials for PV applications.

FIG 1 shows the typical behaviour of a known crystalline silicon solar cell. In particular, FIG 1 shows the solar spectrum (AM1.5) that is converted by known crystalline silicon solar cells. Crystalline silicon has a band gap of 1.12 ev (equivalent to wavelength, λ, of 1100 nm in the near infrared range). From FIG 1, it can be seen that solar photons with wavelength less than 1100 nm can be absorbed. However, the energy of many of these photons is wasted via

thermalization. Photons with wavelength longer than 1100 nm (photon energy less than band gap of silicon solar cells), will be transmitted but not used by the solar cell. Silicon solar cells only absorb light with energies greater than the band gap of 1.12 eV. The part of the solar spectrum below 450 nm is poorly converted into electricity by the solar cells, although this part of the solar spectrum is very high in energy at the surface of the earth.

There is therefore a need in the art for an improved photovoltaic device, having a higher conversion efficiency compared to existing photovoltaic devices.

Summary of the invention

The present invention seeks to address the problems above, and provides a nano-structured material. The nano-structured material may be comprised in a sheet. The sheet may have a suitable thickness. The nano-structured material may be in the form of a layer or film comprising the nano-structured material.

The nano-structured material may be comprised in an apparatus. In particular, the sheet comprising the nano-structured material may be comprised in an apparatus. The apparatus may be a photovoltaic apparatus.

The present invention also provides a photovoltaic apparatus suitable for improving photovoltaic efficiency. In particular, the photovoltaic apparatus comprises at least one nano-structured material. For example, the at least one nano-structured material comprised in the apparatus may be up-conversion and/or down-conversion nano-structured material.

According to a first aspect, the present invention provides a photovoltaic apparatus comprising:

(a) at least one photovoltaic conversion material; and

(b) at least one down-conversion nano-structured material,

wherein the at least one down-conversion nano-structured material comprises at least one dimension of size ≤ 450 nm.

According to a particular aspect, the at least one down-conversion nano-structured material may comprise at least one dimension of size ≤ 400 nm. Even more in particular, the at least one dimension may be of size ≤ 300 nm, ≤ 100 nm or ≤ 50 nm. For example, the at least one down-conversion nano-structured material comprises at least one dimension of size about 70 nm, about 20 nm, about 8 nm or about 1 nm.

According to a particular aspect, the at least one down-conversion nano-structured material may be selected from the group consisting of doped or undoped: rare-earth organic complex, organic material and inorganic material. In particular, the inorganic material may be a metal, a semiconductor material or an insulator material of formula $M^1_mM^2_nX^1_p:M^3_q$, wherein:

(i) each M^1 is the same or different and is selected from the group consisting of: Sr, Zn, Y and La;

(ii) each M^2 is the same or different and is a metal ion or Si;

(iii) each X^1 is the same or different and is selected from the group consisting of: halogens, O, S, and PO_4;

(iv) each M^3 is the same or different and is selected from the group consisting of: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Cu, Mn, Ag, Cu, Zn, Al, Co and Er;

(v) m is $0 \leq m \leq 10$;

(vi) n is $1 \leq n \leq 15$;

(vii) p is $1 \leq p \leq 20$; and

(viii) q is $0 \leq q \leq 10$.

According to a particular aspect, the rare-earth organic complex may comprise: (a) at least one metal ion; and (b) at least one organic chelating material. The at least one metal ion may be a rare earth metal ion. The at least one organic chelating material may be β-diketone and/or a ligand.

According to a particular aspect, the organic material may be any suitable material which comprises at least one of the following atoms: C, H, O and N. For example, the organic material may be fluorescein or derivatives, rhodamine or derivatives, coumarin or derivatives, bodypy or derivatives, cascade blue or derivatives, and Lucifer yellow or derivatives.

According to a particular aspect, the at least one down-conversion nano-structured material may be a semiconductor material. The semiconductor material may be doped or undoped semiconductor. In particular, the semiconductor material may comprise a II-IV or III-V compound. Even more in particular, the semiconductor material may be selected from the group consisting of GaAs, ZnS, CdSe, TiO_2, II-IV compounds and III-V compounds, metal oxides, sulfides, silicates, pyrosilicates, sulfates, phosphates, phosphor-vanadates, (mono, di, tri, hexa, octa, deca, tetradeca, hexadeca)-aluminates, vanadates, tungstates, halogenates, borates, tatatates, niobates, molybdates and oxysulfides.

The at least one down-conversion nano-strcutured material may be a metal. The metal may be any suitable metal. For example, the metal may be gold or silver.

The at least one down-conversion nano-structured material may be an inorganic insulator material of formula $M^1{}_mM^2{}_nX^1{}_p{:}M^3{}_q$, wherein M^1, M^2, M^3, X^1, m, n, p and q are as defined above. For example, each M^2 may be selected from the group

consisting of: Si, transition metal ions, inner transition metal ions, and Group I to Group IV metal ions.

The at least one down-conversion nano-structured material may be selected from the group consisting of: $YM^2O_4:M^3$, $Sr(M^2)_2O_4:M^3$, and $Zn_2M^2O_4:M^3$, wherein each M^2 is the same or different and is selected from the group consisting of: Al, Si and V and each M^3 is the same or different and is selected from the group consisting of: Eu, Mn and Dy. Further examples of the at least one down-conversion material include $Zn_3(PO_4)_2$:Mn, $Cd_3(PO_4)$:Mn, Y_2O_3:Eu, ZnS:Ag, ZnS:Cu,Ag, ZnS:Cu,Al, ZnS:Zn, ZnS:Mn, $LaPO_4$:Ce,Tb, europium phthalate and $Eu(DBM)_3L_2$, wherein DBM is dibenzoylmethane and L is tricaprylylmethylammonium chloride. In particular, the at least one down-conversion nano-structured material may be Zn_2SiO_4:Mn, YVO_4:Eu and $SrAl_2O_4$:Eu,Dy.

According to another aspect of the present invention, there is provided a photovoltaic apparatus comprising:

(a) at least one photovoltaic conversion material; and

(b) at least one up-conversion nano-structured material,

wherein the at least one up-conversion nano-structured material comprises at least one dimension of size ≤ 1100 nm.

According to a particular aspect, the at least one up-conversion nano-structured material may comprise at least one dimension of size ≤ 850 nm, ≤ 650 nm, ≤ 450 nm or ≤ 400 nm. In particular, the at least one up-conversion nano-structured material comprises at least one dimension of size about 10 nm.

According to a particular aspect, the at least one up-conversion nano-structured material may be at least one up-conversion nano-structured material of formula $M^4_rM^5_sX^2_t:M^6_u$, wherein:

(i) each M^4 is the same or different and is selected from the group consisting of: Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra and NH_4;

(ii) each M^5 is the same or different and is a metal ion;

(iii) each X^2 is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As;

(iv) each M^6 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb and Cu;

(v) r is $0 \leq r \leq 10$;

(vi) s is $1 \leq s \leq 10$;

(vii) t is $1 \leq t \leq 10$; and

(viii) u is $1 \leq u \leq 10$.

For example, M^5 may be selected from the group consisting of: transition metal ions, inner transition metal ions and Group I to Group VI metal ions. In particular, each M^5 may be Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu.

According to a particular aspect, the at least one up-conversion nano-structured material may be selected from the group consisting of: $NaM^5F_4:M^6$, $LiM^5F_4:M^6$, $KM^5F_4:M^6$, $RbM^5F_4:M^6$, $CsM^5F_4:M^6$, $BeM^5F_5:M^6$, $Be(M^5)_2F_8:M^6$, $MgM^5F_5:M^6$, $Mg(M^5)_2F_8:M^6$, $CaM^5F_5:M^6$, $Ca(M^5)_2F_8:M^6$, $SrM^5F_5:M^6$, $Sr(M^5)_2F_8:M^6$, $BaM^5F_5:M^6$, $Ba(M^5)_2F_8:M^6$, $M^5F_3:M^6$, $M^5Cl_3:M^6$, $M^5Br_3:M^6$, $M^5I_3:M^6$, $M^5FClBr:M^6$, $M^5OF:M^6$, $M^5OCl:M^6$, $M^5OBr:M^6$, $M^5OS:M^6$, $(M^5)_2S_3:M^6$, wherein each M^5 and M^6 are as defined above. In particular, each M^6 is the same or different and is selected from the group consisting of: Yb, Er, Tm and Ho. In particular, the at least one

up-conversion nano-structured material is $NaYF_4$:Er; $NaYF_4$:Yb,Er; $NaYF_4$:Yb,Tm; $NaYF_4$:Yb,Ho, or a combination thereof. In particular, the at least one up-conversion nano-structured material is selected from the group consisting of: SrS:Eu,Sm, CaS:Eu,Sm, SrS:Ce,Sm and ZnS:Pb,Cu.

The at least one up-conversion nano-structured material may have a structure selected from one of the following: hexagonal, cubic, tetragonal, rhombohedral, orthorhombic, monoclinic, triclinic and a combination thereof. In particular, the at least one up-conversion nano-structured material may have a hexagonal lattice structure.

The at least one up-conversion nano-structured material may be in the form of: nanoparticle(s), nanofilm or monolith. The nanoparticle(s) may comprise a core nanoparticle(s) or a core-shell nanoparticle(s). According to a particular aspect, the nanoparticle may be in the form of a core nanoparticle, and the nanoparticle further comprises at least one organic and/or inorganic material (shell) applied on the core, to obtain a core-shell nanoparticle(s). The shell may be applied continuously or discontinuously on the core.

The shell of the core-shell nanoparticle may comprise a material of formula $M^4_rM^5_sX^2_t$ or $M^4_rM^5_sX^2_t$:M^6_u, wherein each of M^4, M^5, X^2, M^6, r, s, t and u are as defined above. According to a particular aspect, the inorganic shell material may comprise: NaM^5F_4, LiM^5F_4, KM^5F_4, RbM^5F_4, CsM^5F_4, BeM^5F_5, $Be(M^5)_2F_8$, MgM^5F_5, $Mg(M^5)_2F_8$, CaM^5F_5, $Ca(M^5)_2F_8$, SrM^5F_5, $Sr(M^5)_2F_8$, $BaLnF_5$, $Ba(M^5)_2F_8M^5F_3$, M^5F_3, M^5Cl_3, M^5Br_3, M^5I_3, M^5FClBr, M^5OF, M^5OCl, M^5OBr, M^5OS, $(M^5)_2S_3$, wherein each M^5 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; SiO_2; TiO_2; ZnS; or a combination thereof.

The organic shell material may comprise at least one polymer, a surfactant or a lipid, or a combination thereof. Any suitable polymer, surfactant or lipid may be used for the purposes of the present invention.

According to another aspect, the present invention provides a photovoltaic apparatus comprising:

(a) at least one photovoltaic conversion material;

(b) at least one down-conversion nano-structured material according to any aspect of the present invention; and

(c) at least one up-conversion nano-structured material according to any aspect of the present invention.

The photovoltaic apparatus according to any aspect of the present invention may be a solar cell.

The photovoltaic conversion material of the photovoltaic apparatus according to any aspect of the present invention may be in contact with the at least one down-conversion and/or up-conversion nano-structured material. The photovoltaic apparatus according to any aspect of the present invention may further comprise a reflector having at least one reflecting surface and/or an anti-reflective material.

In particular, the photovoltaic apparatus according to any aspect of the present invention may comprise:

(i) at least one layer (A) comprising the at least one photovoltaic conversion material according to any aspect of the present invention; and at least one layer (B) comprising at least one down-conversion nano-structured material as described above, wherein layer B is in contact with layer A;

(ii) at least one layer (A); at least one layer (C) comprising at least one up-conversion nano-structured material according to any aspect of the present invention; and optionally at least one layer (D) comprising

a reflector having at least one reflecting surface, wherein layer A is in contact with layer C and the reflecting surface of layer D is in contact with layer C; or

(iii) at least one layer (A); at least one layer (B); at least one layer (C); and optionally at least one layer (D) having at least one reflecting surface, wherein layer B is in contact with layer A, layer A is in contact with layer C and layer C is in contact with the at least one reflecting surface of layer D.

The at least one photovoltaic conversion material may have a refractive index of 1 to 5 and a dielectric constant of 1 to 15. In particular, the photovoltaic conversion material may comprise at least: a conducting or semiconducting polymer material, a silicon-based material, cadmium telluride (CdTe), copper indium diselenide (CIS), gallium arsenide (GaAs), or dye-sensitized solar cells. For example, the conducting or semiconducting polymer material may be selected from the group consisting of: poly(phenylene) and derivatives thereof, poly(phenylene vinylene) and derivatives thereof, poly(thiophene) and derivatives thereof, poly(thienylenevinylene) and derivatives thereof, and poly(isothianaphthene) and derivatives thereof, organometallic polymers, polymers containing perylene units, poly(squaraines) and their derivatives.

According to another aspect, the present invention provides a method of improving the efficiency of a photovoltaic apparatus comprising the steps of:

(a) providing at least one down-conversion nano-structured material as described above on at least one surface of or in proximity of a photovoltaic material comprised in a photovoltaic apparatus; and/or

(b) providing at least one up-conversion nano-structured material as described above on at least one surface of or in proximity of a photovoltaic material comprised in a photovoltaic apparatus.

The method may further comprise a step of: providing a reflector having at least one reflecting surface, wherein the reflecting surface is provided to be in contact with the at least one up-conversion nano-structured material.

The method may further comprise a step of: providing an anti-reflective material, wherein the anti-reflective material is provided to be in contact with the at least one down-conversion and/or up-conversion nano-structured material.

The present invention also provides a photovoltaic apparatus with improved efficiency prepared according to the method of the present invention.

The present invention also provides a kit comprising a photovoltaic apparatus according to any aspect of the present invention.

Brief description of the figures

FIG 1: Solar spectrum (AM1.5) and solar energy that is converted by a known silicon cell (http://www.vicphysics.org/documents/events/stav2005/spectrum.JPG).

FIG 2: Schematic representation of: (a) NIR-to-visible up-conversion; (b) UV-to-visible down-conversion; and (c) quantum cutting.

FIG 3: Graph showing spectral response vs. wavelengths of 3 types of solar cells, i.e. crystalline Si, amorphous Si and GaAs.

FIG 4: Schematic representation of a photovoltaic apparatus in combination with a layer of down-conversion nano-structured material.

FIG 5: Schematic representation showing the fluorescent mechanism of down-conversion organic rare earth complex.

FIG 6: Schematic representation of a photovoltaic apparatus in combination with a layer of up-conversion nano-structured material.

FIG 7: An illustration of (a) core nanoparticles and (b) core/shell nanoparticles.

FIG 8: An illustration of (a) the core and (b) core/shell structured $NaYF_4$:Yb,Er(Tm)/$NaYF_4$ nanoparticles.

FIG 9: An illustration of (a) polyacrylic acid (PAA) capped $NaYF_4$:Yb,Er(Tm)/$NaYF_4$ nanoparticles and (b) PEG-phospholipids capped $NaYF_4$:Yb,Er(Tm)/$NaYF_4$ nanoparticles.

FIG 10: Structures of three examples of lipids: (a) 18:0 mPEG2000PE, (b) DSPE-PEG(2000) carboxylic acid and (c) DSPE-PEG(2000) Biotin.

FIG 11: Schematic representation of a photovoltaic device in combination with a layer of up-conversion nano-structured material (electron trapping phosphor) and a reflector.

FIG 12: (A) to (F) show schematic representations of various combinations of photovoltaic apparatus.

FIG 13: (a) Fluorescence picture of (i) $NaYF_4$:Yb,Er nanoparticles, (ii) $NaYF_4$:Yb,Tm nanoparticles and (iii) $NaYF_4$:Er nanoparticles. (b) and (c) show the TEM pictures of $NaYF_4$:Yb,Er nanoparticles and $NaYF_4$:Er nanoparticles, respectively at a magnification of 50000 times.

FIG 14: The fluorescence pictures of (a) core, core/shell and PAA coated core/shell $NaYF_4$:Yb,Er and (b) core, core/shell and PAA coated core/shell $NaYF_4$:Yb,Tm nanoparticles. The excitation is 980 nm NIR laser.

FIG 15: Fluorescence spectra of (a) core, core/shell and PAA coated core/shell $NaYF_4$:Yb,Er and (b) core, core/shell and PAA coated core/shell $NaYF_4$:Yb,Tm nanoparticles. The excitation is 980 nm NIR laser.

FIG 16: Excitation and emission spectra of long afterglow down-conversion material, $SrAl_2O_4$:Eu,Dy.

FIG 17: UV-visible absorption spectrum and fluorescent emission spectrum (inset) of $Eu(DBM)_3L_2$ complex. DBM is dibenzoylmethane and L is tricaprylylmethylammonium.

FIG 18: An illustration of the set-up to measure the enhancement of solar cell efficiency in the presence of down-conversion nano-structured material.

Detailed description of the invention

Bibliographic references mentioned in the present specification are for convenience listed in the form of a list of references and added at the end of the examples. The whole content of such bibliographic references is herein incorporated by reference.

Photovoltaic cells or solar cells currently available are only able to absorb and use part of the solar spectrum, mostly in the visible range. Light in the UV or infrared range is usually not fully utilised by the solar cell and converted into electricity. The present invention seeks to improve the conversion of light within the solar spectrum which is under-utilised or unused and incident on the solar cell into electricity.

According to a first aspect of the present invention, there is provided at least one nano-structured material. The nano-structured material may be any suitable material. For the purposes of the present invention, a nano-structured material is defined as being one comprising constituents which has at least one dimension in the nanoscale. For example, the at least one nano-structured material may be a material comprising at least one dimension having size ≤ 2000 nm. For example, ≤1500 nm, ≤1100 nm, ≤1000 nm, ≤850 nm, ≤500 nm, ≤450 nm, ≤350 nm, in particular, ≤ 100 nm, ≤ 75 nm, and even more in particular, less than 50 nm. More in particular, the nano-structured material may comprise at least one dimension of size ≤ 25 nm, and even more in particular the nano-structured material may comprise at least one dimension of size ≤ 10

nm or ≤ 5 nm. The nano-structured material may comprise one, two, three, four, five, six or even more dimension(s), each dimension of size ≤ 2000 nm, ≤ 1000 nm, ≤ 500 nm, ≤100 nm, ≤ 50 nm, less than 50 nm, ≤ 25 nm, ≤ 10 nm or ≤ 5 nm. The dimension may refer to the average diameter of the nano-structured material.

The at least one nano-structured material may be capable of photon conversion processes. Examples of photon conversion processes include up-conversion, down-conversion and quantum cutting. These three processes are shown schematically as FIG 2(a), (b) and (c), respectively. For example, the at least one nano-structured material may be a down-conversion nano-structured material or an up-conversion nano-structured material. In particular, up-conversion nano-structured material harvest the non-utilised sub-band-gap photons in the near infrared range while the down-conversion nano-structured material down shift the under-used UV light to visible light.

In particular, near infrared (NIR)-to-visible up-conversion fluorescence involves absorbing of two or more NIR lower energy photons followed by emitting one higher energy photon in the visible region. Therefore, the quantum efficiency is less than 1. Down-conversion fluorescence involves absorbing one higher energy photon in UV or visible region followed by emitting one lower energy photon in the visible region, its quantum efficiency is less than or equal to one. Quantum cutting fluorescence refers to fluorescence process of absorbing one higher energy UV photon followed by emitting two low energy photons in the visible region. The quantum efficiency exceeds one (more than one photon is emitted for each incoming photon).

The nano-structured material may be part of a composition. The composition may be used in different applications. The composition may be in the form of a sheet or layer. The composition may be applied to devices. For example, the composition may be applied to photovoltaic apparatus such as solar cells.

The nano-structured material may be comprised in a sheet. The sheet may have a suitable thickness. The nano-structured material may be in the form of a layer or film comprising the nano-structured material. The nano-structured material may be comprised in an apparatus. In particular, the sheet comprising the nano-structured material may be comprised in an apparatus. The apparatus may be a photovoltaic apparatus.

According to a particular aspect, the nano-structured material may be provided to an apparatus. For example, the nano-structured material comprised in a sheet may be provided to an assembly in the form of a layer or film comprising the nano-structured material. The assembly may be an apparatus. Even more in particular, the assembly may be a photovoltaic apparatus.

According to a particular aspect, there is provided an apparatus comprising at least one nano-structured material. The apparatus may be a photovoltaic apparatus. In particular, the photovoltaic apparatus may be a solar cell.

In order for a solar cell, such as a silicon solar cell to benefit from spectral modification, wavelengths of 280 nm to 550 nm may be obtained using quantum cutting phosphors, splitting one photon and emitting two (note that 550 nm corresponds to twice the band gap energy of silicon). If this is not feasible, down-conversion may be used to shift the unused photons to the highly responsive spectral range of 500-1100 nm. As for NIR wavelengths longer than 1100 nm, they may be up-converted to visible photons.

According to a particular aspect, the present invention provides a photovoltaic apparatus comprising:

(a) at least one photovoltaic conversion material; and

(b) at least one down-conversion nano-structured material, wherein the at least one down-conversion nano-structured material is selected from the

group consisting of doped or undoped: a rare-earth organic complex, organic material and inorganic material,

wherein the at least one down-conversion nano-structured material comprises at least one dimension of size ≤ 450 nm.

In particular, the doped or undoped inorganic material may be any suitable material. Even more in particular, the inorganic material may comprise a metal, a semiconductor material and/or an insulator material of formula $M^1_mM^2_nX^1_p:M^3_q$ wherein:

(i) each M^1 is the same or different and is selected from the group consisting of: Sr, Zn, Y and La;

(ii) each M^2 is the same or different and is a metal ion or Si;

(iii) each X^1 is the same or different and is selected from the group consisting of: halogens, O, S, and PO_4;

(iv) each M^3 is the same or different and is selected from the group consisting of: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Cu, Mn, Ag, Cu, Zn, Al, Co and Er;

(v) m is $0 \leq m \leq 10$;

(vi) n is $1 \leq n \leq 15$;

(vii) p is $1 \leq p \leq 20$; and

(viii) q is $0 \leq q \leq 10$,

wherein the at least one down-conversion nano-structured material comprises at least one dimension of size ≤ 450 nm.

For solar cells, even if incident light has photon energy greater than the band gap, lights with different wavelengths do not contribute the same to the solar cells. Solar cells are more sensitive to specific wavelengths of photons. FIG 3 shows the spectral response of three types of solar cells (J. A. Merrigan, 1975). It can be seen from FIG 3 that crystalline silicon mainly responds to photon energy from 400 nm to 1100 nm. Amorphous silicon works with photon energy less than 800 nm, and fully uses the UV (280-400 nm). GaAs solar cells work with wavelength between 400 nm and 900 nm. For both crystalline silicon and GaAs, they are less able to absorb the UV light.

The UV light (280-400 nm) accounts for 5% of the solar energy. Down-conversion nano-structured material will be used to down-convert the UV to emit a longer wavelength. Significant enhancement may be possible with proper materials used. The at least one down-conversion nano-structured material may have the following features: high fluorescent efficiency; at least one dimension of size approximately less than the UV wavelength to avoid light scattering and reflection of the incident light; and wider absorption spectrum ranging from about 280 nm to 450 nm and emit with longer wavelengths.

For the purposes of the present invention, a down-conversion nano-structured material is one in which a high energy photon is split into two or more low energy photons. In particular, the down-conversion nano-structured material according to the present invention has a quantum efficiency which is less than or equal to one. The down-conversion nano-structured material according to any aspect of the present invention does not include material which has a quantum efficiency exceeding one. Down-conversion is found in two groups of materials: (i) host materials doped with rare-earth ions, where down-conversion takes place within the ion; and (ii) band-like down-converters, where an Auger-process takes place within the host material and only the emission occurs within the ions. The down-conversion nano-structured material may be any suitable material.

An example of an arrangement of an apparatus according to a first aspect of the present invention is shown in FIG 4. In particular, the at least one down-conversion nano-structured material is in contact with the at least one photovoltaic conversion material. Even more in particular, the apparatus is arranged such that incident light falls on the at least one down-conversion nano-structured material to enable the at least one down-conversion nano-structured material to absorb UV and yield visible light. In such an arrangement, the absorption of high-energy photon in the incident light is facilitated.

The at least one down-conversion nano-structured material may be selected from the group consisting of a doped or undoped: rare-earth organic complex, organic material and inorganic material.

According to a particular aspect, the at least one down-conversion nano-structured material may be a rare-earth organic complex. In particular, the rare-earth organic complex may be any suitable complex comprising an organic backbone with substitution with an inorganic material. Even more in particular, the rare-earth organic complex may comprise: (a) at least one metal ion; and (b) at least one organic chelating material. For example, the at least one metal ion may be a rare earth metal ion. The rare earth metal ion may be selected from the group consisting of at least: La, Pr, Nd, Pm, Gd, Dy, Ho, Er, Tm, Yb, Eu, Tb, Sm and Ce.

The at least one organic chelating material may be β-diketone and/or a ligand . Any suitable β-diketone and ligand for the purposes of the present invention may be used. For example, the β-diketone may be selected from the group consisting of at least one of: dibenzoylmethane, thenoyltrifluoacetone, acytylacetone and tetraphenylporphyrin (TPP). The ligand may be selected from the group consisting of at least: trioctylamine, trioctylphosphine oxide (TOPO), tricaprylylmethylammonium chloride, triisooctylamine, 1,10-phenanthroline and an aromatic compound. The aromatic compound may be salicylic acid or

benzoic acid. The ligand may also comprise any suitable surfactant as described in the Sigma Aldrich catalogue, 2004-2005. In particular, the surfactant used may be at least one or a mixture of the following:

(i) a surfactant, comprising thiol and carboxylic acid functional groups, selected from mercaptosuccinic acid, mercaptobenzoic acid, penicillamine, mercaptopropioinyl glycine, thioldiacetic acid, thiodipropionic acid, and cysteine hydrochloride;

(ii) a surfactant, comprising thiol and amine functional groups, selected from cysteine, mercaptoethylamine, thioguanine, and thioacetamide;

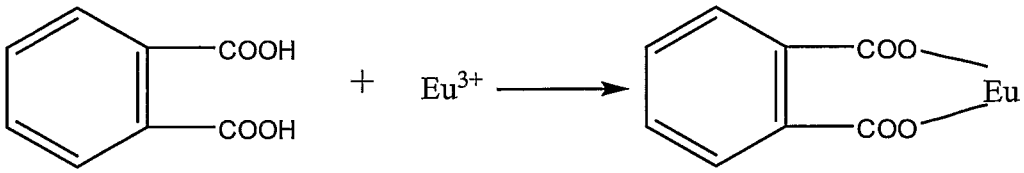
(iii) a surfactant, comprising thiol and hydroxyl groups, selected from mercaptoethanol, thiodiethanol, thioglucose, thioglycerol and cysteine-OH;

(iv) cysteine; and/or

(v) a peptide comprising cysteine.

Even more in particular, the at least one metal ion is a rare-earth metal selected from the group consisting of: Eu, Tb, Sm and Yb; and the at least one organic chelating material is tetraphenylporphyrin (TPP).

Rare-earth organic complex have high down-conversion fluorescent efficiency. For example, Eu and chelating materials react to form Eu-complex, and give off red emitting with high efficiency. Rare-earth organic complexes may be doped into a transparent polymer (like polyacrylic acid and epoxy) and coated onto a solar cell with no visible absorption. An example of a rare-earth organic complex is europium phthalate and $Eu(DBM)_3L_2$, wherein DBM is dibenzoylmethane and L is tricaprylylmethylammonium chloride. In particular, the formation of europium phthalate is shown.



Europium phthalate is capable of absorbing UV light and emitting red light. The mechanism by which a rare-earth organic complex down-converts UV light into visible light is shown in FIG 5. In particular, the organic chelators have strong absorption in UV and elevates electron to its excited states (S1 and S2). Through its triplet state, the electrons are transferred to the excited states of Europium. When electrons come back to the ground states of europium, a visible light emission occurs.

According to a particular aspect, the at least one down-conversion nano-structured material may be a doped or undoped organic material. The organic material may be any suitable material which comprises at least one of the following atoms: C, H, O and N. For example, the organic material may be fluorescein or derivatives, rhodamine or derivatives, coumarin or derivatives, bodypy or derivatives, cascade blue or derivatives, and Lucifer yellow or derivatives.

According to another particular aspect, the at least one down-conversion nano-structured material may be a doped or undoped inorganic material. In particular, the inorganic material may be a metal, a semiconductor or an insulator material of formula $M^1_mM^2_nX^1_p:M^3_q$, wherein M^1, M^2, M^3, X^1, m, n, p and q are as defined above.

For the purposes of the present invention, a metal is defined as a material with no electronic band gap energy; a semiconductor material is defined as a material with electronic band gap energy of less than 2.5 eV; and an insulator material is defined as a material with electronic band gap energy of greater than 2.5 eV.

Any suitable metal may be used for the purposes of the present invention. Examples of metal which can be used as down-conversion nano-structured material include, but are not limited to, silver and gold.

The semiconductor material includes a material whose ability to conduct electricity falls within that of conductors and insulators. For example, the semiconductor material may be CdSe, ZnS, GsAs and TiO_2. Other examples of semiconductor material include II-IV compounds and III-V compounds, metal oxides, sulfides, silicates, pyrosilicates, sulfates, phosphates, phosphor-vanadates, (mono, di, tri, hexa, octa, deca, tetradeca, hexadeca)-aluminates, vanadates, tungstates, halogenates, borates, tatatates, niobates, molybdates and oxysulfides. The semiconductor material may be doped with any suitable material. For example, the semiconductor material may be doped with at least one of the following dopants: B, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Cu, Mn, Ag, Cu, Zn, Al, Co and Er.

The insulator material may be any suitable material. For example, the insulator material may have a formula $M^1_mM^2_nX^1_p:M^3_q$, wherein each of M^1, M^2, M^3, X^1, m, n, p and q are as defined above. Each M^2 may be selected from the group consisting of: Si, transition metal ions, inner transition metal ions, and Group I to Group IV metal ions.

The at least one down-conversion nano-structured material of formula $M^1_mM^2_nX^1_p:M^3_q$ may be selected from the group consisting of: $YM^2O_4:M^3$, $Sr(M^2)_2O_4:M^3$, and $Zn_2M^2O_4:M^3$, wherein each M^2 may be the same or different and may be selected from the group consisting of: Al, Si and V and each M^3 may be the same or different and may be selected from the group consisting of: Eu, Mn and Dy. In particular, the at least one down-conversion nano-structured material is selected from the group consisting of: Zn_2SiO_4:Mn, YVO_4:Eu and $SrAl_2O_4$:Eu,Dy. Other example of down-conversion nano-structured material include: $Zn_3(PO_4)_2$:Mn, $Cd_3(PO_4)$:Mn, Y_2O_3:Eu, ZnS:Ag, ZnS:Cu,Ag, ZnS:Cu,Al,

ZnS:Zn, ZnS:Mn, ZnS:Cu, ZnS:Cu,Co, and $LaPO_4$:Ce,Tb. Even more in particular, the at least one down-conversion nano-structured material of formula $M^1_mM^2_nX^1_p:M^3_q$ may be YVO_4:Eu,Dy, $SrAl_2O_4$:Eu,Dy, ZnS:Mn, ZnS:Cu, ZnS:Cu,Co, YVO_4:Eu and $LaPO_4$:Ce,Tb.

The at least one down-conversion nano-structured material may have at least one dimension less than the incident light and may shift the UV light (wavelength 200 – 400 nm) into visible light (400 – 750 nm). For example, the at least one dimension of the down-conversion nano-structured material may have a size ≤ 450 nm to allow the incident visible light (>400 nm) to go through, without scattering or reflection. According to a particular aspect, the at least one down-conversion nano-structured material may comprise at least one dimension of size ≤ 400 nm, ≤ 350 nm, ≤ 300 nm, ≤ 250 nm, ≤ 200 nm, ≤ 150 nm, ≤ 100 nm, ≤ 70 nm, ≤ 50 nm, ≤ 25 nm, ≤ 20 nm, ≤ 10 nm, ≤ 8 nm, ≤ 5 nm or ≤ 1 nm.

In particular, the at least one down-conversion nano-structured material may be selected from the group consisting of at least: YVO_4:Eu having at least one dimension of about 20 nm; $LaPO_4$:Ce,Tb having at least one dimension of about 8 nm; $SrAl_2O_4$:Eu,Dy having a grain size of about 70 nm; and $Eu(DBM)_3L_2$ having at least one dimension of about 1 nm.

The at least one down-conversion nano-structured material may be in the form of a thin film and arranged to be in contact with the at least one photovoltaic conversion material. As the down-conversion nano-structured material is small, as described above, any incident light which is not absorbed will go through the down-conversion nano-structured material film without scattering. The down-conversion nano-structured material may be doped into a transparent matrix of photovoltaic conversion material to avoid scattering. For the purposes of the present invention, a "matrix" refers to a composition of matter in which two or more different arrays interdigitate, e.g. with the same layer. By way of example,

the two different arrays may be different by virtue of being made from different materials, by virtue of having structures with different orientations, different sizes or some combination of these. The absorbed UV light will down shift to the photovoltaic conversion material to be used in the conversion of light energy into electrical energy.

According to another aspect, the present invention provides a photovoltaic apparatus comprising:

(a) at least one photovoltaic conversion material; and

(b) at least one up-conversion nano-structured material of formula $M^4_rM^5_sX^2_t:M^6_u$, wherein

(i) each M^4 is the same or different and is selected from the group consisting of: Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra and NH_4;

(ii) each M^5 is the same or different and is a metal ion;

(iii) each X^2 is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As;

(iv) each M^6 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb and Cu;

(v) r is $0 \leq r \leq 10$;

(vi) s is $1 \leq s \leq 10$;

(vii) t is $1 \leq t \leq 10$; and

(viii) u is $1 \leq u \leq 10$,

wherein the at least one up-conversion nano-structured material comprises at least one dimension of size ≤ 1100 nm.

For the purposes of the present invention, an up-conversion nano-structured material is one in which two or more low energy photons are combined to form one high energy photon. In particular, the up-conversion nano-structured material according to any aspect of the present invention has quantum efficiency less than 1. An up-conversion material also comprises a material which is capable of storing light energy when exposed to ultraviolet or visible light and this light energy may subsequently be released as visible light when the material is stimulated with infrared radiation. An up-conversion material may consist of host-material doped with rare earth or transition metal ion (also referred to as the active ion). The optical properties of the rare earth ions are only weakly influenced by the host-material because the energy levels involved in the optical transitions are shielded by filled outer shells. In contrast, for transition metal ions, the electrons responsible for the optical transitions are not shielded and the crystal field of the host-material determines the emission and absorption spectra. In particular, the at least one up-conversion nano-structured material according to any aspect of the present invention are material which have a broad absorption range and are capable of absorbing near infrared from about 800 – 1700 nm and generating high energy photons in the visible range which can then be utilised by a solar cell to convert light energy into electrical energy.

An example of an arrangement of an apparatus according to a second aspect of the present invention is shown in FIG 6. In particular, the at least one up-conversion nano-structured material is in contact with the at least one photovoltaic conversion material. For example, the at least one up-conversion nano-structured material is in contact with the surface of the photovoltaic conversion material opposite to the surface of the photovoltaic conversion material on which incident light falls. The at least one up-conversion nano-

structured material absorbs the back light of the photovoltaic apparatus and store within the photovoltaic conversion material. By incident NIR excitation from the photovoltaic conversion material, visible light is released and contribute to the photovoltaic conversion material for use in converting from light energy to electrical energy. In this way, NIR spectra from about 800 – 1700 nm may be utilised. Even more in particular, the apparatus is arranged such that incident light, such as incident sunlight, with photon energy greater than the band gap of the photovoltaic conversion material will be absorbed and the sub-band-gap photons will be transmitted to the at least one up-conversion nano-structured material. The converted visible photons from the at least one up-conversion nano-structured material will be used by the overlying at least one photovoltaic conversion material and improve the efficiency of the photovoltaic conversion material and therefore the efficiency of the photovoltaic apparatus.

Any suitable up-conversion nano-structured material may be used for the purposes of the present invention. For example, the at least one nano-structured material may be prepared according to the method described in WO 2007/078262. According to a particular aspect, the at least one up-conversion nano-structured material has a formula $M^4_rM^5_sX^2_t:M^6_u$, wherein each of M^4, M^5, M^6, X^2, r, s, t and u are as defined above.

Each M^5 according to any aspect of the present invention may be the same or different, and may be any suitable metal ion. For example, each M^5 may be the same or different and may be a transition metal ion, inner transition metal ion, or any one of Group I to Group VI metal ion. In particular, each M^5 may be selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

Each M^4 may be the same or different and is selected from the group consisting of: Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra and NH_4. Each M^6 may be the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr,

Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb and Cu or a combination thereof, such as Yb-Er, Yb-Ho and Yb-Tm.

M^6 according to any aspect of the present invention may act as the dopant. A dopant may be an impurity which is added to a compound in low concentrations to alter some properties of the compound. For example, a dopant may be added in a concentration ranging from one part in a thousand to one part in ten million. It would be understood that a dopant does not alter the crystal structure of the compound it is added to. For example, a dopant may be added to a nano-structured material of any aspect of the present invention so that the nano-structured material can have additional or enhanced properties. The properties include, but are not limited to, optical properties, magnetic properties, electrical properties and fluorescence.

According to a particular aspect, the at least one up-conversion nano-structured material according to any aspect of the invention comprising M^6 may have fluorescence properties. Fluorescence refers to the emission of light in any wavelength excited with energy source. The energy source may be a light source, electric source, thermal source, magnetic source or a combination thereof. The light source may be at least one of UHV, UV, NIR, visible or X-ray. The light can be of any wavelength. The wavelength of the source may be shorter than the emission. For example, UV excitation with emission in the visible range. The wavelength may be longer than the emission, e.g. NIR excitation with visible emission. The energy source may also be referred to as the excitation source. In particular, the nano-structured material can be excited with NIR. The NIR may be emitted at visible wavelength. The NIR may be emitted at 980 nm. The excitation source may be a laser source e.g. 980 nm NIR laser.

The at least one up-conversion nano-structured material may be selected from the group consisting of: $NaM^5F_4:M^6$, $LiM^5F_4:M^6$, $KM^5F_4:M^6$, $RbM^5F_4:M^6$,

$CsM^5F_4:M^6$, $BeM^5F_5:M^6$, $Be(M^5)_2F_8:M^6$, $MgM^5F_5:M^6$, $Mg(M^5)_2F_8:M^6$, $CaM^5F_5:M^6$, $Ca(M^5)_2F_8:M^6$, $SrM^5F_5:M^6$, $Sr(M^5)_2F_8:M^6$, $BaM^5F_5:M^6$, $Ba(M^5)_2F_8:M^6$, wherein each M^5 and M^6 are as defined above. In particular, each M^5 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and each M^6 is the same or different and is selected from the group consisting of: Yb, Er, Tm and Ho. Even more in particular, the at least one up-conversion nano-structured material is $NaYF_4$:Er, $NaYF_4$:Yb,Er, $NaYF_4$:Yb,Tm, $NaYF_4$:Yb,Ho, $LiYF_4$:Yb,Er, $BaYF_5$:Yb,Er, $NaLaF_4$:Yb,Er, LaF_3:Yb,Er, CeF_3:Yb,Er, GdF_3:Yb,Er, YF_3:Yb,Er, YOF:Yb,Er, LaF_3:Yb,Tm, CeF_3:Yb,Tm, GdF_3:Yb,Tm, YF_3:Yb,Tm or YOF:Yb,Tm.

The up-conversion nano-structured material may also comprise doubly activated alkaline earth sulphide and selenides, zinc selfides and selenides and cadmium sulfides and selenides. Such up-conversion nano-structured material has good sensitivity, storage-ability and rapid time response. Examples of the at least one up-conversion nano-structured material may include SrS:Eu,Sm, CaS:Eu,Sm, SrS:Ce,Sm and ZnS:Pb,Cu.

The at least one up-conversion nano-structured material may have a structure selected from the group consisting of: hexagonal, cubic, tetragonal, rhombohedral, orthorhombic, monoclinic, triclinic and a combination thereof. It will be understood that for the purposes of the present invention, the lattice structure of the at least one up-conversion nano-structured material describes the grouping of the material according to the axial system. Each lattice structure consists of a set of three axes in a particular geometrical arrangement. The nano-structured material's lattice structure may play a role in determining some of its properties, such as its electric properties and optical properties.

In particular, the at least one up-conversion nano-structured material has a hexagonal lattice structure. For example, the at least one up-conversion nano-structured material may be hexagonal phase $NaYF_4$:Er, hexagonal phase

$NaYF_4$:Yb,Er, hexagonal phase $NaYF_4$:Yb,Tm or hexagonal phase $NaYF_4$:Yb,Ho.

The at least one up-conversion nano-structured material may have at least one dimension of size ≤ 1100 nm. The at least one up-conversion nano-structured material having such dimensions is advantageous as the nano-structured material minimises reflection and scattering of visible light. According to a particular aspect, the at least one up-conversion nano-structured material may comprise at least one dimension of size ≤ 1000 nm, ≤ 900 nm, ≤ 850 nm, ≤ 800 nm, ≤ 700 nm, ≤ 650 nm, ≤ 600 nm, ≤ 500 nm, ≤ 450 nm, ≤ 400 nm, ≤ 300 nm, ≤ 200 nm, ≤ 100 nm, ≤ 50 nm, ≤ 25 nm, ≤ 20 nm, ≤ 10 nm, ≤ 8 nm or ≤ 5 nm.

The at least one up-conversion nano-structured material may be in the form of: nanoparticle(s), nanofilm, or monolith. For example, the nano-structured material may be at least one nanoparticle and the average diameter of the nanoparticle(s) is $\leq$ 1100 nm, $\leq$ 1000 nm, $\leq$100 nm, $\leq$ 50 nm, < 50 nm, $\leq$ 25 nm, $\leq$ 10 nm or $\leq$ 5 nm. In particular, the average diameter of the nanoparticle(s) is < 50 nm, $\leq$ 25 nm, $\leq$ 10 nm or $\leq$ 5 nm. More in particular, the average diameter of the nanoparticle(s) is $\leq$ 10 nm.

The at least one up-conversion nano-structured material may be at least one nanofilm. The nanofilm may have a thickness between about 0.1 nm to about 1 mm. In particular, the nanofilm thickness may be the same or less than about 500 nm, about 400 nm, about 300 nm, about 200 nm, about 100 nm, about 50 nm, about 25 nm, about 20 nm, about 15 nm, about 10 nm or about 5 nm. The nanofilm may be a single layer or multiple layers, and wherein each layer of the nanofilm is the same or different from the other layer. The nanofilms may be prepared by depositing particles using methods such as dip coating or spin coating.

Up-conversion nano-structured material such as $NaYF_4$:Er, $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm are capable of absorbing near infrared from 1480 – 1580 nm and 920 – 1020 nm, and generating high energy photons in the visible range. In particular, $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm nanoparticles are able to convert near infrared of 920-1010 nm into visible light, while $NaYF_4$:Er nanoparticles are able to convert near infrared of 1480-1880 nm into visible light, which can be used by the photovoltaic conversion material.

The nanoparticle(s) may comprise core nanoparticle(s) and/or core-shell nanoparticle(s). The shell may be the same or different material as the core. An illustration of the core nanoparticle and core-shell nanoparticle is shown in FIG 7(a) and 7(b), respectively. FIG 7(a) shows a core nanoparticle with at least one kind of surfactant on its surface. FIG 7(b) shows a core-shell nanoparticle with at least one kind of surfactant on the shell. FIG 8 shows a nano-structured material where the core and the shell are of the same material, $NaYF_4$. For example, the nanoparticle may be a core nanoparticle and the nanoparticle further comprises at least one organic and/or inorganic material (shell) applied on the core, to obtain a core-shell nanoparticle(s).

As mentioned above, the at least one up-conversion nanoparticle may comprise an organic and/or inorganic material (shell). The organic and/or inorganic material (shell) may be applied continuously or discontinuously on the core. According to a particular aspect, the shell material has the formula $M^4_rM^5_sX^2_t$ or $M^4_rM^5_sX^2_t$:M^6_u, wherein each of M^4, M^5, X^2, M^6, r, s, t and u are as defined above.

For example, the inorganic shell material may comprise a material selected from the group consisting of: NaM^5F_4, LiM^5F_4, KM^5F_4, RbM^5F_4, CsM^5F_4, BeM^5F_5, $Be(M^5)_2F_8$, MgM^5F_5, $Mg(M^5)_2F_8$, CaM^5F_5, $Ca(M^5)_2F_8$, SrM^5F_5, $Sr(M^5)_2F_8$, $BaLnF_5$, $Ba(M^5)_2F_8M^5F_3$, M^5F_3, M^5Cl_3, M^5Br_3, M^5I_3, M^5FClBr, M^5OF, M^5OCl, M^5OBr, M^5OS, $(M^5)_2S_3$, wherein each M^5 is as defined above. In particular, each

M^5 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; SiO_2; TiO_2; ZnS; or a combination thereof.

According to another particular aspect, the organic shell material may comprise at least one polymer, a surfactant, a lipid, or a combination thereof. For example, the polymer may be selected from the group consisting of: polystyrene (PS), polyethylene (PE), polymethyl methacrylate (PMMA), polylactic acid (PLA) and a combination thereof. For the purposes of the present invention, a surfactant will be understood to be on which is a surface active agent that lowers the surface tension. The surfactant may contain both hydrophilic and hydrophobic components and may be semi-soluble in both organic and aqueous solvents. For example, surfactants tend to clump up when in solution, forming a surface between fluid and air with hydrophobic tails in the air and the hydrophilic heads in the fluid.

The shell material may confer certain properties onto the up-conversion nano-structured material. For example, the shell may make the up-conversion nano-structured material more hydrophilic, hydrophilic or amphiphilic.

According to a further aspect, the at least one up-conversion nano-structured material may have its surface modified. The surface of the up-conversion nano-structured material may be modified by adding at least one surfactant, lipid, polymer, inorganic material, or a mixture thereof. The surface of the nano-structured material may be modified to confer certain properties onto the nano-structured material. For example, the surface of the nano-structured material may be modified to make the nano-structured material more hydrophilic, hydrophilic or amphiphilic. The nano-structured material may be made more hydrophilic by surfactant(s) and/or lipid(s).

According to a particular aspect, the nano-structured material may be surface modified by any one of the following ways:

(a) Surfactant/lipids modification:

Nano-structured material + surfactant(s) ⟶ nano-structured material-Surfactants complex

(b) Surfactant(s)/lipid(s) replacement:

Nano-structured material-Surfactant(1) + Surfactant (2) ⟶ Nano-structured material-surfactant(2)

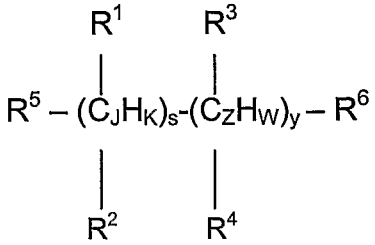
(c) Surfactant attached on the surfactant on the nano-structure material surface

Nanoparticles-Surfactant(1) + Surfactant (2) ⟶ Nano-structured material-Surfactant(1)-Surfactant(2)

It will be understood that in the above, surfactant and lipid may be used interchangeably. An illustration of surface modified nano-structured material is shown in FIG 9.

The surface of the nano-structured material may be modified by at least one lipid. The lipid may be any suitable lipid. For example, the lipid may be phospholipid, long-chain aliphatic hydrocarbon, lipid multichain, comb-shaped lipid-polymer steroid, fullerene, polyaminoacid, native or denatured protein, aromatic hydrocarbon, or partially or completely fluorinated lipid. In particular, the lipid may have the structure as shown in FIG 10 (a), (b) and (c).

In particular, the surface is modified by at least one surfactant. The at least one surfactant may be adsorbed onto the surface of the at least one up-conversion nano-structured material. The surfactant according to any aspect of the present invention may be hydrophilic, hydrophobic and/or amphiphilic. The surfactant may have the following formula:



(Formula I)

wherein:

each J is the same or different, and $1 \leq J \leq 9$;

each K is the same or different, and $0 \leq K \leq 9$;

each s is the same or different, and $0 \leq s \leq 9$;

each Z is the same or different, and $1 \leq Z \leq 9$;

each W is the same or different, and $0 \leq W \leq 9$;

each y is the same or different, and $0 \leq y \leq 9$;

each R^1, R^2, R^3, R^4 and R^5 is the same or different, and is independently selected from the group consisting of: H, substituted or unsubstituted C_1-C_6 alkyl, substituted or unsubstituted C_1-C_6 aryl, HS, COOH, NH_2 and OH;

each R_6 is the same or different, and is selected from the group consisting of: COOH, NH_2, OH, P=0 and P;

with the proviso that $s + y < 10$.

As used herein, the term "alkyl" refers to a straight or branched, monovalent, saturated aliphatic chain of preferably 1 to 6 carbon atoms, including normal, iso, neo and tertiary. "Alkyl" includes, but is not limited to, methyl, ethyl, propyl, isopropyl, butyl, iso-butyl, sec butyl, tert butyl, amyl, isoamyl, neoamyl, hexyl, isohexyl, neohexyl, and the like; cycloalkyl group such as cyclopropyl,

cyclobutyl, cyclopentyl, cyclohexyl and the like, the cycloalkyl group may be substituted. The alkyl may be optionally substituted with substituents selected from the group consisting of lower alkyl, lower alkoxy, lower alkylsulfanyl, lower alkylsulfenyl, lower alkylsulfonyl, oxo, hydroxy, mercapto, amino optionally substituted by alkyl, carboxy, carbamoyl optionally substituted by alkyl, aminosulfonyl optionally substituted by alkyl, silyloxy optionally substituted by alkoxy, alkyl, or aryl, silyl optionally substituted by alkoxy, alkyl, or aryl, nitro, cyano, halogen, or lower perfluoroalkyl, multiple degrees of substitution being allowed. Such an "alkyl" group may contain one or more O, S, S(O), or $S(O)_2$, P, P(O), $P(O)_2$ atoms.

The term "aryl" refers to a benzene ring or to an optionally substituted benzene ring system fused to one or more optionally substituted benzene rings, optionally substituted with substituents selected from the group consisting of lower alkyl, lower alkoxy, lower alkylsulfanyl, lower alkylsulfenyl, lower alkylsulfonyl, oxo, hydroxy, mercapto, amino optionally substituted by alkyl, carboxy, tetrazolyl, carbamoyl optionally substituted by alkyl, aminosulfonyl optionally substituted by alkyl, acyl, aroyl, heteroaroyl, acyloxy, aroyloxy, heteroaroyloxy, alkoxycarbonyl, silyloxy optionally substituted by alkoxy, alkyl, or aryl, silyl optionally substituted by alkoxy, alkyl, or aryl, nitro, cyano, halogen, or lower perfluoroalkyl, multiple degrees of substitution being allowed. Examples of aryl include, but are not limited to, phenyl, biphenyl, naphthyl, furanyl, pyrrolyl, thiophenyl, pyridinyl, indolyl, benzofuranyl, benzothiophenyl, quinolinyl, isoquinolinyl, imidazolyl, thiazolyl, pyrazinyl, pyrimidinyl, purinyl and pteridinyl and the like.

The term “lower” refers to a group having between one to six carbon atoms.

Any suitable surfactant as described in the Sigma Aldrich catalogue, 2004-2005 may be used for the present invention. In particular, the surfactant used may be at least one or a mixture of the following:

(i) a surfactant, comprising thiol and carboxylic acid functional groups, selected from mercaptosuccinic acid, mercaptobenzoic acid, penicillamine, mercaptopropioinyl glycine, thioldiacetic acid, thiodipropionic acid, and cysteine hydrochloride;

(ii) a surfactant, comprising thiol and amine functional groups, selected from cysteine, mercaptoethylamine, thioguanine, and thioacetamide;

(iii) a surfactant, comprising thiol and hydroxyl groups, selected from mercaptoethanol, thiodiethanol, thioglucose, thioglycerol and cysteine-OH;

(iv) cysteine; and/or

(v) a peptide comprising cysteine.

For example, in the surfactant(s) of Formula (I), s + y has the following ranges: 1-9, 1-8, 1-7, 1-6, 1-5, 1-4, 1-3, 1-2, or 1. In particular, s + y is 1-4, preferably 1 or 2, and each of R^1, R^2, R^3, and R^4, independently, is not present or is H. More in particular, surfactant(s) according to any aspect of the present invention may be $HSCH_2COOH$ and/or $HS(CH_2)_2COOH$. The cysteine-containing peptide of (v) may be a peptide of the following sequence: CDPGYIGSR, which refers to the 925-933 laminin fragment. In particular, the surfactant is polyacrylic acid, polyethylene glycol 600 (HOOC-PEG-COOH), 11-aminoundecanoic acid (AUA) or a mixture thereof.

The at least one up-conversion nano-structured material may be arranged to be in contact with the at least one photovoltaic conversion material. As the up-conversion nano-structured material is small, as described above, minimal light scattering will occur. The up-conversion nano-structured material may be doped into a transparent matrix. For the purposes of the present invention, a "matrix" refers to a composition of matter in which two or more different arrays interdigitate, e.g. with the same layer. By way of example, the two different

arrays may be different by virtue of being made from different materials, by virtue of having structures with different orientations, different sizes or some combination of these. For example, the up-conversion nano-structured material may be doped to form a transparent polymer matrix. In particular, the polymer matrix is an epoxy matrix. This allows for doping a larger amount of up-conversion nano-structured material into the matrix to better utilise the NUR without changing the transparency of the polymer, and therefore enhancing the utilisation of up-converted visible light in the photovoltaic conversion material. The absorbed NIR light will be released as visible light to the photovoltaic conversion material to be used in the conversion of light energy into electrical energy.

According to another aspect, the present invention provides a photovoltaic apparatus comprising:

(a) at least one photovoltaic conversion material;

(b) at least one down-conversion nano-structured material as described above; and

(c) at least one up-conversion nano-structured material as described above.

The photovoltaic apparatus may be a solar cell.

Any suitable photovoltaic conversion material may be used for the purposes of the present invention. For example, the at least one photovoltaic conversion material may have a refractive index of about 1 to about 5 and a dielectric constant of about 1 to about 15.

According to a particular aspect, the photovoltaic conversion material may comprise at least: a conducting or semiconducting polymer material, a silicon-based material, cadmium telluride (CdTe), copper indium diselenide (CIS), gallium arsenide (GaAs) or dye-sensitized solar cells.

For example, the conducting or semiconducting polymer material may be selected from the group consisting of: poly(phenylene) and derivatives thereof, poly(phenylene vinylene) and derivatives thereof, poly(thiophene) and derivatives thereof, poly(thienylenevinylene) and derivatives thereof, and poly(isothianaphthene) and derivatives thereof, organometallic polymers, polymers containing perylene units, poly(squaraines) and their derivatives. The poly(phenylene vinylene) and derivative thereof may be poly(2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV) or poly(para-phenylene vinylene) (PPV). The poly(thiophene) and derivatives thereof may be selected from the group consisting of: poly(3-octylthiophene-2,5,-diyl), regioregular, poly(3-octylthiophene-2,5,-diyl), regiorandom, poly(3-hexylthiophene-2,5-diyl), regioregular, and poly(3-hexylthiophene-2,5-diyl), regiorandom. In particular, the photovoltaic conversion material may comprise P3HT (poly(3-hexylthiophene)). P3HT is an optically transparent material with a high electrical conductivity. The silicon-based material may be crystalline silicon, amorphous silicon or a combination thereof. An example of a dye-sensitized solar cell may be such as that described in Brian O'Regan and Michael Grätzel, 1991.

The photovoltaic apparatus according to any aspect of the present invention may further comprise a reflector having at least one reflecting surface and/or an anti-reflective material. In particular, the photovoltaic apparatus may comprise a reflector when the photovoltaic apparatus comprises at least one up-conversion nano-structured material.

FIG 11 shows an example of a photovoltaic apparatus comprising a photovoltaic conversion material, at least one up-conversion nano-structured material and a reflector. For most photovoltaic apparatus, only incident sunlight from the top is used to generate electricity. However, the advantage provided by the apparatus illustrated in FIG 11 is that light from the back will be utilised as well. The apparatus shown in FIG 11 has three layers, the top layer being the photovoltaic conversion material, the bottom layer comprises a one-way

reflector with a reflecting surface coated with the up-conversion nano-structured material. When incident light shines on the photovoltaic conversion material from the front surface, photons with energy larger than band gap energy will be absorbed by the photovoltaic material and generate electricity. Sub-band-gap photons are transmitted to excite the up-conversion nano-structured material to generate additional visible photons. Light from the back of the apparatus then goes in and re-charges the up-conversion nano-structured material, and awaiting the next incoming NIR photons from the front surface to excite them to release visible photons again. The cycle then repeats itself. A one-way reflector allows the light from the back or bottom of the apparatus to come in and re-charge the up-conversion nano-structured material. The up-conversion nano-structured material has great electron trapping capacity, and therefore even very weak photons from the back of the apparatus can be effectively absorbed by the up-conversion nano-structured material.

The photovoltaic apparatus according to any aspect of the present invention may further comprise an anti-reflective material. In particular, the anti-reflective material may be applied to the surface of the nano-structured material to decrease the reflection and enhance the absorption of the incident light. Any suitable anti-reflective material may be used. For example, the anti-reflective material may be MgF_2, SiO_2, Al_2O_3, Si_3N_4, TiO_2 and Ta_2O_5. In particular, the anti-reflective material may be applied to the top of the down-conversion nano-structured material to decrease the reflection and enhance the absorption of the incident light.

According to a particular aspect, the photovoltaic apparatus as described above is such that the photovoltaic conversion material is in contact with the at least one nano-structured material. For example, the photovoltaic conversion material and the nano-structured material may be in the form of layers and the two layers may be in contact with each other.

According to a further particular aspect, the photovoltaic apparatus comprises:

(i) at least one layer (A) comprising the at least one photovoltaic conversion material and at least one layer (B) comprising at least one down-conversion nano-structured material as described above, wherein layer B is in contact with layer A;

(ii) at least one layer (A), at least one layer (C) comprising at least one up-conversion nano-structured material as described above, and optionally at least one layer (D) comprising a reflector having at least one reflecting surface, wherein layer A is in contact with layer C and the reflecting surface of layer D is in contact with layer C; or

(iii) at least one layer (A), at least one layer (B), at least one layer (C) and optionally at least one layer (D) having at least one reflecting surface, wherein layer B is in contact with layer A, layer A is in contact with layer C and layer C is in contact with the at least one reflecting surface of layer D.

Possible arrangements of the photovoltaic apparatus are shown in FIG 12. In particular, FIG 12 shows the following possible arrangements: (A) shows a photovoltaic apparatus comprising a first layer of down-conversion nano-structured material 1204 and a second layer of photovoltaic conversion material 1202; (B) shows a photovoltaic apparatus comprising first layer of an anti-reflective material 1206, a second layer of down-conversion nano-structured material 1204 and a third layer of photovoltaic conversion material 1202; (C) shows a photovoltaic apparatus comprising a first layer of photovoltaic conversion material 1202 and a second layer of up-conversion nano-structured material 1208; (D) shows a photovoltaic apparatus comprising a first layer of photovoltaic conversion material 1202, a second layer of up-conversion nano-structured material 1208 and a third layer of reflective material 1210; (E) shows

a photovoltaic apparatus comprising a first layer of down-conversion nano-structured material 1204, a second layer of photovoltaic conversion material 1202 and a third layer of up-conversion nano-structured material 1208; and (F) shows a photovoltaic apparatus comprising a first layer of an anti-reflective material 1206, a second layer of down-conversion nano-structured material 1204, a third layer of photovoltaic conversion material 1202, a fourth layer of up-conversion nano-structured material 1208 and a fifth layer of reflective material 1210. It would be readily understood that the illustrations are only examples and that many variations may be made without departing from the present invention.

Alternatively, the at least one photovoltaic conversion material and the at least one nano-structured material may not contact each other but may be arranged such that the photovoltaic conversion material and the nano-structured material are in close proximity to one another. An example of a possible arrangement is shown in Figure 1 of Slooff et al, 2005. In particular, the photovoltaic apparatus may be a luminescent concentrator. The concentrator may comprise a transparent matrix material which may be in the form of a flat plate, with photovoltaic conversion material connected to one or more sides of the matrix. The matrix may comprise the nano-structured material. Part of the light emitted by the nano-structured material is guided towards the photovoltaic conversion material by total internal reflection. The advantage of such an arrangement is that both direct light and diffuse light is collected, thereby further improving the efficiency of the photovoltaic apparatus. In particular, a concentrator makes use of relatively inexpensive materials such as plastic lenses and metal housings to capture the solar energy shining on a fairly large area and focus that energy onto a smaller area, where the photovoltaic conversion material is. The at least one nano-structured material according to any aspect of the present invention may be coated on the material which captures the solar energy shining on them.

The at least one nano-structured material according to any aspect of the present invention when used in photovoltaic apparatus may be useful for several reasons. For example, light scattering would be minimised. In particular, since the nano-structured material have at least one dimension of size less than the incoming radiation, light scattering would be avoided. Further, given the size of the nano-structured material, a more even and uniform distribution of the material may be achieved when the nano-structured material is applied to a photovoltaic apparatus. This may increase the efficiency of the photovoltaic apparatus. With the nano-structured material in the nanoscale, surface modification may also be achieved more easily as compared to surface modification on bulk materials.

The present invention also provides a method of improving the efficiency of a photovoltaic apparatus comprising the steps of:

(a) providing at least one down-conversion nano-structured material as described above on at least one surface of or in proximity of a photovoltaic material comprised in a photovoltaic apparatus; and/or

(b) providing at least one up-conversion nano-structured material as described above on at least one surface of or in proximity of a photovoltaic material comprised in a photovoltaic apparatus.

The at least one down-conversion nano-structured material and/or the at least one up-conversion nano-structured material may be in the form of layers. In particular, a layer of at least one down-conversion nano-structured material and/or a layer of at least one up-conversion nano-structured material may be provided to be in contact with at least one photovoltaic material. The efficiency of the photovoltaic apparatus may be improved by the provision of the at least one down-conversion nano-structured material and/or the at least one up-conversion nano-structured material, as described above. For example, the at least one down-conversion nano-structured material absorbs UV light and down

shifts to visible light which is then utilised by the photovoltaic conversion material to convert light energy into electrical energy. Similarly, the at least one up-conversion nano-structured material absorbs NIR light and releases visible light to the photovoltaic conversion material to be used in the conversion of light energy into electrical energy.

Depending on the material of the at least one photovoltaic conversion material comprised in the photovoltaic apparatus, different photovoltaic conversion material may require different nano-structured material to be provided to the photovoltaic apparatus. For example, crystalline silicon solar cells, which are capable of absorbing light of 400 – 1100 nm, both up-conversion and down-conversion nano-structured material can be provided. For amorphous silicon solar cells, light from 280 – 800 nm can be well absorbed by amorphous silicon, and therefore only up-conversion nano-structured material may be provided to the apparatus. In particular, for single crystalline and polycrystalline silicon solar cells, sunlight with wavelength shorter than 1100 nm may be absorbed by silicon. Therefore, $NaYF_4$:Er nanoparticles or $NaYF_4$:Er/$NaYF_4$ core/shell nanoparticles can be applied to the solar cell. These nanoparticles may be used in crystalline silicon solar cells to utilise the photons with wavelength between 1480-1580 nm. For other types of solar cells like amorphous silicon (1.7ev, wavelength = 729nm), both $NaYF_4$:Er, $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm may be used, absorbing 1480-1580 nm and 920-1010 nm NIR and up-convert into the visible range.

The method according to the present invention may further comprise the step of: providing a reflector having at least one reflecting surface, wherein the reflecting surface is provided to be in contact with the at least one up-conversion nano-structured material; and/or providing an anti-reflective material. The anti-reflective material may be in contact with the at least one down-conversion and/or up-conversion nano-structured material. As explained above, the provision of the reflector improves the up-conversion of NIR light into visible

light, thereby improving the amount of visible light available for conversion from light energy into electricity by the photovoltaic conversion material.

The advantage of the method of the present invention is that the at least one down-conversion nano-structured material and the at least one up-conversion nano-structured material may be provided as additional components to existing photovoltaic apparatus such as solar cells. Further, as the photovoltaic conversion material and the nano-structured material are not integrated as a single component, each of the photovoltaic conversion material and the nano-structured material may be optimised independently.

The present invention also provides a photovoltaic apparatus obtainable by the method described above. In particular, the photovoltaic apparatus obtainable by the method described above may have an improved conversion efficiency from light energy into electricity compared to a photovoltaic apparatus which does not comprise the at least one nano-structured material according to any aspect of the present invention.

The present invention also provides a kit comprising a photovoltaic apparatus according to any aspect of the present invention. The kit may also comprise written instructions on the use of the photovoltaic apparatus.

Having now generally described the invention, the same will be more readily understood through reference to the following examples which are provided by way of illustration, and are not intended to be limiting of the present invention.

EXAMPLES

Example 1

Up-conversion nano-structured material

$NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm NIR-to-visible up-conversion nanoparticles (also referred to as phosphors) are regarded as one of the most efficient up-conversion fluorescent materials. They absorb NIR at the wavelength range of 920-1010 nm. Hence two or three absorbed NIR photons may be combined to generate a higher energy photon in the visible (520 nm, 540 nm and 650 nm) range. The up-conversion efficiency (emitted visible power per absorbed NIR power) is approximately 5% with 980 nm excitation (K W Kramer et al, 2004). Gibart et al (Gibart et al, 1996) first applied up-conversion phosphors on a GaAs (1.43 eV, corresponding to 867 nm wavelength) solar cell. A response of the cell was observed at energy of 1.391eV under excitation of 1 W/0.039 cm^2.

Without doping Yb, $NaYF_4$:Er is also a good up-conversion phosphors that absorbs NIR photons in the range of 1480 to 1580 nm. Shalav et al. (A Shalav et al, 2005) placed $NaYF_4$:Er on the rear side of a bifacial cell, observing a response of the cell under excitation of 1523 nm, with external quantum yield (EQE) of 2.5%.

For both Gibart et al. and Shalav et al., the phosphors they used were prepared by solid state reaction with micron particle size (1-3 micron). Such big particle size strongly scatters the visible light (0.4-0.75 micron). For such large particle size, low doping concentration to minimize scattering resulted in low conversion efficiency, whereas high doping concentration led to decreased layer transparency (thus preventing the converted visible light from reaching the overlying solar material). Therefore, due to the size-related poor doping, the solar enhancement was very limited.

For the purposes of the present invention, $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm NIR-to-Visible up-conversion nanoparticles were prepared according to the method disclosed in WO 2007/078262. Intense up-conversion fluorescence was observed under 980 nm excitation. Using a JEOL, JEM 3010 transmission electron microscope (TEM), it was determined that the nanoparticles were

approximately 10 nm with very narrow size distribution. The synthesized nanoparticles were easily dispersed in organic solvents such as hexane and formed a transparent colloidal solution. FIG 13 shows the nanoparticles and their colloidal solution (0.1 wt.-%) under 980 nm NIR excitation. Green, blue and red up-conversion nanoparticles were prepared. FIG 13 (a) shows the (i) green, (ii) blue and (iii) red fluorescence, given off by $NaYF_4$:Yb,Er, $NaYF_4$:Yb,Tm and YOF:Yb,Er, respectively. FIG 13 (b) and (c) shows the TEM images of $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm.

For the $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm nanoparticles, after coated with an undoped $NaYF_4$ shell, significant enhancements of up-conversion fluorescence were observed. The hydrophobic core/shell nanoparticles were rendered hydrophilic by a subsequent amphiphilic coating of PAA. A schematic diagram of a core, core/shell and PAA coated core/shell $NaYF_4$:Yb,Tm nanoparticle is shown in FIG 8 (a), (b) and FIG 9 (a) respectively.

FIG 14 (a) and (b) shows the fluorescence pictures of core, core/shell and PAA coated core/shell $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm nanoparticles, respectively. The excitation is 980 nm NIR laser. FIG 15 (a) and (b) shows the fluorescence spectra of core, core/shell and PAA coated core/shell of $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm nanoparticles, respectively. Up-conversion fluorescence enhancements of 7.4 and 29.6 times were obtained for $NaYF_4$:Yb,Er and $NaYF_4$:Yb,Tm, respectively, after coating with an undoped $NaYF_4$ shell. For the PAA coated core/shell particles, fluorescence intensity of about 57% for $NaYF_4$:Yb,Er, and about 66.9% for $NaYF_4$:Yb,Tm, was observed, compared to the core/shell counterparts.

Down-conversion nano-structured material

a) YVO_4:Eu and $LaPO_4$:Ce,Tb nanoparticles

Down-conversion fluorescent nanoparticles of YVO_4:Eu and $LaPO_4$:Ce,Tb were prepared following the method described in A Huignard et al, 2002, and V Buissette et al, 2006, respectively. These nanoparticles are approximately 20 nm and 8 nm in size, respectively, as determined using TEM (JEOL, JEM 3010). Under 254 nm UV excitation, green and red emitting fluorescence was observed. In particular, YVO_4:Eu and $LaPO_4$:Ce,Tb emitted red and green emissions, respectively, under UV.

The colloidal solution of YVO_4:Eu and $LaPO_4$:Ce,Tb nanoparticles are stable for years without any optical change. This is advantageous as nanoparticles provided on the front surface of solar cells to form a thin film would remain stable over time. As the nanoparticles are very small in size, no light scattering occurred, and light passed through the nanoparticles and entered the solar cells, if light was not absorbed. On the other hand, UV light was absorbed by the nanoparticles and converted into visible light, which is more easily absorbed by the solar cells (not including amorphous silicon).

b) $SrAl_2O_4$:Eu,Dy nanoparticles

Long afterglow phosphors of $SrAl_2O_4$:Eu,Dy were also prepared with grain size of 70 nm. The size was determined using TEM (JEOL, JEM 3010) and scanning electron microscope (SEM). $SrAl_2O_4$:Eu,Dy is a very efficient down-conversion fluorescent material with efficiency of about 90%. FIG 16 shows the excitation and emission spectra of $SrAl_2O_4$:Eu,Dy. As shown FIG 16, excitation covered from 250 nm to 450 nm, with emission peak at 520 nm. Accordingly, $SrAl_2O_4$:Eu,Dy is an excellent down-conversion fluorescent material for solar cells. $SrAl_2O_4$:Eu,Dy almost fully absorbed the solar spectrum from 250 nm to 450 nm, and emitted visible fluorescence at 520 nm.

Further, as $SrAl_2O_4$:Eu,Dy is an afterglow material, it can glow in the dark for over 12 hours. After coating onto solar cells, $SrAl_2O_4$:Eu,Dy acts as a down-converter during the day, which converts the UV light into visible light. At night,

the $SrAl_2O_4$:Eu,Dy nanoparticles will continue to shine on the solar cells with its afterglow, thus enabling the generation of electricity.

c) Eu-complex $Eu(DBM)_3L_2$

Down-conversion fluorescent materials of rare earth organic complex were also prepared. These complex consists of rare earth ions (Eu, Tb, Sm and Ce), β-diketones including dibenzoylmethane, thenoyltrifluoacetone, acytylacetone, and/or other ligands including trioctylamine, trioctylphosphine oxide (TOPO), tricaprylylmethylammonium chloride, triisooctylamine, 1,10-phenanthroline, aromatic compound (e.g., salicylic acid, benzoic acid). Under 254 nm and 365 nm UV excitation, red and green fluorescence were observed from Eu-$(dibenzoylmethane)_3$-$(tricaprylylmethylammonium)_2$ and Tb-$(acetylacetone)_3$-phenanthroline, respectively, using a luminescent spectrometer (Perkin-Elmer, LS55B).

Fig 17 is the UV-visible absorption and emission spectra of Eu-complex $Eu(DBM)_3L_2$, wherein DBM refers to dibenzoylmethane, and L refers to tricaprylylmethylammonium chloride. This complex has a strong absorption in the UV range from 230 nm to 410 nm, and gives off red emission of 612 nm (see inset of FIG 17). The size of $Eu(DBM)_3L_2$ was determined to be about 1 nm. The size of the rare-earth organic complex was estimated by calculation. In particular, the length of the complex is considered in terms of the number of atoms and based on the size of each atom, the size of the complex is determined.

Down-conversion fluorescent materials of rare earth organic complexes can be dissolved in organic solutions like chloroform, and form transparent solution. Under UV light excitation, strong fluorescent emission was observed from these solutions as well.

Example 2

To test their enhancement to solar cell conversion efficiency, an experiment as shown in FIG 18 was set up. A commercial polycrystalline silicon solar cell (Silicon Solar Inc, polycrystalline solar cell, with 5x5 cm^2 size and epoxy encapsulation) 1802 was used for the testing. A UV lamp 1804 having dual wavelength of 254 nm and 365 nm was used as excitation. A power-meter 1806 was used to measure the current and voltage.

For comparison, glass slides 1808 with and without down-conversion fluorescent materials as described in Example 1 above were used. Glass with down-conversion fluorescent materials was prepared by dissolving $Eu(DBM)_3L_2$ and 1% w/w PMMA resin in chloroform. Two concentrations of $Eu(DBM)_3L_2$ were tested, i.e. 1% w/w of $Eu(DBM)_3L_2$ in chloroform and 2% w/w of $Eu(DBM)_3L_2$ in chloroform. A drop (about 0.1 mL) of the solution prepared was dip-coated (spin coating and other dispersion may also be done) onto one surface of the glass slide which would be in contact with the solar cell when the glass slide is placed on the solar cell. The glass slide had dimensions 2.5 cm x 7.5 cm. After the chloroform evaporated, a transparent thin film of $Eu(DBM)_3L_2$ in PMMA was formed on the glass slide. The glass slides were then cured for about 2 hours. Glass slides with 1% w/w $Eu(DBM)_3L_2$ in chloroform, 2% w/w $Eu(DBM)_3L_2$ in chloroform, and without the $Eu(DBM)_3L_2$ were placed on separate solar cells, and the current (I) and voltage (V) of the solar cells (excited at 254 nm and 365 nm separately) were measured with five readings each, each reading being taken one minute apart. The power output of the solar cells was calculated as P=IV. Tables 1 to 11 provide the results obtained. The glass slides comprising the down-conversion nano-structured material gave off a bright red emission under UV excitation.

Reading	1	2	3	4	5	Average
x 2000 μA	25	25	24	24	24	24.4
x 20V	1.15	1.12	1.12	1.11	1.10	1.12

Table 1: Current and voltage reading of solar cells without any glass slide and without $Eu(DBM)_3L_2$ under 254 nm UV excitation. Average power = 0.0273 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	23	22	22	22	22	22.2
x 20V	1.04	1.02	1.01	1.01	1.00	1.02

Table 2: Current and voltage reading of solar cells with two glass slides without $Eu(DBM)_3L_2$ placed at the centre of the solar cells under 254 nm UV excitation. Average power = 0.0226 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	30	29	28	27	26	28
x 20V	1.26	1.23	1.20	1.17	1.15	1.20

Table 3: Current and voltage reading of solar cells with two glass slides coated with 1% w/w $Eu(DBM)_3L_2$ placed at the centre of the solar cells under 254 nm UV excitation. Average power = 0.0337 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	47	46	44	42	40	43.8
x 20V	1.73	1.69	1.64	1.60	1.56	1.64

Table 4: Current and voltage reading of solar cells with two glass slides coated with 2% w/w $Eu(DBM)_3L_2$ placed at the centre of the solar cells under 254 nm UV excitation. Average power = 0.0728 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	61	59	57	56	55	57.6
x 20V	2.06	2.02	1.99	1.96	1.94	1.99

Table 5: Current and voltage reading of solar cells with two glass slides coated with 2% w/w $Eu(DBM)_3L_2$ on both surfaces of each of the glass slides placed at the centre of the solar cells under 254 nm UV excitation. Average power = 0.115 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	222	219	216	215	214	217
x 20V	3.79	3.78	3.77	3.76	3.75	3.77

Table 6: Current and voltage reading of solar cells without any glass slide and without $Eu(DBM)_3L_2$ under 365 nm UV excitation. Average power = 0.818 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	191	187	187	186	185	187
x 20V	3.61	3.60	3.59	3.58	3.56	3.59

Table 7: Current and voltage reading of solar cells with two glass slides without $Eu(DBM)_3L_2$ placed at the centre of the solar cells under 365 nm UV excitation. Average power = 0.671 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	216	214	210	207	202	210
x 20V	3.67	3.65	3.63	3.61	3.59	3.63

Table 8: Current and voltage reading of solar cells with two glass slides coated with 1% w/w $Eu(DBM)_3L_2$ placed at the centre of the solar cells under 365 nm UV excitation. Average power = 0.762 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	249	238	233	229	225	235
x 20V	3.83	3.78	3.75	3.72	3.71	3.76

Table 9: Current and voltage reading of solar cells with two glass slides coated with 2% w/w $Eu(DBM)_3L_2$ placed at the centre of the solar cells under 365 nm UV excitation. Average power = 0.883 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	248	239	233	228	225	235
x 20V	3.82	3.77	3.73	3.71	3.69	3.75

Table 10: Current and voltage reading of solar cells with two glass slides coated with 2% w/w $Eu(DBM)_3L_2$ on both surfaces of each of the glass slides placed at the centre of the solar cells under 365 nm UV excitation. Average power = 0.881 mW.

Reading	1	2	3	4	5	Average
x 2000 μA	260	256	253	250	248	253
x 20V	3.91	3.89	3.88	3.87	3.85	3.88

Table 11: Current and voltage reading for the solar cells of Table 10 were taken again after 2 hours (i.e. solar cells with two glass slides coated with 2% w/w $Eu(DBM)_3L_2$ on both surfaces of each of the glass slides placed at the centre of the solar cells under 365 nm UV excitation). Average power = 0.982 mW.

It was found that under 365 nm excitation, an increase of power efficiency of about 46% was observed for the glass slides coated with the down-conversion nano-structured material, and an increase of 409% was observed under 254 nm excitation. In particular, a comparison of the power of Table 1 and Table 5 shows about a three fold increase. A comparison of the powers of Table 7 and Table 10 shows a maximum of 32% increase in power and a 46% increase when the power of Table 7 is compared to that of Table 11. Further, coated glass slides shown in Table 10 when compared to bare solar cells of Table 6 show about 8% increase in power generation. After the coated glass slides of were cured for 2 hours (Table 11), the power generation increased to 20% compared to the bare solar cells of Table 6.

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Claims

1. A photovoltaic apparatus comprising:

(a) at least one photovoltaic conversion material; and

(b) at least one down-conversion nano-structured material, wherein the at least one down-conversion nano-structured material is selected from the group consisting of a doped or undoped: rare-earth organic complex, organic material and inorganic material,

wherein the at least one down-conversion nano-structured material comprises at least one dimension of size ≤ 450 nm.

2. The apparatus according to claim 1, wherein the inorganic material comprises a material selected from the group consisting of: a metal, a semiconductor material and an insulator having a formula $M^1_mM^2_nX^1_p:M^3_q$ wherein:

(i) each M^1 is the same or different and is selected from the group consisting of: Sr, Zn, Y and La;

(ii) each M^2 is the same or different and is a metal ion or Si;

(iii) each X^1 is the same or different and is selected from the group consisting of: halogens, O, S, and PO_4;

(iv) each M^3 is the same or different and is selected from the group consisting of: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Cu, Mn, Ag, Cu, Zn, Al, Co and Er;

(v) m is $0 \leq m \leq 10$;

(vi) n is $1 \leq n \leq 15$;

(vii) p is $1 \leq p \leq 20$; and

(viii) q is $0 \leq q \leq 10$.

3. The apparatus according to claim 1, wherein the rare-earth organic complex comprises: (a) at least one metal ion; and (b) at least one organic chelating material.

4. The apparatus according to claim 3, wherein the at least one metal ion is a rare earth metal ion and the at least one organic chelating material is β-diketone and/or a ligand.

5. The apparatus according to claim 4, wherein the rare earth metal ion is selected from the group consisting of: La, Pr, Nd, Pm, Gd, Dy, Ho, Er, Tm, Yb, Eu, Tb, Sm and Ce.

6. The apparatus according to claim 4 or claim 5, wherein the β-diketone is selected from the group consisting of at least one of dibenzoylmethane, thenoyltrifluoacetone, acytylacetone and tetraphenylporphyrin (TPP).

7. The apparatus according to any one of claims 4 to 6, wherein the ligand is selected from the group consisting of at least one of: trioctylamine, trioctylphosphine oxide (TOPO), tricaprylylmethylammonium chloride, triisooctylamine, 1,10-phenanthroline and an aromatic compound.

8. The apparatus according to claim 7, wherein the aromatic compound is salicylic acid or benzoic acid.

9. The apparatus according to any one of claims 1 to 8, wherein the organic material is selected from the group consisting of: fluorescein or derivatives, rhodamine or derivatives, coumarin or derivatives, bodypy or derivatives, cascade blue or derivatives, and Lucifer yellow or derivatives.

10. The apparatus according to claim 2, wherein the metal is gold or silver.

11. The apparatus according to claim 2, wherein the semiconductor material is CdSe, ZnS, GaAs, TiO_2, II-IV compounds and III-V compounds, metal oxides, sulfides, silicates, pyrosilicates, sulfates, phosphates, phosphor-vanadates, (mono, di, tri, hexa, octa, deca, tetradeca, hexadeca)-aluminates, vanadates, tungstates, halogenates, borates, tatatates, niobates, molybdates and oxysulfides.

12. The apparatus according to claim 11, wherein the semiconductor material is doped with at least one dopant selected from the group consisting of: B, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Cu, Mn, Ag, Cu, Zn, Al, Co and Er.

13. The apparatus according to any one of claims 2 to 12, wherein each M^2 is selected from the group consisting of: Si, transition metal ions, inner transition metal ions, and Group I to Group IV metal ions.

14. The apparatus according to any one of claims 1 to claim 13, wherein the at least one down-conversion nano-structured material is selected from the group consisting of: $YM^2O_4:M^3$, $Sr(M^2)_2O_4:M^3$, and $Zn_2M^2O_4:M^3$, wherein each M^2 is the same or different and is selected from the group consisting of: Al, Si and V and each M^3 is the same or different and is selected from the group consisting of: Eu, Mn and Dy.

15. The apparatus according to claim 14, wherein the at least one down-conversion nano-structured material is selected from the group consisting of: Zn_2SiO_4:Mn, YVO_4:Eu and $SrAl_2O_4$:Eu,Dy.

16. The apparatus according to any one of claims 1 to 13, wherein the at least one down-conversion nano-structured material is selected from the group consisting of: $Zn_3(PO_4)_2$:Mn, $Cd_3(PO_4)$:Mn, Y_2O_3:Eu, ZnS:Ag, ZnS:Cu,Ag, ZnS:Cu,Al, ZnS:Zn, ZnS:Mn, ZnS:Cu, ZnS:Cu,Co,

$LaPO_4$:Ce,Tb, europium phthalate and $Eu(DBM)_3L_2$, wherein DBM is dibenzoylmethane and L is tricaprylylmethylammonium chloride.

17. The apparatus according to any one of claims 1 to 16, wherein the at least one down-conversion nano-structured material comprises at least one dimension of size ≤ 400 nm.

18. The apparatus according to any one claims 1 to 17, wherein the at least one down-conversion nano-structured material comprises at least one dimension of size ≤ 300 nm.

19. The apparatus according to any one of claims 1 to 18, wherein the at least one down-conversion nano-structured material comprises at least one dimension of size ≤ 100 nm.

20. The apparatus according to any one of claims 1 to 19, wherein the at least one down-conversion nano-structured material comprises at least one dimension of size ≤ 50 nm.

21. A photovoltaic apparatus comprising:

(a) at least one photovoltaic conversion material; and

(b) at least one up-conversion nano-structured material of formula $M^4_rM^5_sX^2_t:M^6_u$, wherein:

(i) each M^4 is the same or different and is selected from the group consisting of: Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra and NH_4;

(ii) each M^5 is the same or different and is a metal ion;

(iii) each X^2 is the same or different and is selected from the group consisting of: halogens, O, S, Se, Te, N, P and As;

(iv) each M^6 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb and Cu;

(v) r is $0 \leq r \leq 10$;

(vi) s is $1 \leq s \leq 10$;

(vii) t is $1 \leq t \leq 10$; and

(viii) u is $1 \leq u \leq 10$,

wherein the at least one up-conversion nano-structured material comprises at least one dimension of size ≤ 1100 nm.

22. The apparatus according to claim 21, wherein each M^5 is selected from the group consisting of: transition metal ions, inner transition metal ions, and Group I to Group IV metal ions.

23. The apparatus according to claim 21 or claim 22, wherein the at least one up-conversion nano-structured material is selected from the group consisting of: $NaM^5F_4:M^6$, $LiM^5F_4:M^6$, $KM^5F_4:M^6$, $RbM^5F_4:M^6$, $CsM^5F_4:M^6$, $BeM^5F_5:M^6$, $Be(M^5)_2F_8:M^6$, $MgM^5F_5:M^6$, $Mg(M^5)_2F_8:M^6$, $CaM^5F_5:M^6$, $Ca(M^5)_2F_8:M^6$, $SrM^5F_5:M^6$, $Sr(M^5)_2F_8:M^6$, $BaM^5F_5:M^6$, $Ba(M^5)_2F_8:M^6$, wherein each M^5 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, and each M^6 is the same or different and is selected from the group consisting of: Yb, Er, Tm and Ho.

24. The apparatus according to claim 23, wherein the at least one up-conversion nano-structured material is $NaYF_4$:Er, $NaYF_4$:Yb,Er, $NaYF_4$:Yb,Tm, $NaYF_4$:Yb,Ho, or a combination thereof.

25. The apparatus according to claim 21 or claim 22, wherein the at least one up-conversion nano-structured material is selected from the group consisting of: SrS:Eu,Sm, CaS:Eu,Sm, SrS:Ce,Sm and ZnS:Pb,Cu.

26. The apparatus according to any one of claims 21 to 25, wherein the at least one up-conversion nano-structured material comprises at least one dimension of size ≤ 850 nm.

27. The apparatus according to any one of claims 21 to 26, wherein the at least one up-conversion nano-structured material comprises at least one dimension of size ≤ 650 nm.

28. The apparatus according to any one of claims 21 to 27, wherein the at least one up-conversion nano-structured material comprises at least one dimension of size ≤ 450 nm.

29. The apparatus according to any one of claims 21 to 28, wherein the at least one up-conversion nano-structured material comprises at least one dimension of size ≤ 400 nm.

30. The apparatus according to any one of claims 21 to 29, wherein the at least one up-conversion nano-structured material has a structure selected from the group consisting of: hexagonal, cubic, tetragonal, rhombohedral, orthorhombic, monoclinic, triclinic and a combination thereof.

31. The apparatus according to claim 30, wherein the at least one up-conversion nano-structured material has a hexagonal structure.

32. The apparatus according to any one of claims 21 to 31, wherein the at least one up-conversion nano-structured material is in the form of: nanoparticle(s), nanofilm or monolith.

33. The apparatus according to claim 32, wherein the nanoparticle(s) comprise core nanoparticle(s) and/or core-shell nanoparticle(s).

34. The apparatus according to claim 32 or claim 33, wherein the nanoparticle is in the form of a core nanoparticle, and the nanoparticle further comprises at least one organic and/or inorganic material (shell) applied on the core, to obtain a core-shell nanoparticle(s).

35. The apparatus according to claim 34, wherein the shell material has the formula $M^4_rM^5_sX^2_t$ or $M^4_rM^5_sX^2_t{:}M^6_u$, wherein each of M^4, M^5, X^2, M^6, r, s, t and u are as defined claim 21.

36. The apparatus according to claim 34 or claim 35, wherein the inorganic shell material comprises: NaM^5F_4, LiM^5F_4, KM^5F_4, RbM^5F_4, CsM^5F_4, BeM^5F_5, $Be(M^5)_2F_8$, MgM^5F_5, $Mg(M^5)_2F_8$, CaM^5F_5, $Ca(M^5)_2F_8$, SrM^5F_5, $Sr(M^5)_2F_8$, $BaLnF_5$, $Ba(M^5)_2F_8M^5F_3$, M^5F_3, M^5Cl_3, M^5Br_3, M^5I_3, M^5FClBr, M^5OF, M^5OCl, M^5OBr, M^5OS, $(M^5)_2S_3$, wherein each M^5 is the same or different and is selected from the group consisting of: Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; SiO_2; TiO_2; ZnS; or a combination thereof.

37. The apparatus according to claim 34, wherein the organic shell material comprises at least one polymer, a surfactant or a lipid, or a combination thereof.

38. The apparatus according to claim 37, wherein the at least one polymer is selected from the group consisting of: polystyrene (PS), polyethylene (PE), polymethyl methacrylate (PMMA) and polylactic acid (PLA).

39. The apparatus according to any one of claims 33 to 38, wherein the shell is applied continuously or discontinuously on the core.

40. A photovoltaic apparatus comprising:

(a) at least one photovoltaic conversion material;

(b) at least one down-conversion nano-structured material as defined in any one of claims 1 to 20; and

(c) at least one up-conversion nano-structured material as defined in any one of claims 21 to 39.

41. The apparatus according to any one of the preceding claims, wherein the photovoltaic apparatus is a solar cell.

42. The apparatus according to any one of the preceding claims, wherein the photovoltaic conversion material has a refractive index of about 1 to about 5 and a dielectric constant of about 1 to about 15.

43. The apparatus according to any one of the preceding claims, wherein the photovoltaic conversion material comprises at least: a conducting or semiconducting polymer material, a silicon-based material, cadmium telluride (CdTe), copper indium diselenide (CIS), gallium arsenide (GaAs) or dye-sensitized solar cell.

44. The apparatus according to claim 43, wherein the conducting or semiconducting polymer material is selected from the group consisting of: poly(phenylene) and derivatives thereof, poly(phenylene vinylene) and derivatives thereof, poly(thiophene) and derivatives thereof, poly(thienylenevinylene) and derivatives thereof, and poly(isothianaphthene) and derivatives thereof, organometallic polymers, polymers containing perylene units, poly(squaraines) and their derivatives.

45. The apparatus according to claim 44, wherein the poly(phenylene vinylene) and derivative thereof is poly(2-methoxy-5-(2-ethyl-hexyloxy)-

1,4-phenylene vinylene (MEH-PPV) or poly(para-phenylene vinylene) (PPV).

46. The apparatus according to claim 44, wherein the poly(thiophene) and derivatives thereof is selected from the group consisting of: poly(3-octylthiophene-2,5,-diyl), regioregular, poly(3-octylthiophene-2,5,-diyl), regiorandom, poly(3-hexylthiophene-2,5-diyl), regioregular, and poly(3-hexylthiophene-2,5-diyl), regiorandom.

47. The apparatus according to claim 43, wherein the silicon-based material is crystalline silicon, amorphous silicon or a combination thereof.

48. The apparatus according to any one of the preceding claims, further comprising a reflector having at least one reflecting surface.

49. The apparatus according to any one of the preceding claims, further comprising an anti-reflective material.

50. The apparatus according to any one of the preceding claims, wherein the at least one photovoltaic conversion material is in contact with the at least one nano-structured material.

51. The apparatus according to claim 50, wherein the apparatus comprises:

(i) at least one layer (A) comprising the at least one photovoltaic conversion material and at least one layer (B) comprising at least one down-conversion nano-structured material as defined in any one of claims 1 to 20, wherein layer B is in contact with layer A;

(ii) at least one layer (A), at least one layer (C) comprising at least one up-conversion nano-structured material as defined in any one of claims 21 to 39, and optionally at least one layer (D) comprising a reflector having at least one reflecting surface, wherein layer A is

in contact with layer C and the reflecting surface of layer D is in contact with layer C; or

(iii) at least one layer (A), at least one layer (B), at least one layer (C) and optionally at least one layer (D) having at least one reflecting surface, wherein layer B is in contact with layer A, layer A is in contact with layer C and layer C is in contact with the at least one reflecting surface of layer D.

52. A method of improving the efficiency of a photovoltaic apparatus comprising the steps of:

(a) providing at least one down-conversion nano-structured material as defined in any one of claims 1 to 20 on at least one surface of or in proximity of a photovoltaic material comprised in a photovoltaic apparatus; and/or

(b) providing at least one up-conversion nano-structured material as defined in any one of claims 21 to 39 on at least one surface of or in proximity of a photovoltaic material comprised in a photovoltaic apparatus.

53. The method according to claim 52, further comprising the step of: providing a reflector having at least one reflecting surface, wherein the reflecting surface is provided to be in contact with the at least one up-conversion nano-structured material.

54. The method according to claim 52 or claim 53, further comprising the step of: providing an anti-reflective material, wherein the anti-reflective material is provided to be in contact with the at least one down-conversion and/or up-conversion nano-structured material.

55. A photovoltaic apparatus obtainable by the method according to any one of claims 52 to 54.

56. A kit comprising a photovoltaic apparatus according to any one of claims 1 to 51.