(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
18 August 2016 (18.08.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/130761 A1

(51) International Patent Classification:
H01L 31/00 (2006.01)

(21) International Application Number:
PCT/US2016/017482

(22) International Filing Date:
11 February 2016 (11.02.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/115,667 13 February 2015 (13.02.2015) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: SOLAR CELL EMPLOYING PHOSPHORESCENT MATERIALS

(57) Abstract: A solar cell device having a solid state light absorber region that incorporates a donor- acceptor particle structure. The particle structure includes acceptor particles that generate a flow of electrons in the solid state light absorber region in response to absorbed photons; and donor particles comprising a phosphorescent material, wherein each donor particle is coupled to a group of acceptor particles, and wherein the phosphorescent material absorbs high energy photons and emits lower energy photons that are absorbed by the acceptor particles.

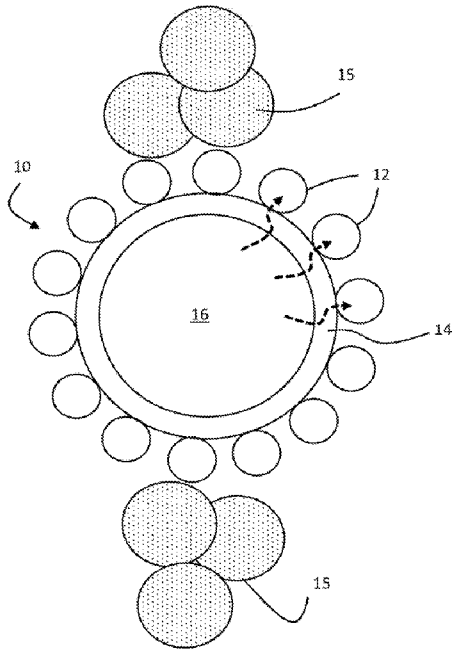

Figure 1

WO 2016/130761 A1

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

SOLAR CELL EMPLOYING PHOSPHORESCENT MATERIALS

PRIORITY CLAIM

This application claims priority to co-pending US provisional patent application "Solar Cell Employing Phosphorescent Materials," serial number 62/115,667 filed on February 13, 2015, the content of which is hereby incorporated by reference.

TECHNICAL FIELD

[0001] The subject matter of this invention relates to solar cells employing phosphorescent materials, and more particularly to solar cells having a solid state absorber region that integrates phosphor particles with light acceptor particles.

BACKGROUND

[0002] Converting solar energy to electricity is the one of the cleanest methods of producing useable energy. Among the various renewable energy technologies available, solar cells hold significant promise. One major drawback of this technology is the lack of flexibility, e.g., solar cells only have the ability to generate power during daylight hours and thus cannot provide an uninterrupted power supply without incorporating additional components. Another drawback is the relatively low efficiency of known devices. Hence, a solar cell with improved efficiency that can generate power during non-daylight hours and/or that enables efficient storage of energy generated during daylight hours is desirable.

SUMMARY

[0003] The disclosed solution describes a solar cell device that has improved efficiency in converting light to electrical energy and the ability to output power in the dark after a period of excitation in light. The device incorporates a phosphorescent material within controlled proximity of the light absorber used in solar cells. The phosphorescent material is designed and synthesized so as to match its emission wavelength with the absorption spectrum of the light absorber.

[0004] The aforementioned phosphorescent material comprises a donor chromophore (donor particles) that absorbs high energy photons of solar light and emits light of low energy photons over extended time periods. The transfer of energy from the phosphorescent material to the absorber (acceptor particles) results in the generation of additional electron-hole pairs in the solar cell as compared to those produced in the absence of the phosphorescent material, and leads to an improvement in the efficiency of the solar cell. A device comprising the energy transfer system described herein can be adapted for various solar cell technologies.

[0005] A solid state light absorber region is provided that includes a donor-acceptor particle structure having acceptor particles adsorbed on a large surface area of inert nanoparticles that serve as current collectors. Upon excitation, a generation, injection, and flow of electrons in the solid state light absorber region results in response to absorbed photons. Donor particles are provided comprising a phosphorescent material that are coupled to groups of acceptor particles such that the phosphorescent material absorbs high energy photons and emits lower energy photons that are absorbed by the acceptor particles.

[0006] In a first aspect, the invention provides a solar cell device, comprising: a solid state light absorber region that includes a donor-acceptor particle structure having: acceptor particles adsorbed on an inert nanoparticles current collector, which causes a flow of electrons in the solid state light absorber region in response to absorbed photons; and donor

particles comprising a phosphorescent material, wherein each donor particle is coupled to a group of acceptor particles, and wherein the phosphorescent material absorbs high energy photons and emits lower energy photons that are absorbed by the acceptor particles.

[0007] In a second aspect, the invention provides a dye sensitive solar cell (DSSC) device, comprising: a counter electrode; an electrolyte region; a transparent back contact; and a transparent electrode disposed between the electrolyte region and transparent back content, wherein the transparent electrode includes a donor-acceptor particle structure having: acceptor particles adsorbed on an inert nanoparticles current collector, which upon absorption of photons, results in a flow of free electrons in the acceptor particles, injection of electrons into the inert nanoparticles current collector, and transport of injected electrons by the inert nanoparticles current collector to the transparent back contact; and donor particles comprising a phosphorescent material, wherein each donor particle is coupled to a group of acceptor particles, and wherein the phosphorescent material absorbs high energy photons and emits lower energy photons that are absorbed by the acceptor particles.

[0008] In a third aspect, the invention provides a method of forming a dye sensitive solar cell (DSSC) device, comprising: providing a first and a second transparent back contact; forming a transparent electrode on the first transparent back contact wherein the transparent electrode includes a donor-acceptor particle structure having: acceptor particles adsorbed on an inert nanoparticles current collector; and donor particles comprising a phosphorescent material, wherein each donor particle is coupled to a group of acceptor particles, and wherein the phosphorescent material absorbs high energy photons and emits lower energy photons that are absorbed by the acceptor particles; forming a counter electrode on the second transparent back contact; and forming an electrolyte region between the counter electrode and transparent electrode; wherein the transparent electrode forms a light absorption region, which upon absorption of photons results in a flow of free electrons in the acceptor particles, injection of

electrons into the inert nanoparticles current collector and transport of injected electrons by the inert nanoparticles current collector to the first transparent back contact.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] These and other features of this invention will be more readily understood from the following detailed description of the various aspects of the invention taken in conjunction with the accompanying drawings in which:

[0010] Figure 1 depicts a donor-acceptor particle structure according to embodiments.

[0011] Figure 2 depicts a dye sensitive solar cell according to embodiments.

[0012] Figure 3 depicts a graph showing spectral matching of donor and acceptor particles according to embodiments.

[0013] The drawings are not necessarily to scale. The drawings are merely schematic representations, not intended to portray specific parameters of the invention. The drawings are intended to depict only typical embodiments of the invention, and therefore should not be considered as limiting the scope of the invention. In the drawings, like numbering represents like elements.

DETAILED DESCRIPTION

[0014] A solar cell device and associated method for forming the device are disclosed having a solid state light absorber region or chromophore that includes coated phosphor "donor" particles placed in close proximity to associated "acceptor" particles. While both types of particles act as chromophores (light absorbers), the donor particles include a phosphorescent material that absorbs high energy photons of solar light and emits light of low energy photons over extended time periods. The phosphorescent material is selected so as to enable spectral

overlap of its emission wavelength with the absorption spectrum of the acceptor particles. The transfer of energy from the phosphorescent material to the acceptor particles results in the generation of additional electron-hole pairs in the absorber chromophore as compared to those produced in the absence of the phosphorescent material, and leads to the improvement in the efficiency of the solar cell. In addition, because the phosphorescent material continues to emit low energy photons even after the removal of an excitation light source (e.g., the sun in the present case), the resulting solar cell device has the ability to output power in the dark after a period of excitation in light.

[0015] In an illustrative embodiment, the donor-acceptor particle structure is implemented in a solid state form with inorganic phosphor particles having a very high phosphorescence efficiency in which the distance between each donor particle and associated acceptor particles is carefully controlled to optimize energy transfer between the two. The use of inorganic phosphorescent materials allows emission of radiation for many hours in darkened conditions, which can be used to power a solar cell device in the absence of light. Experimental results in a dye sensitive solar cell application show approximately a 60% improvement in the solar cell device's efficiency under illumination using simulated sunlight and 300 times improvement in the dark. Because the energy transfer is achieved in a solid state, the present approach is not restricted to organic phosphors embedded in liquid electrolytes, such as photoelectrochemical (PEC) solar cells, but can instead be adapted for a wide variety of known solar cells.

[0016] Referring now to the drawings, Figure 1 depicts a donor-acceptor particle structure 10 that includes a phosphor (donor) particle 16 having a coating or spacer 14 coupled to a group of acceptor particles 12. The acceptor particles 12 are adsorbed on inert nanoparticles that serve as current collectors, the structure generally being referred to as an "inert nanoparticles current collector" 15. When incorporated into a solar cell device, the phosphorescent

material that makes up the phosphor particle 16 is excited by high energy photons of sunlight, which is transferred to the acceptor particles 12 to both enhance efficiency during lighted conditions and allow for extended periods of use (e.g., several hours) in darkened conditions.

[0017] Figure 2 depicts an illustrative embodiment of a dye sensitized solar cell (DSSC) device 20 that employs the abovementioned donor-acceptor particle structure 10. Device 20 generally includes a first transparent back contact 22, a top electrode 24 (i.e., anode) that incorporates the donor-acceptor particle structure 10 and inert nanoparticles current collector 15 to form a solid state light absorbing region, an electrolyte 26, a counter electrode 28 (cathode) and a second transparent back contact 30. The illustrative solar cell device 20 is generally implemented using a standard dye sensitized solar cell (DSSC) architecture, with the additional phosphor material incorporated with the acceptor particles in the top electrode 24.

[0018] In the illustrative DSSC embodiment 20, phosphor particles 16 may for example comprise $SrAl_2O_4$ coated with a thin layer of polycrystalline TiO_2 film that forms the spacer 14. Acceptor particles 12 may for example be comprised of an absorber such as dye or quantum dot material adsorbed on a TiO_2 nanoparticle current collector. The TiO_2 film (i.e., spacer 14) prevents the direct contact of the phosphor material 16 with the electrolyte 26, thus preventing the quenching of phosphorescent signals by the iodide/triiodide or other redox couples. The spacer 14 also serves as a barrier against direct charge transfer between the phosphor particle 16 and the acceptor particles 12, and serves as an electrical conduit for injected electrons from the excited dye to the back contact 30 of the solar cell. TiO_2 is transparent to the visible light (e.g., λ=520 nm) emitted by the phosphor particles 16. In one illustrative embodiment, the thickness of the TiO_2 spacer may be in the range of 8-10 nm.

[0019] DSSC device 20 generally includes a solid dye structure formed within the top electrode 24 for catching photons of incoming light, which convert the energy into excited

electrons. The excited electrons are then injected into a conduction band of the TiO_2 nanoparticles in the electrode 24, and conducted away (upward in Figure 2) to the first transparent back contact 22 by the layer's TiO_2 nanoparticles current collector 15 (Figure 1). Electrolyte 26 closes the circuit 32 allowing the electrons to return to the dye within electrode layer 24. The movement of the electrons through the electrical circuit 32 can be used to run electrical devices and thus produce usable work. By incorporating the donor-acceptor particle structure 10 into the top electrode 24, the number of electron hole pairs is increased, thus improving efficiency. Furthermore, because the phosphorescent material continues to emit energy for many hours after excitation, the device will continue to output electricity in darkened conditions.

[0020] Although described in a DSSC embodiment, the described donor-acceptor particle structure 10 may likewise be incorporated into other types of devices, such as quantum dot solar cells, polymer solar cells and thin film solar cells.

[0021] In the case of a DSSC device, the following illustrative fabrication process may be utilized, with reference to Figures 1 and 2. First, a light emitting phosphor 16 is selected, such as a green ($Sr_{0.95}Eu_{0.02}Dy_{0.03}Al_2O_4$) or blue ($Sr_{2.90}Eu_{0.03}Dy_{0.07}Al_4SiO_{11}$) emitting phosphor having particle diameters of approximately 230 mesh and 300 mesh respectively. Next the phosphor particles 16 are coated with a film (i.e., spacer) 14. This may for example be done by repeatedly spraying a mixture of 0.1 M titanium (IV) isopropoxide and 1.2 M acetylacetonate in ethanol on the phosphor particles 16 dispersed on a silicon wafer maintained at 400 °C. After the deposition, the particles may be annealed at 500 °C for 30 minutes to remove trace organics. The thickness of the coating may be in range of 8-10 nm, which may be accomplished with 40 deposition cycles.

[0022] TiO_2 nanoparticles may be prepared as a transparent TiO_2 paste with hydrothermal synthesis using titanium (IV) isopropoxide as the precursor. For example, the procedure may

utilize the drop wise addition of 3.7 mL of the precursor to a beaker containing a mixture of 1 mL of 2-propanol, 8 ml of acetic acid, and 25 mL distilled water kept over an ice bath.

[0023] The mixture can then be heated at 80 °C for 25 minutes. The entire contents can then be transferred to an autoclave and heated to a temperature of 250 °C for approximately 13 hours. The resulting particles are repeatedly washed with distilled water, centrifuged, and finally suspended in ethanol until further use. Particles obtained by this procedure comprise pure anatase phase of TiO_2 with an average particles size of ~20 nm. Scattering TiO_2 nanoparticles may be prepared by dispersing 10 grams of P25 (Degussa) powder in 30 mL of ethanol. The mixture may then be sonicated for 30 minutes.

[0024] The top electrode 24 may be fabricated as follows. First, a fluorine-doped tin oxide coated glass (FTO substrate – i.e., first transparent back contact 22) is coated with a transparent blocking layer of TiO_2, such as the provided by SOLARONIX®, and annealed in a furnace at 500°C for 30 minutes, which is then followed with a deposition of thick transparent TiO_2 nanoparticles. The film is then dried and coated with 150 μm of paste containing scattering TiO_2 nanoparticles and TiO_2 coated $SrAl_2O_4$. The volumetric ratio of TiO_2 to phosphor particles may for example be in the range of approximately 10:1. The film is then annealed at 500°C for 60 minutes to achieve a total film thickness of approximately 100 microns. Before sensitization with ruthenium dye (e.g., N719, SIGMA ALDRICH®), the substrate is immersed in 0.02M $TiCl_4$ solution for 10 minutes, and annealed again at 450°C for 60 minutes. The resulting substrate is then immersed in a 0.5 mM N719 dye dissolved in 1:1 (v/v) ratio of acetonitrile and tert-butyl alcohol at 4°C to form top electrode 24.

[0025] A platinum counter electrode 28 may be prepared by applying a thin coating of chloroplatinic acid on a second FTO substrate (i.e., second transparent back contact 30), followed by annealing at 500°C for 1 hour.

[0026] The electrodes 24, 28 may be assembled using a 200 μm-thick hot-melt film (Surlyn 1702, SOLARNIX®) as spacer between the transparent electrode 24 and counter electrode 28. An electrolyte 26, e.g., consisting of 0.6 M PMII, 0.05 M I_2, 0.05M tertbutyl pyridine (0.04 M) and 0.025M guanidinium thiocyanate in 4:1 (v/v) ratio of acetonitrile and valeronitrile, may be injected through a small, predrilled hole in the counter electrode 28.

[0027] As noted herein, the emission spectra of the donor particles should be selected to overlap the absorption spectra of the acceptor particle to maximize efficiency of the device. Figure 3, for example, shows the absorption and emission spectra of N719 dye dissolved in tert-butyl alcohol along with the emission spectra of $SrAl_2O_4$ (dispersed on a copper foil) recorded at room temperature at an excitation wavelength of 373 nm. The absorption spectrum of N719 dye shows an absorption peak at 520 nm and has a good spectral overlap with the emission range of $SrAl_2O_4$, which is necessary for efficient excitation energy transfer. $SrAl_2O_4$ has a broad excitation spectrum from 460-250 nm, and thus can be excited by solar radiation. The phosphor exhibits a broad band photoluminescence (PL) with maximum intensity occurring at 520 nm.

[0028] The foregoing description of various aspects of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously, many modifications and variations are possible. Such modifications and variations that may be apparent to an individual in the art are included within the scope of the invention as defined by the accompanying claims.

CLAIMS

1. A solar cell device, comprising:

a solid state light absorber region that includes a donor-acceptor particle structure having:

acceptor particles adsorbed on an inert nanoparticles current collector, which results in a flow of electrons in the solid state light absorber region in response to absorbed photons; and

donor particles comprising a phosphorescent material, wherein each donor particle is coupled to a group of acceptor particles, and wherein the phosphorescent material absorbs high energy photons and emits lower energy photons that are absorbed by the acceptor particles.

2. The solar cell device of claim 1, wherein the acceptor particles comprise an absorber adsorbed on an inert TiO_2 nanoparticles current collector.

3. The solar cell device of claim 1, wherein the donor particles includes a coating that provides a spacer between each donor particle and group of acceptor particles.

4. The solar cell device of claim 3, wherein the spacer comprises TiO_2.

5. The solar cell device of claim 1, wherein an emission spectrum of the donor particles overlaps with an absorption spectrum of the acceptor particles.

6. The solar cell device of claim 1, wherein the solid state light absorber region forms an electrode.

7. The solar cell device of claim 1 that comprises a device selected from a group consisting of: a dye sensitive solar cell, a quantum dot solar cell, a polymer solar cell, and a thin film solar cell.

8. A dye sensitive solar cell (DSSC) device, comprising:

a counter electrode;

an electrolyte region;

a transparent back contact; and

a transparent electrode disposed between the electrolyte region and transparent back content, wherein the transparent electrode includes a donor-acceptor particle structure having:

acceptor particles adsorbed on an inert nanoparticles current collector, which upon absorption of photons, results in a flow of free electrons in the acceptor particles, injection of electrons into the inert nanoparticles current collector, and transport of injected electrons by the inert nanoparticles current collector to the transparent back contact; and

donor particles comprising a phosphorescent material, wherein each donor particle is coupled to a group of acceptor particles, and wherein the phosphorescent material absorbs high energy photons and emits lower energy photons that are absorbed by the acceptor particles.

9. The DSSC device of claim 8, wherein the acceptor particles comprise a dye, quantum dot or other absorber material anchored onTiO_2 nanoparticles.

10. The DSSC device of claim 8, wherein the donor particles include a coating that provides a spacer between each donor particle and group of acceptor particles.

11. The DSSC of claim 10, wherein the spacer comprises TiO_2.

12. The DSSC of claim 8, wherein an emission spectrum of the donor particles overlaps with an absorption spectrum of the acceptor particles.

13. The DSSC of claim 8, wherein a volumetric ratio of acceptor particles to donor particles is approximately 10:1.

14. The DSSC of claim 9, wherein the donor-acceptor particle structure and TiO_2 nanoparticles are coated onto a substrate.

15. A method of forming a dye sensitive solar cell (DSSC) device, comprising:

providing a first and a second transparent back contact;

forming a transparent electrode on the first transparent back contact, wherein the transparent electrode includes a donor-acceptor particle structure having:

acceptor particles adsorbed on an inert nanoparticles current collector; and

donor particles comprising a phosphorescent material, wherein each donor particle is coupled to a group of acceptor particles, and wherein the phosphorescent material absorbs high energy photons and emits lower energy photons that are absorbed by the acceptor particles;

forming a counter electrode on the second transparent back contact; and

forming an electrolyte region between the counter electrode and transparent electrode;

wherein the transparent electrode forms a light absorption region, which upon absorption of photons results in a flow of free electrons in the acceptor particles, injection of electrons into the inert nanoparticles current collector and transport of injected electrons by the inert nanoparticles current collector to the first transparent back contact.

16. The method of claim 15, wherein the acceptor particles comprise a dye adsorbed on a TiO_2 nanoparticles current collector.

17. The method of claim 15, wherein the donor particles include a coating that provides a spacer between each donor particle and group of acceptor particles.

18. The method of claim 17, wherein the spacer comprises TiO_2.

19. The method of claim 15, wherein an emission spectrum of the donor particles overlaps with an absorption spectrum of the acceptor particles.

20. The method of claim 15, wherein a volumetric ratio of acceptor particles to donor particles is approximately 10:1.

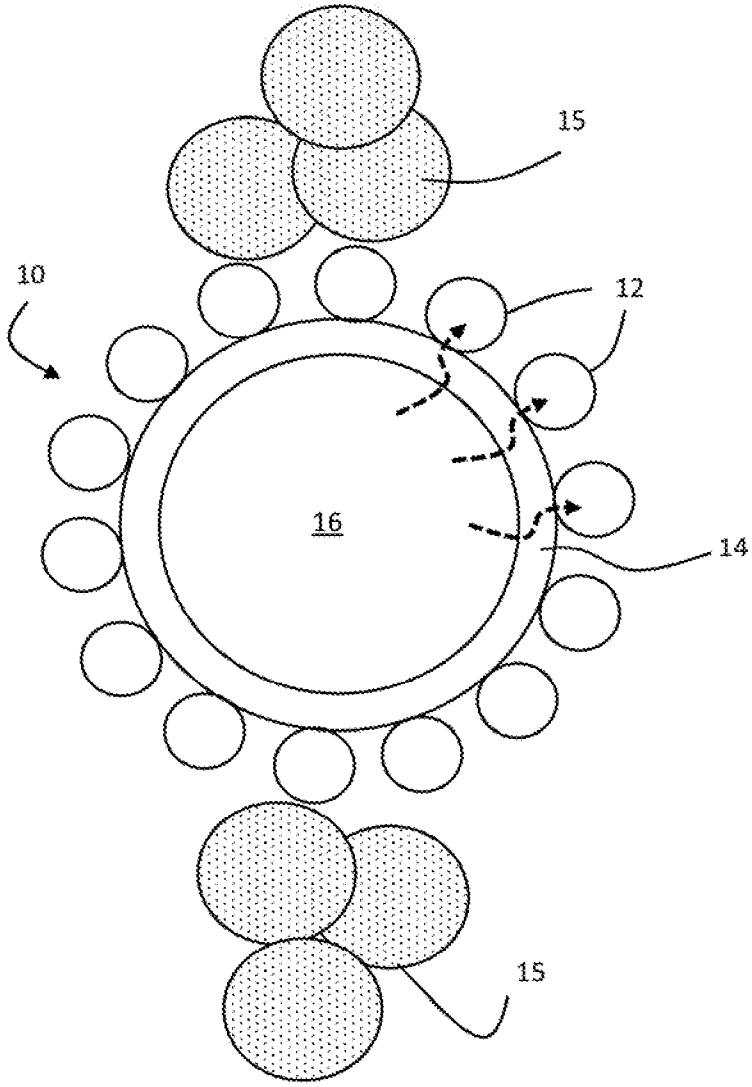

Figure 1

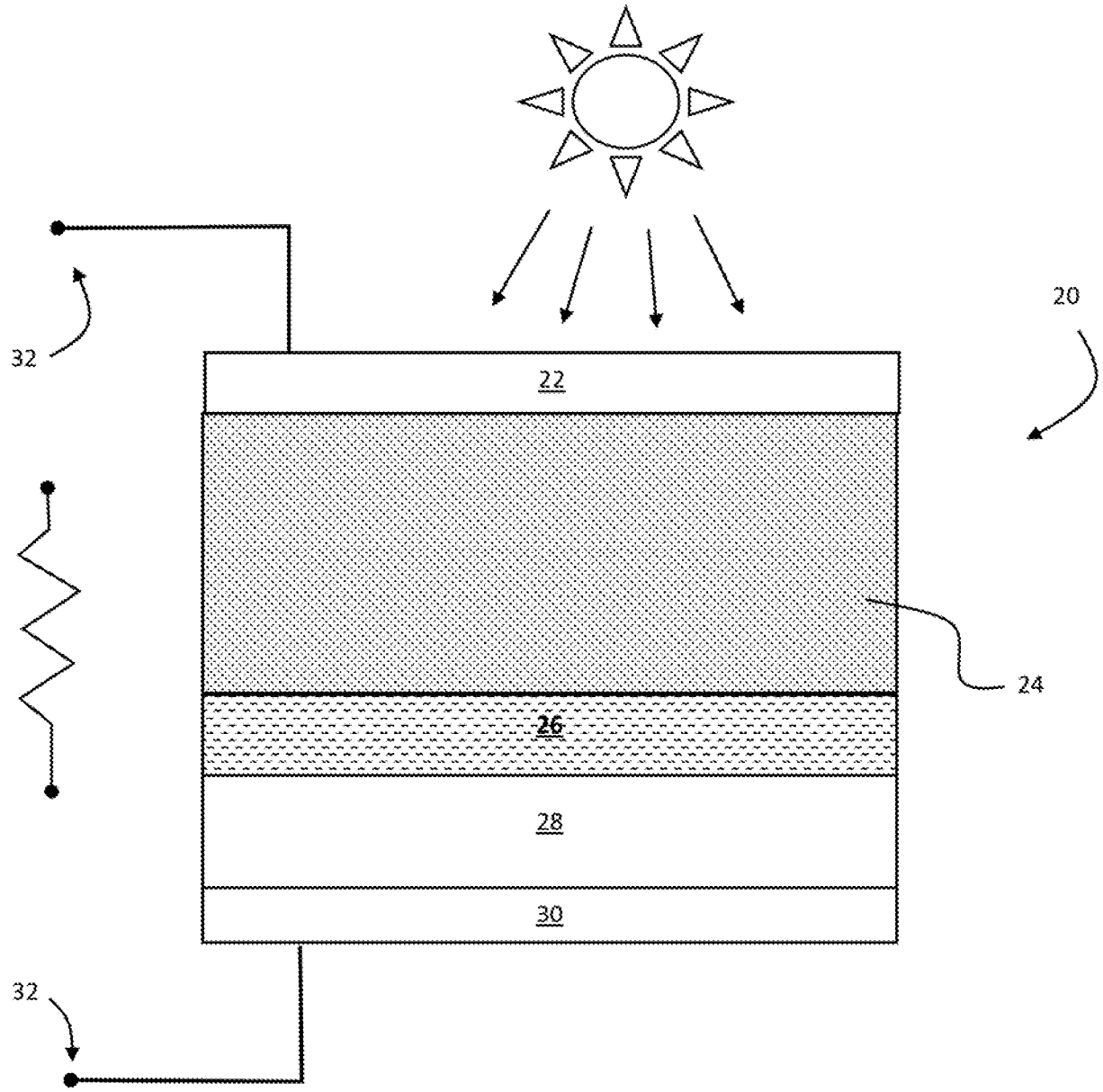

Figure 2

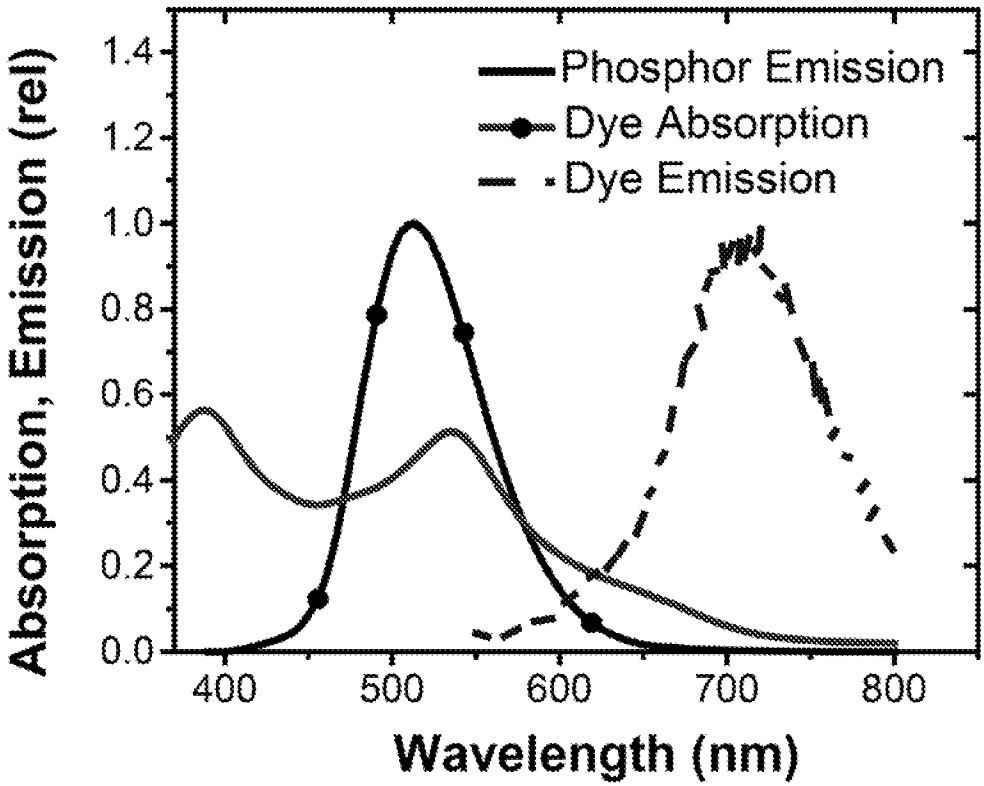
Absorption, Emission (rel)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800
Wavelength (nm)
Phosphor Emission
Dye Absorption
Dye Emission

Figure 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/017482

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01L 31/00 (2016.01)
CPC - H01L 31/055 (2016.01)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - H01L 21/00, 31/00, 31/042 (2016.01)
CPC - H01L 21/02631, 31/055, 31/022425 (2016.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC- 136/252, 256, 257, 263; 438/85; 977/948, 949 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patents, ProQuest
Search terms used: phosphor, nanoparticles, donor, acceptor, current collector, solar cell, dye sensitized, down converting

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2007/0151601 A1 (JUNG et al) 05 July 2007 (05.07.2007) entire document	1-20
Y	US 2011/0315219 A1 (HASAN et al) 29 December 2011 (29.12.2011) entire document	1-20
Y	US 2014/0076404 A1 (TAN et al) 20 March 2014 (20.03.2014) entire document	4, 11, 18
A	US 2013/0161555 A1 (HANAYA et al) 27 June 2013 (27.06.2013) entire document	1-20
A	US 2009/0173381 A1 (KANG et al) 09 July 2009 (09.07.2009) entire document	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 April 2016	21 APR 2016
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774