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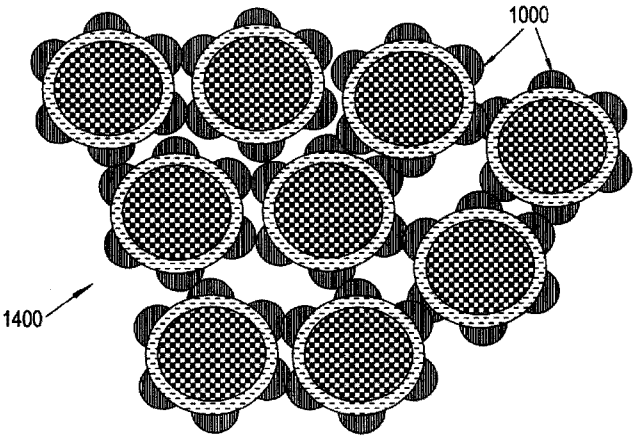
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(54) Title: COMPONENTS OF PHOTOVOLTAIC CELLS, CELLS CONSTRUCTED THEREFROM AND RELATED MANUFACTURING PROCESSES

Fig.7



(57) Abstract: A nano-sized photon collector (NSPC) comprising: (a) a nano-sized crystalline semiconducting particle, at least a portion of which is not insulated; (b) a quantum dot photon collector particle(PC); and(c) an insulating coating comprising silica on at least a portion of said PC.

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TITLE: COMPONENTS OF PHOTOVOLTAIC CELLS, CELLS CONSTRUCTED THEREFROM AND RELATED MANUFACTURING PROCESSES

FIELD OF THE INVENTION

This invention relates to photovoltaic cells and their production.

BACKGROUND OF THE INVENTION

The increasing world population contributes to an increased demand for electricity. Traditionally, combustion of fossil fuels has been a major source of electricity.

Electricity from fossil fuels is supplemented by various alternative electricity generation strategies such as hydroelectric power, geothermal energy, solar energy collected as heat and wind energy. According to each of these strategies, input energy is collected and transformed to mechanical energy which turns turbines that generate electricity.

Direct production of electricity from incident solar radiation using photovoltaic cells is also known, although this method has not been developed commercially to a great degree.

Photovoltaic cells have undergone significant theoretical development since their original conception. A recent review of this development is presented by Basham *et al.* (*Perspective: FÖrster Resonance Energy Transfer in Dye-Sensitized Solar Cells* (2010) ACSNANO 4(3):1253-1258). A specific application of FÖrster Resonance Energy Transfer in the context of photovoltaic cells was presented by Buhbut *et al.* (*Built-in Quantum Dot Antennas in Dye-Sensitized Solar Cells* (2010) ACSNANO 4(3):1293-1298). Each of these publications is fully incorporated herein by reference. It is believed that one of ordinary skill in the art would be well acquainted with the contents of each of these publications.

SUMMARY OF THE INVENTION

A broad aspect of the invention relates to generation of electricity using Fret enhanced dye sensitized solar cells (FE-DSSC).

As used in this specification and the accompanying claims the term "dye sensitized solar cell" or "DSSC" refers to a photovoltaic cell with semiconductor formed between the anode and an electrolyte. Principles of operation of DSSC were described, for example by O'Regan and Gratzel (*A Low-Cost, High-Efficiency Solar-Cell Based on Dye-Sensitized Colloidal TiO_2 Films* (1991) Nature 353: 737– 740). This publication is fully incorporated herein by reference. It is believed that one of ordinary skill in the art would be well acquainted with the contents of this publication.

As used in this specification and the accompanying claims the term "FRET" refers to the physical phenomenon "Förster resonance energy transfer". Although this phenomenon is

sometimes referred to as "fluorescence resonance energy transfer", FRET is not limited to fluorescent compounds in the context of various exemplary embodiments of the invention.

As used in this specification and the accompanying claims the term a "Fret enhanced dye sensitized solar cell (FE-DSSC)" indicates a DSSC wherein a portion of the harvested energy results from FRET as described, for example, by Basham *et al.* (2010; *op. cit.*).

One aspect of some embodiments of the invention relates to a nano-sized photon collector (NSPC) from which anodes can be constructed. According to various exemplary embodiments of the invention the NSPC has an average largest dimension of 1, 2, 5, 10, 20, 40, 50 or 100 nanometers or lesser or intermediate sizes. According to various exemplary embodiments of the invention, variation from this largest dimension may be $\pm$1; $\pm$5; $\pm$10; $\pm$20; $\pm$30; $\pm$40; $\pm$50 or $\pm$75% or intermediate or greater values. In some exemplary embodiments of the invention, an anode of the NSPC is constructed of a metal oxide, for example titanium dioxide. In some exemplary embodiments of the invention, a photon collector of the NSPC comprises one or more quantum dots.

In some exemplary embodiments of the invention, the quantum dot(s) of the NSPC are at least partially coated with an insulating layer.

One aspect of some embodiments of the invention relates to use of silica in preparation of an insulating layer on quantum dots (PC). Optionally, the silica in the insulating layer contributes to a reduction in chemical and/or photochemical degradation of the quantum dots. In some exemplary embodiments of the invention, an insulating layer which contributes to conductivity of the dots is applied, optionally in addition to the layer containing silica.

As used in this specification and the accompanying claims the term "insulating coating"; "insulating layer"; "insulating...from contact"; "insulated ...from contact" and "insulated" and variations thereof indicate presence of a layer that blocks contact between an indicated element (e.g. photon collector and/or nano-sized crystalline semiconducting particle) and electrolyte. Note that the term insulation does not necessarily mean blocking electric current. On the contrary, in various embodiments of the invention, the insulator may be conductive or include a conductive portion. In some exemplary embodiments of the invention, blocking of contact contributes to a reduction in rate of chemical and/or photochemical degradation.

As used in this specification and the accompanying claims the term "photon collector particle", "PC" and "quantum dot" each refer to an element capable of absorbing energy from photon radiation in a first spectrum band and emitting energy in a second spectrum band. Optionally, the energy is emitted as FRET energy.

The first spectrum band is referred to as the photon collector element absorption spectrum band and the second spectrum band is referred to as the photon collector emission spectrum band. In some exemplary embodiments of the invention, quantum dots serve as photon collectors.

According to various exemplary embodiments of the invention any electrolyte may be used in a FRET enhanced dye-sensitized solar cell (FSC). Optionally, a solid electrolyte is employed.

As used in this specification and the accompanying claims the term "electron injector" or "EI" refers to a particle or a molecule capable of absorbing energy from photon radiation in a given spectrum band and, as a result of said absorption, donating an electron to a substance that is in at least one of a direct and an indirect contact. The spectrum band of the electron injector is the electron injector absorption spectrum band.

In some exemplary embodiments of the invention, the electron injector is a particle or a molecule capable of absorbing the photon collector emission spectrum band and, as a result of said absorption, is capable of donating an electron to a substance that is in at least one of a direct and an indirect contact.

-In some exemplary embodiments of the invention, an anode of the FSC includes multiple nano-sized semiconducting particles. Optionally, the anode includes titanium oxide. In some exemplary embodiments of the invention, at least some of the nano-sized semiconducting particles include semiconducting material which is at least partially crystalline.

One aspect of some embodiments of the invention relates to providing an insulating coating between anodic semiconducting particles and quantum dots attached thereto. In some exemplary embodiments of the invention, quantum dots are coated with insulating material and then attached to anodic semiconducting particles.

Another aspect of some embodiments of the invention relates to a discontinuous insulating coating applied selectively to portions of quantum dots not in contact with anodic semiconducting particles. In some exemplary embodiments of the invention, some portions of a surface of anodic semiconducting particles not in contact with the quantum dots are coated with a dye. Optionally, the dye is an electron injector (EI). Optionally, some portions of a surface of anodic semiconducting particles not in contact with the quantum dots are in contact with surrounding electrolyte.

Another aspect of some embodiments of the invention relates to a linker molecule which keeps quantum dots at a desired distance from anodic semiconducting particles. Optionally, the

specific EI and/or electrolyte employed can contribute to the desired distance. In some exemplary embodiments of the invention, a bi-functional linker molecule containing at least two functional groups with affinity to the PC and the anode; for example carboxylic group, amine group, phosphine group or thiol group is employed. Examples for such linker molecules include, but are not limited to thioglycolyic acid, thioethanol, dicarboxylic acids (e.g. glutaric acid, pimelic acid, azeietic acid or decandioic acid). Optionally, mercapto-propionic acid serves as a linker molecule.

It will be appreciated that the various aspects described above relate to the solution of technical problems associated with operational efficiency of photovoltaic cells.

Alternatively or additionally, it will be appreciated that the various aspects described above relate to the solution of technical problems related to useful life photovoltaic cells.

In some exemplary embodiments of the invention, there is provided a nano-sized photon collector (NSPC) including: (a) a nano-sized crystalline semiconducting particle, at least a portion of which is not insulated;

(b) a quantum dot photon collector particle (PC); and (c) an insulating coating including silica on at least a portion of the PC.

Optionally, the NSPC includes at least one electron injector (EI).

Optionally, the NSPC is configured so that energy emitted by the PC particle is transferred to the EI.

Optionally, the NSPC is configured so that a virtual photon emitted by the PC particle is transferred to the EI which injects an electron into the semiconducting particle.

Optionally, the NSPC is configured so that energy emitted by the PC particle includes at least one of FRET and radiative energy.

Optionally, the nano-sized semiconducting particle includes a metal dioxide, optionally titanium dioxide.

Optionally, the insulating coating includes an oxide.

Optionally, the insulating coating includes at least two layers.

In some exemplary embodiments of the invention, there is provided a method including: (a) providing isolated quantum dot photon collector particles (PC); and (b) insulating a surface of the PC with a layer including silica to produce insulated PC.

Optionally, the insulating includes at least one of: (a) passivating, (b) modifying, (c) capping, (d) substituting, (e) electro-deposition and combinations thereof.

Optionally, the insulating includes applying a layer of an oxide to the surface of the PC.

Optionally, the oxide includes at least one of TiO_2, SiO_2 and Al_2O_3.

Optionally, the layer includes at least two layers.

In some exemplary embodiments of the invention, there is provided a method including: (a) providing a nano-sized crystalline semiconducting particle; (b) applying one or more quantum dot photon collector particles (PC) to the nano-sized semiconducting particle; and (c) insulating at least a portion of the PC while leaving at least a portion of the nano-sized semiconducting particle un-insulated; so that a nano-sized photon collector particle (NSPC) is produced.

Optionally, the insulating occurs prior to the applying.

Optionally, the PC are insulated with silica prior to the applying.

Optionally, the method includes insulating at least a portion of the PC with silica.

In some exemplary embodiments of the invention, there is provided a method including:

providing a nano-sized crystalline semiconducting particle; coating at least a portion of a surface of the crystalline particle with an amorphous semiconductor layer;

forming at least one quantum dot photon collector particle (PC) on the coated portion of the surface; applying an additional amorphous semiconductor layer to the PC; and

applying electron injector (EI) to an uncoated portion of the nano-sized crystalline semiconducting particle; to produce a nano-sized photon collector (NSPC).

Optionally, the coating and the applying each independently include at least one process selected from the group consisting of: crystallizing, chemically reducing, pH adjustment, precipitation, oxidation, condensation, polymerization, complexation and substitution.

In some exemplary embodiments of the invention, there is provided a method including:

providing quantum dot photon collector particles (PC) with a surface insulated at least with a layer including silica; forming a nano-sized semiconducting particle on the PC; and applying electron injector (EI) to produce a nano-sized photon collector (NSPC).

Optionally, the forming includes at least one process selected from the group consisting of: crystallizing, chemical reduction, pH adjustment, precipitation, oxidation, condensation, polymerization, complexation and substitution.

Optionally, the surface of the PC is also insulated with at least one layer not including silica.

In some exemplary embodiments of the invention, there is provided a method including:

(a) providing a nano-sized crystalline semiconducting particle with electron injector (EI) on at least a portion of its surface; (b) applying one or more insulated quantum dot photon

collector particles (PC) to the nano-sized semiconducting particle ; so that a nano-sized photon collector(NSPC) particle is produced.

Optionally, the applying includes attachment via a linker molecule.

In some exemplary embodiments of the invention, there is provided a FRET enhanced dye-sensitized solar cell (FSC) including (a) an electrolyte, (b) a plurality of nano-sized photon collectors (NSPC) according to claim 1 arranged so that the insulating coating on the PC blocks direct contact between the PC and the electrolyte; and (c) at least one electron injector (EI).

Optionally, at least some of the at least one EI is in direct contact with the nano-sized semiconducting particle.

Optionally, at least some of the at least one EI is in contact with the nano-sized semiconducting particle via an electrically conductive insulating coating on the PC.

Optionally, at least some of the at least one EI is in direct contact with the electrolyte.

Optionally, at least some of the at least one EI is in contact with the electrolyte via an electrically conductive insulating coating.

Throughout this specification and the accompanying claims singular language is sometime used for clarity. Such use of singular language indicates also a plurality of the recited element and/or multiple repetition of the recited action. By way of example: Recitation of "a nano-sized semiconducting particle" refers also to a plurality of such particles; and recitation of "a quantum dot photon collector particle (PC)" refers also to a plurality of such particles.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although suitable methods and materials are described below, methods and materials similar or equivalent to those described herein can be used in the practice of the present invention. In case of conflict, the patent specification, including definitions, will control. All materials, methods, and examples are illustrative only and are not intended to be limiting.

As used herein, the terms "comprising" and "including" or grammatical variants thereof are to be taken as specifying inclusion of the stated features, integers, actions or components without precluding the addition of one or more additional features, integers, actions, components or groups thereof. This term is broader than, and includes the terms "consisting of" and "consisting essentially of" as defined by the Manual of Patent Examination Procedure of the United States Patent and Trademark Office.

The phrase "consisting essentially of" or grammatical variants thereof when used herein are to be taken as specifying the stated features, integers, steps or components but do not preclude

the addition of one or more additional features, integers, steps, components or groups thereof but only if the additional features, integers, steps, components or groups thereof do not materially alter the basic and novel characteristics of the claimed composition, device or method.

The term "method" refers to manners, means, techniques and procedures for accomplishing a given task including, but not limited to, those manners, means, techniques and procedures either known to, or readily developed from known manners, means, techniques and procedures by practitioners of architecture and/or computer science.

Percentages (%) of chemicals typically supplied as powders or crystals (e.g. TiO_2 and SiO_2) are W/W (weight per weight) unless otherwise indicated. Percentages (%) of chemicals typically supplied as liquids (e.g. Triton X-100) are W/W (weight per weight) unless otherwise indicated.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying figures. In the figures, identical and similar structures, elements or parts thereof that appear in more than one figure are generally labeled with the same or similar references in the figures in which they appear. Dimensions of components and features shown in the figures are chosen primarily for convenience and clarity of presentation and are not necessarily to scale. The attached figures are:

Fig. 1 is a schematic representation of a quantum dot according to some exemplary embodiments of the invention with the insulating coating visible;

Fig. 2 is a schematic representation of a core/shell quantum dot according to some exemplary embodiments of the invention with the insulating coating visible;

Fig. 3 is a schematic representation of a nano-sized photon collector (NSPC) according to an exemplary embodiment of the invention;

Fig. 4 is a schematic representation of a portion of an NSPC according to another exemplary embodiment of the invention;

Fig. 5 is a schematic representation of the NSPC of Fig. 4 in its entirety;

Fig. 6 is a schematic representation of an NSPC according to another additional exemplary embodiment of the invention;

Fig. 7 is a schematic representation of a cluster or aggregate of the NSPC of Fig. 3;

Fig. 8 is a schematic representation of a cluster or aggregate of the NSPC of Fig. 5;

Fig. 9 is a schematic representation of a cluster or aggregate of the NSPC of Fig. 6;

Fig. 10 is a schematic representation of the NSPC of Fig. 5 in FSC with electron injector (EI) particles distributed;

Fig. 11 is a schematic representation of the NSPC of Fig. 3 in FSC with electron injector (EI) particles distributed;

Fig. 12 is a schematic representation of the NSPC of Fig. 5 in FSC with electron injector (EI) particles attached only to the semiconductor;

Fig. 13 is a schematic representation of the NSPC of Fig. 3 in FSC with electron injector (EI) particles attached only to the semiconductor;

Fig. 14 is a schematic representation quantum dots as depicted in Fig. 1 linked via a linker molecule to a semiconductor particle with electron injector (EI) particles attached thereto;

Fig. 15 is a schematic representation of an optional TIO2 NS anode attached to an aggregate as depicted in Fig. 7;

Fig. 16 is a schematic representation of an optional TIO2 NS anode attached to an aggregate as depicted in Fig. 8;

Fig. 17 is a simplified flow diagram of a method according to some exemplary embodiments of the invention;

Fig. 18 is a simplified flow diagram of another method according to some exemplary embodiments of the invention;

Fig. 19 is a simplified flow diagram of a third method according to some exemplary embodiments of the invention;

Fig. 20 is a simplified flow diagram of a fourth method according to some exemplary embodiments of the invention;

Fig. 21 is a simplified flow diagram of a fifth method according to some exemplary embodiments of the invention;

Fig. 22 is a TEM (transmission electron microscopy) micrograph of quantum dot photon collectors (PC) with an insulating coating according to an exemplary embodiment of the invention;

Fig. 23 is a TEM (transmission electron microscopy) micrograph of quantum dot photon collectors (PC) with an insulating coating according to another exemplary embodiment of the invention;

Fig. 24 is a TEM micrograph of aggregates of quantum dot photon collectors (PC) with an insulating coating according to another exemplary embodiment of the invention;

Fig. 25 is a TEM micrograph of quantum dot photon collectors (PC) with multiple layers of insulating coating according to another exemplary embodiment of the invention; and

Fig. 26 is a TEM micrograph of nano-sized crystalline semiconducting particles with patches of an insulating coating applied to a portion of their surface according to an exemplary embodiment of the invention.

DETAILED DESCRIPTION OF EMBODIMENTS

Various exemplary embodiments of the invention relate to components of FRET enhanced dye sensitized solar cells, cells constructed of such components and methods to produce the components and/or the solar cells.

Specifically, some embodiments of the invention can be used to increase efficiency of photovoltaic cells and/or increase their useful lifetime and/or reduce production costs thereof. In some exemplary embodiments of the invention, an increase in efficiency results at least in part from bringing more EI into a proper spatial relationship with PC. In some exemplary embodiments of the invention, an increase in useful lifetime results at least in part from protection of PC from chemical and/or photochemical degradation. In some exemplary embodiments of the invention, a decrease in production cost results at least in part from a reduction in use of materials which do not contribute directly to production of electricity.

The principles and operation of components, cells and methods according to exemplary embodiments of the invention may be better understood with reference to the drawings and accompanying descriptions.

Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details set forth in the following description or exemplified by the Examples. The invention is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

Exemplary quantum dot photon collector particles (PC)

Some exemplary embodiments of the invention relate to quantum dot photon collector particles (PC) with an insulating coating which serves to block contact between the PC element and a surrounding electrolyte. In some exemplary embodiments of the invention, coated quantum dot collector particles PC are produced separately and used as raw materials in production of photovoltaic cells and/or their components.

Fig. 17 is a simplified flow diagram of a method for production of quantum dot PC with an insulating coating according to some exemplary embodiments of the invention indicated generally as 1700.

Depicted exemplary method 1700 includes providing 1710 isolated quantum dot photon collector particles (PC) and insulating 1720 a surface of the PC from contact with a surrounding electrolyte to produce insulated PC 1730. In some exemplary embodiments of the invention, insulating 1720 includes application and/or creation of a layer including silica. Optionally, the layer includes two or more layers. Optionally, at least one of these layers does not include silica. In some exemplary embodiments of the invention, two or more PC may be grouped together in a single layer (see Fig. 23 and explanatory text in Example 2) According to various exemplary embodiments of the invention insulating 1720 includes one or more of passivating, modifying, capping, substituting and electro-deposition.

In some exemplary embodiments of the invention, insulating 1720 includes applying 1722 a layer of an oxide to the surface of the PC. Optionally, the oxide includes one or more of TiO_2, SiO_2 and Al_2O_3. According to various exemplary embodiments of the invention a thickness of the applied oxide layer is less than 15, optionally 10, optionally 5, optionally 1 nm or intermediate or lesser thickness. In some exemplary embodiments of the invention, application is via the sol-gel process.

In some exemplary embodiments of the invention, method 1700 is applied to a uniform quantum dot PC comprising a single layer of material. Fig. 1 illustrates the insulated PC 1730 which results in such a case as insulated quantum dot 100. Insulated quantum dot 100 includes a conventional uniform quantum dot 110 and an insulating layer 120 surrounding it. In some exemplary embodiments of the invention, layer 120 includes silica. Optionally, layer 120 includes a wide band gap semiconductor such as titania.

In some exemplary embodiments of the invention, method 1700 is applied to a core /shell quantum dot PC comprising two layers of material. Fig. 2 illustrates the insulated PC 1730 which results in such a case as insulated quantum dot 200. Insulated quantum dot 300 includes a conventional core/shell quantum including a core 208 and a shell 210 surrounded by insulating layer 220. In some exemplary embodiments of the invention, layer 220 includes silica. Optionally, layer 220 includes a wide band gap semiconductor such as titania.

Exemplary nano-sized subunits

Some exemplary embodiments of the invention, relate to nano-sized photon collectors (NSPC).

These NSPC are useful in construction of photovoltaic cells. Although the NSPC can be provided without electrolyte, they are most easily described in terms of which portion(s) of the NSPC would be in contact with electrolyte, or insulated from such contact, in an assembled photovoltaic cell.

Fig. 3 schematically depicts an exemplary NSPC indicated generally as 1000. Exemplary NSPC 1000 includes nano-sized crystalline semiconducting particle(s) 1010 which are partially un-insulated from contact with a surrounding electrolyte (not depicted). In some exemplary embodiments of the invention, particles 1010 are constructed of crystalline TiO_2. In use, particles 110 function as an anode. Depicted exemplary NSPC 1000 also includes a quantum dot photon collector particle (PC) 1020 and an insulating coating 1040 on at least a portion of the PC (in the depicted embodiment, the entire PC is coated). In some exemplary embodiments of the invention, insulating coating 1040 includes silica. Optionally, insulating coating 1040 includes two or more layers. In some exemplary embodiments of the invention, one of these layers does not include silica.

Optionally, insulating coating 1040 is at least partially composed of a product of modifying the material of which PC 1020 is constructed. In the depicted embodiment, insulating coating 1040 is partially covered by semiconducting particles 1010.

Fig. 4 schematically depicts another exemplary NSPC configuration indicated generally as 1100. In the depicted embodiment the nano-sized crystalline semiconducting particle 1110 is porous and quantum dot photon collector particle (PC) 1120 is located in a pore of 1110. Part of 1120 is contacting an inner surface of the pore in 1110 and this contact insulates it from surrounding electrolyte (not shown). Insulating coating 1040 on the potentially exposed portion of 1120 prevents contact of the PC with the surrounding electrolyte. Optionally, insulating coating 1040 is formed by chemical modification of the surface PC 1120. As in the previous embodiment, a portion of nano-sized crystalline semiconducting particle 1110 is not insulated from contact with the electrolyte.

Fig. 4 schematically depicts yet another exemplary NSPC configuration indicated generally as 1200. In the depicted embodiment, nano-sized crystalline semiconducting particle 1210 forms an aggregate and quantum dot PC 1220 is positioned within the aggregate. Here again, that portion of PC 1220 that is potentially exposed to surrounding electrolyte is covered by insulating coating 1240. As in the previous two embodiments, a portion of nano-sized crystalline semiconducting particle 1210 is not insulated from contact with the electrolyte.

Fig. 5 schematically depicts still another exemplary NSPC configuration indicated generally as 900. In the depicted embodiment, nano-sized crystalline semiconducting particles 910 surround a PC 920 provided as a core. Those sections of the core that are not covered by particles 910 are coated by insulating coating 940 which prevents contact of PC 920 with surrounding electrolyte.

According to various exemplary embodiments of the invention NSPC, for example of the types depicted in Figs. 3 to 6, are provided with at least one electron injector (EI). In these exemplary embodiments, the NSPC are configured so that energy emitted by the PC particle(s) is transferred to the EI. Optionally, energy emitted by the PC particle includes FRET and/or radiation.

In some exemplary embodiments of the invention, a virtual photon emitted by the PC particle is transferred to the EI, which injects an electron into the anodic semiconducting particle.

In some exemplary embodiments of the invention, the nano-sized semiconducting particle comprises a metal dioxide. Metal dioxides suitable for use in this context include, but are not limited to, titanium dioxide and zinc oxide.

Alternatively or additionally, the insulating coating comprises an oxide.

Exemplary assembly possibilities

As indicated above, nano-sized photon collectors (NSPC) useful in construction of photovoltaic cells. In some exemplary embodiments of the invention, a plurality of NSPC are assembled into a cluster or aggregate. In some exemplary embodiments of the invention, such a cluster or aggregate is then incorporated into a photovoltaic cell. In other exemplary embodiments of the invention, the clustering or aggregation occurs during incorporation of individual NSPC into the photovoltaic cell.

Fig. 7 is a schematic representation of a cluster or aggregate of NSPC indicated generally as 1400. Aggregate 1400 includes a plurality of NSPC 1000 as depicted in Fig. 3 and described in detail hereinabove.

Fig. 8 is a schematic representation of a cluster or aggregate of NSPC indicated generally as 1300. Aggregate 1300 includes a plurality of NSPC 1200 as depicted in Fig. 5 and described in detail hereinabove.

In both figs 7 and 8 the nano-sized crystalline semiconducting particles of the individual NSPC are in contact with one another so that they can function collectively as an anode. Each of these nano-sized crystalline semiconducting particles is at least partially in contact with

surrounding electrolyte. Each of the quantum dot PC within the aggregate remains insulated from the surrounding electrolyte.

Fig. 9 is a schematic representation of a cluster or aggregate of NSPC indicated generally as 1500. Aggregate 1500 includes a plurality of NSPC 900 as depicted in Fig. 6 and described in detail hereinabove. The depicted exemplary embodiment includes electron injector (EI) 1550 represented schematically as black dots. AS shown, EI may be provided on the nano-sized crystalline semiconducting particles and/or on the insulating coating of the PC. The arrangement of the individual NSPC in an aggregate increases a likelihood that each molecule of EI will be at an appropriate distance to absorb energy emitted by one or more PC.

Exemplary electron injector (EI) distribution possibilities

According to various exemplary embodiments of the invention an electron injector (EI) serves to transfer energy from the quantum dot PC to the nano-sized crystalline semiconducting particles, which serve as the anode. In some exemplary embodiments of the invention, use of an EI contributes to an increase in the amount of electricity generated in response to incident radiation (e.g. sunlight).

In some exemplary embodiments of the invention, the EI is added during assembly of individual NSPC. In other exemplary embodiments of the invention, the EI is added during assembly of aggregates and/or assembly of an FSC.

Fig. 10 is a schematic representation of a single NSPC indicated generally as 300 in an FSC with electron injector (EI) particle distribution depicted. NSPC 300 is similar to that depicted in Fig. 5 in that a portion of PC 320 contacts nano-sized crystalline semiconducting particle 310 directly. The remainder of PC 320 is covered by an insulating coating 330 which separates PC 320 from surrounding electrolyte (not depicted). In the depicted embodiment EI 350 are in contact with insulating coating 330 and/or a surface of anodic particle 310. Optionally, contact of EI 350 with anodic particle 310 contributes to an increase in efficiency of energy transfer from EI 350 to particle 310. Alternatively or additionally, since some of EI 350 contact insulating coating 330, use of a coating 330 which allows electron injection contributes to an increase in efficiency of energy transfer to particle 310.

Fig. 11 is a schematic representation of a single NSPC indicated generally as 400 in an FSC with electron injector (EI) particle distribution depicted. NSPC 400 is similar to that depicted in Fig. 3 in that each PC 420 is fully encapsulated by insulating coating 430 so that it contacts neither nano-sized crystalline semiconducting particle 410 nor surrounding electrolyte (not depicted). As in the previous embodiment, EI 450 is in contact with insulating coating 430

and/or a surface of anodic particle 410. Optionally, contact of EI 450 with anodic particle 410 contributes to an increase in efficiency of energy transfer to particle 410. Alternatively or additionally, since some of EI 450 contact insulating coating 430, use of a coating 430 which allows electron injection contributes to an increase in efficiency of energy transfer to particle 410.

Fig. 12 is a schematic representation of a single NSPC indicated generally as 402 in an FSC with electron injector (EI) particle distribution depicted. NSPC 402 has some PC 420, which are fully encapsulated by insulating coating 430 as in Fig 11, and some PC 421 which contact a surface of anodic particle 410 and are partially encapsulated by insulating coating 430 as in Fig. 10. Both PC 420 and 421 are fully insulated from the surrounding electrolyte. In contrast to the embodiments depicted in Figs. 10 and 11, EI 450 in the depicted embodiment are each contact with a surface of anodic particle 410. As in the previously described embodiments, contact of EI 450 with anodic particle 410 contributes to an increase in efficiency of energy transfer to particle 410. Alternatively or additionally, since EI 450 each contact particle 410, a coating 430 which allows electron injection should not decrease efficiency of energy transfer to particle 410.

Fig. 13 is a schematic representation of a single NSPC indicated generally as 404 in an FSC with electron injector (EI) particle distribution depicted. NSPC 404 is similar to NSPC 402 of Fig. 12 except that all of the PC are of type 420 which are fully encapsulated by insulating coating 430.

Fig. 14 is a schematic representation of an exemplary NSPC indicated generally as 700 in a FSC with quantum dots 720 fully encapsulated by an insulating coating 740 linked via a linker molecule 760 to an anodic semiconductor particle 710 with electron injector (EI) particles 750 attached thereto. The depicted exemplary arrangement is amenable to use of a non-conductive material for coating 740 as in the embodiments of Figs. 12 and 13. Because neither PC 720 nor coating 740 contacts the surface of anodic particle 710, there is more surface available for occupation by EI 750. In some exemplary embodiments of the invention, application of EI 750 to a greater percentage of the surface of particle 710 contributes to an increase in efficiency of NSPC 700.

Fig. 15 is a schematic representation of an anode for an FSC indicated generally as 1501. Depicted exemplary anode 1501 includes a transparent conducting oxide pale 1510. Optionally plate 1510 comprises TiO_2. An aggregate 1400 of NSPC as depicted in Fig. 7 is attached to plate 1510. Electric current generated in aggregate 1400 flows out through plate 1510. .

Fig. 16 is a schematic representation of an anode for an FSC indicated generally as 1601. Anode 1601 employs an aggregate 1300 as depicted in Fig. 8 but is similar in other respects to anode 1501.

Exemplary methods to produce NSPC

Fig. 18 is a simplified flow diagram of an exemplary method to produce a nano-sized photon collector particle (NSPC) indicated generally as 1800. Depicted exemplary method 1800 includes providing 1810 a nano-sized crystalline semiconducting particle and applying 1820 one or more quantum dot photon collector particles (PC) to the nano-sized semiconducting particle. The depicted exemplary method also includes insulating 1830 at least a portion of the PC while leaving at least a portion of the nano-sized semiconducting particle un-insulated. This produces a nano-sized photon collector particle (NSPC) 1840. In some exemplary embodiments of the invention, insulating 1830 occurs prior to applying 1820. Optionally, insulating 1830 is performed according to method 1700 of Fig. 17.

In some exemplary embodiments of the invention method 1800 includes applying 1850 EI to the NSPC. Optionally, at least a portion of the EI is applied to an un-insulated portion of the nano-sized crystalline semiconducting particle. In some exemplary embodiments of the invention, substantially all of the EI is applied to the un-insulated portion of the nano-sized crystalline semiconducting particle after forming the anode. In some exemplary embodiments of the invention, applying 1850 is conducted prior to applying 1820.

In some exemplary embodiments of the invention, method 1800 includes insulating at least a portion of said PC with silica. Optionally, the PC are insulated with silica prior to applying 1820.

Fig. 19 is a simplified flow diagram of another exemplary method to produce an NSPC indicated generally as 1900. Depicted exemplary method 1900 includes providing 1910 a nano-sized crystalline semiconducting particle and coating 1920 at least a portion of a surface of the crystalline particle with an amorphous semiconductor layer. In some exemplary embodiments of the invention, the coating has a thickness of at least 1 nm.

Depicted exemplary method 1900 also includes forming 1930 at least one quantum dot photon collector particle (PC) on the coated portion of the surface and applying 1940 an additional amorphous semiconductor layer to the PC. In some exemplary embodiments of the invention, at least a portion of the nano-sized crystalline semiconducting particle remains

uncoated after coating 1920 and applying 1940. Optionally, coating 1920 and applying 1940 use a same amorphous semiconductor or different amorphous semiconductors.

Depicted exemplary method 1900 includes applying 1950 electron injector (EI) to produce a nano-sized photon collector (NSPC) 1960. Optionally, at least a portion of the EI is applied 1950 to an uncoated portion of the nano-sized crystalline semiconducting particle. In some exemplary embodiments of the invention, substantially all of the EI is applied 1950 to an uncoated portion of the nano-sized crystalline semiconducting particle by staining after anode formation.

According to various exemplary embodiments of the invention coating 1920 and applying 1940 each independently include at least one of crystallizing, chemically reducing, pH adjustment, precipitation, oxidation, condensation, polymerization, complexation and substitution.

Fig. 20 is a simplified flow diagram of a third exemplary method to produce an NSPC indicated generally as 2000. Depicted exemplary method 2000 includes providing 2010 quantum dot photon collector particles (PC) with an insulated surface. In some exemplary embodiments of the invention, the surface of the PC is insulated at least with a layer including silica. Optionally, the surface of the PC is also insulated with at least one layer not including silica. Optionally, exemplary method 1700 can be used for providing 2010. Depicted method 2000 also includes forming 2020 a nano-sized semiconducting particle on said PC and applying 2030 electron injector (EI) to produce a nano-sized photon collector (NSPC) 2040.

In some exemplary embodiments of the invention, forming 2020 includes at least one of crystallizing, chemical reduction, pH adjustment, precipitation, oxidation, condensation, polymerization, complexation and substitution.

In some exemplary embodiments of the invention, applying 2030 is primarily, optionally almost exclusively, to the nano-sized semiconducting particle. In some exemplary embodiments of the invention, applying 2030 is by staining the surface in a solution before or after anode formation.

Fig. 21 is a simplified flow diagram of a fourth exemplary method to produce an NSPC indicated generally as 2100. Depicted exemplary method 2100 includes providing 2110 a nano-sized crystalline semiconducting particle with electron injector (EI) on at least a portion of its surface and applying 2120 one or more insulated quantum dot photon collector particles (PC) to the nano-sized semiconducting particle so that a nano-sized photon collector particle 2130 (NSPC) is produced.

In some exemplary embodiments of the invention, applying 2120 includes attachment via a linker molecule.

Exemplary photovoltaic cells

Some exemplary embodiments of the invention relate to FRET enhanced dye-sensitized solar cells (FSC). FSC according to these exemplary embodiments of the invention, the FSC includes an electrolyte. According to various exemplary embodiments of the invention any electrolyte is suitable for the FSC of the present invention. Optionally, a solid electrolyte or a liquid electrolyte can be employed.

FSC according to these exemplary embodiments also include a plurality of nano-sized photon collectors (NSPC) as described hereinabove arranged so that the insulating coating on the PC blocks direct contact between the PC and the electrolyte.

FSC according to these exemplary embodiments also include at least one electron injector (EI). Although EI are depicted schematically as "particles" in the figures, in actual practice they may not be particulate.

In some exemplary embodiments of the invention, at least some of the at least one EI is in direct contact with the crystalline nano-sized semiconducting particle. Alternatively or additionally, at least some of the at least one EI is in contact with the crystalline nano-sized semiconducting particle via an amorphous insulating coating on the PC.

In some exemplary embodiments of the invention, at least some of the at least one EI is in direct contact with the electrolyte. Alternatively or additionally, at least some of the at least one EI is in contact with said electrolyte via an electrically conductive insulating coating. Whether contact between the EI and the electrolyte is direct, or via an amorphous insulating coating, the coating should allow efficient injection of electrons to the anode while also preventing recombination processes with the electrolyte.

As used in this specification and the accompanying claims the term "*electrolyte*" refers to any electrical mediator. Electrolytes can be liquid and/or solid and/or gel and/or polymers and/or semiconductors.

Exemplary insulation considerations

According to various exemplary embodiments of the invention, 70%, 80%, 90%, 99%, or substantially 100% or intermediate percentages of the PC of the FRET enhanced dye-sensitized solar cell (FSC) are insulated from surrounding electrolyte by means of the insulator.

In some exemplary embodiments of the invention, the insulator is a product of chemical conversion material present in the quantum dots. According to various exemplary embodiments

of the invention conversion of one or more of Si, Ge, Sn, Se, Te, B, C, P, Co, Au, BN, BP, BAs, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, BeS, BeSe, BeTe, MgS, MgSe, GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbO, PbS, PbSe, PbTe, CuF, CuCl, CuBr, CuI, Si3N4, Ge3N4, Al2O3, (Al, Ga, In)2 (S, Se, Te)3, Al2CO, poly vinyl butyral, poly vinyl acetate (PVA), polyethylene glycols, epoxies, urethanes, silicone and derivatives of silicone, fluorinated silicones and vinyl and hydride substituted silicones, acrylic polymers and copolymers formed from monomers or oligomers including polymers such as, methylmethacrylate, butylmethacrylate and laurylmethacrylate, styrene based polymers and crosslinked polystyrene polymers, poly(methyl (meth)acrylate) (PMMA), poly(ethylene glycol dimethacrylate) (PEGMA), poly(thioether), silane monomers, PMMA, PEGMA, PVA, thiol co-monomer, silane monomers, 3-(trimethoxysilyl)-propylmethacrylate (TMOPMA), tetramethoxysilane (TEOS)), poly(ethylene glycol) (PEG), poly(N- isopropylacrylamide), poly(N-alkylacrylamide), poly(N-n-propylacrylamide), poly(N- isopropylmethacrylamide), a peptide, a polypeptide, poly(ethylene oxide)-poly(propylene oxide)- poly(ethylene oxide), poly(DTEC), dextran-polylactide, elastin-like polypeptides, a polyester, polylactide, poly(L-lactic acid), poly(D,L-lactic acid), poly(lactide-co-glycolides), biotinylated poly(ethylene glycol-block-lactic acid), poly(alkylcyanoacrylate), poly(epsilon-caprolactone), polyanhydride, poly(bis(p-carboxyphenoxy) propane-sebacic acid), polyorthoester, polyphosphoester, polyphosphazene, polystyrene, polyurethane, poly(amino acid), poly(ethylene oxide), poly(ethylene oxide)-polypropylene-poly(ethylene oxide), poly(lactic acid)-g-poly(vinyl alcohol), poly(ethylene oxide)-poly(L-lactic acid), poly(D,L-lactic-co-glycolic acid)-poly(ethylene glycol), poly(L-lactide- ethylene glycol), poly(ethylene glycol)-co-poly(hydroxyl Acid), polyvinyl alcohol), poly(lactic acid- co-lysine)-poly(aspartic acid), poly(-caprolactone-co-trimethylene carbonate), poly(L-lactic acid-co- glycolic acid-co-L-serine), poly(propylene fumarate), oligo(poly(ethylene glycol) fumarate), poly(propylene furmarate-co-ethylene glycol), poly(ethylene glycol) di[ethylphosphatidyl(ethylene glycol)methacrylate], poly(N-isopropylacrylamide)-poly(ethylene glycol), poly(N- isopropylacrylamide)-gelatin, poly(N-isopropylacrylamide-acrylic acid) produces an insulating coating on at least a portion of the PC.

Since the quantum dot PC are typically provided as core/shell structures such as CdSe/ZnS, InP/ZnS, PbSe/PbS, CdSe/CdS, CdTe/CdS, CdTe/ZnS some exemplary embodiments of the invention relate to chemical conversion of shell material.

According to various exemplary embodiments of the invention the chemical conversion can include, for example, passivating and/or modifying and/or capping and/or substituting and/or electro-deposition. According to various exemplary embodiments of the invention the insulating coating includes one or more of metal oxides, nitrides, sulfides, silicates, aluminates, oxynitrides, organic polymers.

In some exemplary embodiments of the invention, the semiconducting material and the insulator comprise the same compound. Optionally, the compound is titanium oxide. In some exemplary embodiments of the invention, the PC element is essentially surrounded by the semiconducting material which insulates the photon collector element from the electrolyte. Optionally, the PC element is essentially surrounded by a layer including silica.

Exemplary efficiency considerations

In some exemplary embodiments of the invention, the FSC is configured so that at least a desired fraction of incident photons are absorbed by the NSPC. Optionally, 30%, 50%, 70%, 90%, 99% or substantially 100% or intermediate percentages of incident photons are absorbed by the NSPC.

In some exemplary embodiments of the invention, 70%, 80%, 90%, 99%, or substantially 100% or intermediate percentages of the photon collector elements are in proximity to EI.

As used in this specification and the accompanying claims the term "in proximity to said at least one electron injector" means within a distance that enables efficient energy transfer to the electron injector via FRET. Optionally, efficient energy transfer is a transfer of at least 70%, optionally 80%, optionally 90% optionally 99% or intermediate or greater percentages of the energy.

Alternatively or additionally, "in proximity to said at least one electron injector" indicates a distance of less than 10 nm, optionally less than 5 nm, optionally less than 2 nm.

According to various exemplary embodiments of the invention EI particles may be in direct and/or indirect contact with the nano-sized semiconducting particle. Alternatively or additionally, EI particles may be in direct and/or indirect contact with the electrolyte.

There can be a tradeoff between efficient injection of electrons to the nano-sized semiconducting particle and recharging of the EI with electrons from the electrolyte.

Exemplary quantum dot materials

According to various exemplary embodiments of the invention quantum dots can comprise Si, Ge, Sn, Se, Te, B, C, P, Co, Au, BN, BP, BAs, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, InSb, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, ZnO, ZnS,

ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, BeS, BeSe, BeTe, MgS, MgSe, GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbO, PbS, PbSe, PbTe, CuF, CuCl, CuBr, CuI, Si3N4, Ge3N4, Al2O3, (Al, Ga, In)2 (S, Se, Te)3, Al2CO, poly vinyl butyral, poly vinyl acetate (PVA), polyethylene glycols, epoxies, urethanes, silicone and derivatives of silicone, fluorinated silicones and vinyl and hydride substituted silicones, acrylic polymers and copolymers formed from monomers or oligomers including polymers such as, methylmethacrylate, butylmethacrylate and laurylmethacrylate, styrene based polymers and crosslinked polystyrene polymers, poly(methyl (meth)acrylate) (PMMA), poly(ethylene glycol dimethacrylate) (PEGMA), poly(thioether), silane monomers, PMMA, PEGMA, PVA, thiol co-monomer, silane monomers, 3-(trimethoxysilyl)-propylmethacrylate (TMOPMA), tetramethoxysilane (TEOS)), poly(ethylene glycol) (PEG), poly(N- isopropylacrylamide), poly(N-alkylacrylamide), poly(N-n-propylacrylamide), poly(N- isopropylmethacrylamide), a peptide, a polypeptide, poly(ethylene oxide)-poly(propylene oxide)- poly(ethylene oxide), poly(DTEC), dextran-polylactide, elastin-like polypeptides, a polyester, polylactide, poly(L-lactic acid), poly(D,L-lactic acid), poly(lactide-co-glycolides), biotinylated poly(ethylene glycol-block-lactic acid), poly(alkylcyanoacrylate), poly(epsilon-caprolactone), polyanhydride, poly(bis(p-carboxyphenoxy) propane-sebacic acid), polyorthoester, polyphosphoester, polyphosphazene, polystyrene, polyurethane, poly(amino acid), poly(ethylene oxide), poly(ethylene oxide)-polypropylene-poly(ethylene oxide), poly(lactic acid)-g-poly(vinyl alcohol), poly(ethylene oxide)-poly(L-lactic acid), poly(D,L-lactic-co-glycolic acid)-poly(ethylene glycol), poly(L-lactide- ethylene glycol), poly(ethylene glycol)-co-poly(hydroxyl Acid), polyvinyl alcohol), poly(lactic acid- co-lysine)-poly(aspartic acid), poly(-caprolactone-co-trimethylene carbonate), poly(L-lactic acid-co- glycolic acid-co-L-serine), poly(propylene fumarate), oligo(poly(ethylene glycol) fumarate), poly(propylene furmarate-co-ethylene glycol), poly(ethylene glycol) di[ethylphosphatidyl(ethylene glycol)methacrylate], poly(N-isopropylacrylamide)-poly(ethylene glycol), poly(N- isopropylacrylamide)-gelatin, poly(N-isopropylacrylamide-acrylic acid) and an appropriate combination of two or more such materials or a deriavations thereof.

Exemplary core- shell luminescent nanocrystals for use as quantum dots include, but are not limited to, (represented as Core/Shell), CdSe/ZnS, InP/ZnS, PbSe/PbS, CdSe/CdS, CdTe/CdS, CdTe/ZnS, $CuInS_2$, $CuInSe_2$ and a combination thereof.

Exemplary Electron Injector (EI) Materials.

In some exemplary embodiments of the invention, the electron For is a dye. Suitable EI dyes include, but are not limited to anthocyanins, porphyrins, phthalocyanines, merocyanines,

cyanines, squarates, eosins, and metal-containing dyes such as Ruthenium Dyes, RuL2(NCS)2 (L=2,2'-bipyridyl-4,4'-dicarboxylic acid (N3 dye); tris (isothiocyanato)-ruthenium (II)-2, 2' : 6', 2"- terpyridine-4,4', 4"- tricarboxylic acid; cis-bis (isothiocyanato) bis (2,2'-bipyridyl-4, 4'-dicarboxylato)-rutlienium (II) bis-tetrabutylammonium ; cis-bis (isocyanato) (2,2'-bipyridyl- 4, 4'dicarboxylato) ruthenium (II); and tris (2,2'-bipyridyl-4, 4'-dicarboxylato) ruthenium (II) dichloride, [RuL2(NCS)2]: 2 TBA (L=L=2,2'-bipyridyl-4,4'-dicarboxylic acid, TBA=tetra-n-butylammonium (N719 dye), RuLL'(NCS)2 (L=2,2'-bipyridyl-4,4'-dicarboxylic acid, L'= 4,4'-dinonyl-2,2'-bipyridine (Z907 dye), [RuL(NCS)3]: 3 TBA (L= 2,2':6',2"-terpyridyl-4,4',4"-tricarboxylic acid, TBA=tetra-n-butylammonium (N749 dye), PolypyridiniumRuII-complexes, organic dyes, coumarin-dyes, squaraine dyes, indole-dyes and combinations thereof.

It is expected that during the life of this patent many additional types of quantum dot (PC) will be developed and the scope of the invention is includes the use of all such new types of PC *a priori.*

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims.

Specifically, a variety of numerical indicators have been utilized. It should be understood that these numerical indicators could vary even further based upon a variety of engineering principles, materials, intended use and designs incorporated into the invention. Additionally, components and/or actions ascribed to exemplary embodiments of the invention and depicted as a single unit may be divided into subunits. Conversely, components and/or actions ascribed to exemplary embodiments of the invention and depicted as sub-units/individual actions may be combined into a single unit/action with the described/depicted function.

Alternatively, or additionally, features used to describe a method can be used to characterize an apparatus and features used to describe an apparatus can be used to characterize a method.

It should be further understood that the individual features described hereinabove can be combined in all possible combinations and sub-combinations to produce additional embodiments of the invention. The examples given above are exemplary in nature and are not intended to limit the scope of the invention which is defined solely by the following claims. Specifically, although various exemplary embodiments of the invention have been described in the context of

photovoltaic cells and methods for their production, many of these embodiments might also be used in other applications.

All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention.

As used in this specification, the terms "include" and "have" and their conjugates mean "including but not necessarily limited to".

Additional objects, advantages, and novel features of various embodiments of the invention will become apparent to one ordinarily skilled in the art upon examination of the following examples, which are not intended to be limiting. Additionally, the various embodiments and aspects of the invention as delineated hereinabove and as claimed in the claims section below finds experimental support in the following examples.

EXAMPLES

Reference is now made to the following examples, which together with the above description; illustrate the invention in a non limiting fashion.

EXAMPLE 1:

Silica coated quantum dots

In order to demonstrate the feasibility of applying an insulating coating to a quantum dot photon collector particle (PC), silica particles were applied to CdSe/ZnS quantum dots as follows:

A mixture of 1 gr Triton X-100 and 13.2mL cyclohexane was prepared and stirred for 24 hours. One (1) mL of CdSe/ZnS quantum dots in Cyclohexane (0.25 mg/ml) was added to the mixture and the stirring continued for another 24 hours. At this point, 200 μL ammonia water solution (30%) was added and stirred for 120 min to produce a stable reverse micro-emulsion.

The formation of silica particles was triggered by addition of 100 μL TEOS followed by stirring for a growth time of 24 h.

Fig 22 is a TEM micrograph of the resultant quantum dots with an insulating coating of SiO_2 clearly visible as grey band 2230 around the CdSe/ZnS core/shell structure2210. The coated quantum dots in Fig. 22 are of the type represented schematically in Fig. 2.

This example illustrates that production of quantum dots with an insulating coating is feasible. Optionally, these coated quantum dots can be used as raw materials in production of

photovoltaic cells and/or employed in various method described hereinabove. The applied insulating coating prevents contact of the coated quantum dots with surrounding electrolyte. In this exemplary embodiment, SiO_2 can protect the coated quantum dots from degradation which would result from contact with surrounding electrolyte. Although silica was used in this example other metal oxides and/or nitrides, and/or sulfides and/or silicates and/or aluminates and/or oxynitrides and/or organic polymers could be used to impart resistance to chemical and/or photochemical degradation.

EXAMPLE 2:

Multiple quantum dots in silica shell

In order to demonstrate the feasibility of applying an insulating coating to a multiple quantum dot photon collector particles (PC) concurrently, silica particles were applied to CdSe/ZnS quantum dots as follows:

A mixture of 1 gr Triton X-100 and 15 mL cyclohexane was stirred for 24h.

One (1) mL CdSe/ZnS quantum dots in Cyclohexane (0.5 mg/ml) added to the solution and the stirring continued for 24 hr. At this point, 300μL ammonia solution was added and stirred for 120 min to produce a stable reverse micro-emulsion.

The formation of silica particles was triggered by addition of 500 μL TEOS followed by stirring for a growth time of 24 h.

Fig 23 is a TEM micrograph of the resultant quantum dots with an insulating coating of SiO_2 2320 clearly visible as a contiguous layer binding them into an aggregate around the CdSe/ZnS quantum dots 2310 structure. The coated quantum dots in Fig. 23 are functionally similar to the type represented schematically in Fig. 2.

This example illustrates that it is possible to increase the ratio of active material (quantum dots) to insulation material while still achieving the desired insulation from surrounding electrolyte. This increased ratio of active material to insulation material contributes to an increase in efficiency as measured by electric output and/or to a decrease in price per unit of electric output. In some exemplary embodiments of the invention, achievement of this increase stems from grouping two or more quantum dots togerher in a single insulating layer as depicted in the figure.

As described above for Example 1, other materials could be substituted for silica.

EXAMPLE 3:

Titania coated quantum dots

In order to demonstrate the feasibility of using titania to produce an insulating coating for quantum dots instead of silica as in example 1, titania particles were applied to CdSe/ZnS quantum dots as follows:

A mixture of 0.8 gr Triton X-100 and 12 mL cyclohexane was stirred for 24h.

One (1) mL CdSe/ZnS quantum dots (0.25 mg/ml) was added to the solution and the stirring continued for 24 h. At this point, 250 μL ammonia water solution (10%) was added and stirred for 2 hr .The formation of titania particles was triggered by addition of 300 μL TBOT solution followed by stirring for a growth time of 24 h.

Fig 24 is a photomicrograph of the resultant quantum dots with an insulating coating of TiO_2 clearly visible as grey band 2430 around the CdSe/ZnS core/shell structure 2410. The coated quantum dots in Fig. 24 are of the type represented schematically in Fig. 2.

This example confirms the results of example 1 and demonstrates that titania may be deposited in a manner similar to that described for silica above. The coated quantum dots produced in this example are characterized by good electrical conductivity due to the titania coating. Although titania was used in this example, other wide band gap semiconductors such as, for example, ZnO, doped titania and SnO2 can be used to impart good conductivity to quantum dots. Optionally, combinations of two or more materials can be employed.

Alternatively or additionally, a coating strategy as described above in example 2 could be implemented with titania or another wide band gap semiconductor.

EXAMPLE 4:

Preparation of quantum dots with a dual layer of insulation

In order to demonstrate the feasibility of applying multiple layers of insulating coating to quantum dots, a titania coating was applied to quantum dots previously coated with silica as follows:

5 ml of silica coated QD micro emulsion (prepared as in example 1) were mixed with 5ml cyclohexane solution containing Triton X-100 (0.15M). Formation of a titania coating was initiated by adding TBOT ($1.65 \cdot 10^{-3}$ M) followed by rapidly by addition of 20 μl H_2SO_4 (98%) to the resultant micro-emulsion.

Fig 25 is a TEM micrograph of the resultant quantum dots with a coating of titania over the silica coating 2530 (two layers appear as a single grey band) surrounding quantum dots 2510.

This example demonstrates that application of multiple insulating layers to quantum dots is feasible. The coated quantum dots produced in this example are characterized by good electrical conductivity due to the titania coating and good resistance to chemical and/or photochemical degradation due to the silica coating.

Some particles containing only coating, without quantum dots, are visible in Fig. 25. Adjustment of relevant reaction parameters should be able to reduce the prevalence of such "empty" particles.

As described above in Examples 1 and 4, other materials could be substituted for silica and titania to protect the quantum dots from degradation and improve conductivity respectively.

Alternatively or additionally, the coating strategy of example 2 may be combined with the idea of applying 2 layers of coating.

EXAMPLE 5:

Selective insulation of a portion of a nano-sized crystalline semiconducting particle

In order to demonstrate the feasibility of applying an insulating coating to a portion of a surface of a nano-sized crystalline semiconducting particle, patches of Cadmium sulfide were applied to Titania nanoparticles.

In order to accomplish this, 5.57gr Titania nanoparticles at pH=2.1; 50 gr DMF and 2 gr 2.2% CdCl2 solution were introduced into a closed Erlenmeyer flask (100 ml).

The flask was mixed at room temperature till a white suspension formed. At this point, nitrogen gas was bubbled through the solution and 0.02 gr of sulfur was added. This produced a white suspension with a small amount of sulfur crystals. The sulfur containing suspension was shaken for 3 days in sunlight. At the end of this time, the white TiO2 particles in the suspension were yellowish in color.

Fig. 26 is a TEM micrograph in which black patches of Cadmium sulfide coating are clearly visible on the grey Titania surface. The size of the patches in received in this experiment was from 3.6 to 5.4 nm as indicated.

These results show that it is possible to coat only a portion of a nano-sized crystalline semiconducting particle with an insulating coating. Such partially coated particles are useful in various exemplary embodiments of the invention described above.

CLAIMS:

1. 1. A nano-sized photon collector (NSPC) comprising:

(a) a nano-sized crystalline semiconducting particle, at least a portion of which is not insulated;

(b) a quantum dot photon collector particle (PC); and

(c) an insulating coating comprising silica on at least a portion of said PC.

2. An NSPC according to claim 1, comprising at least one electron injector (EI).

3. An NSPC according to claim 2, configured so that energy emitted by said PC particle is transferred to the EI.

4. An NSPC according to claim 2, configured so that a virtual photon emitted by said PC particle is transferred to the EI which injects an electron into the semiconducting particle.

5. An NSPC according to claim 1, configured so that energy emitted by said PC particle includes at least one of FRET and radiative energy.

6. An NSPC according to claim 1, wherein said nano-sized semiconducting particle comprises a metal dioxide, optionally titanium dioxide.

7. An NSPC according to claim 1, wherein said insulating coating comprises an oxide.

8. An NSPC according to claim 1, wherein said insulating coating comprises at least two layers.

9. A method for producing an insulated PC comprising:

(a) providing isolated quantum dot photon collector particles (PC); and

(b) insulating surfaces of said PC with a layer comprising silica .

10. A method according to claim 9, wherein said insulating comprises at least one of: (a) passivating, (b) modifying, (c) capping, (d) substituting, (e) electro-deposition and combinations thereof.

11. A method according to claim 9, wherein said insulating comprises applying a layer of an oxide to said surfaces of said PC.

12. A method according to claim 9, wherein said oxide includes at least one of TiO_2, SiO_2 and Al_2O_3.

13. A method according to claim 9, wherein said layer comprises at least two layers.

14. A method for producing a nano-sized photon collector particle (NSPC) comprising:

(a) providing a nano-sized crystalline semiconducting particle;

(b) applying one or more quantum dot photon collector particles (PC) to said nano-sized semiconducting particle; and

(c) insulating at least a portion of said PC while leaving at least a portion of said nano-sized semiconducting particle un-insulated;

so that a nano-sized photon collector particle (NSPC) is produced.

15. A method according to claim 14, wherein said insulating occurs prior to said applying.

16. A method according to claim 14, wherein said PC are insulated with silica prior to said applying.

17. A method according to claim 14, comprising insulating at least a portion of said PC with silica.

18. A method for producing a nano-sized photon collector (NSPC). comprising:

providing a nano-sized crystalline semiconducting particle;

coating at least a portion of a surface of said crystalline particle with an amorphous semiconductor layer;

forming at least one quantum dot photon collector particle (PC) on said coated portion of said surface;

applying an additional amorphous semiconductor layer to said PC; and

applying electron injector (EI) to an uncoated portion of said nano-sized crystalline semiconducting particle;

to produce said nano-sized photon collector (NSPC).

19. A method according to claim 18, wherein said coating and said applying each independently comprise at least one process selected from the group consisting of: crystallizing, chemically reducing, pH adjustment, precipitation, oxidation, condensation, polymerization, complexation and substitution.

20. A method for producing a nano-sized photon collector (NSPC).

comprising:

providing quantum dot photon collector particles (PC) with surfaces insulated at least with a layer comprising silica;

forming a nano-sized semiconducting particle on said PC; and

applying an electron injector (EI) to produce said nano-sized photon collector (NSPC).

21. A method according to claim 20, wherein said forming comprises at least one process selected from the group consisting of: crystallizing, chemical reduction, pH adjustment, precipitation, oxidation, condensation, polymerization, complexation and substitution.

22. A method according to claim 20, wherein said surface of said PC is also insulated with at least one layer not comprising silica.

23. A method for producing a nano-sized photon collector(NSPC) particle comprising:

(a) providing a nano-sized crystalline semiconducting particle with an electron injector (EI) on at least a portion of its surface;

(b) applying one or more insulated quantum dot photon collector particles (PC) to said nano-sized semiconducting particle ;

so that said nano-sized photon collector(NSPC) particle is produced.

24. A method according to claim 23, wherein said applying includes attachment via a linker molecule.

25. A FRET enhanced dye-sensitized solar cell (FSC) comprising (a) an electrolyte,

(b) a plurality of nano-sized photon collectors (NSPC) according to claim 1 arranged so that said insulating coating on said PC blocks direct contact between said PC and said electrolyte; and

(c) at least one electron injector (EI).

26. An FSC according to claim 25, wherein at least some of said at least one EI is in direct contact with said nano-sized semiconducting particle.

27. An FSC according to claim 25, wherein at least some of said at least one EI is in contact with said nano-sized semiconducting particle via an electrically conductive insulating coating on said PC.

28. An FSC according to claim 25, wherein at least some of said at least one EI is in direct contact with said electrolyte.

29. An FSC according to claim 25, wherein at least some of said at least one EI is in contact with said electrolyte via an electrically conductive insulating coating.

AMENDED CLAIMS
Received by the International Bureau on 25.Dec.2011 (25.12.2011)

1. A nano-sized photon collector (NSPC) comprising:
    a. a nano-sized crystalline semiconducting particle, at least a portion of which is not coated;
    b. a non-injecting Quantum Dot Photon Collector particle (PC); and
    c. a protective coating comprising silica on a least a portion of said PC, that when applied gives the PC lasting protection from corrosive action of electrolytes.

2. An NSPC according to claim 1, comprising at least one electron injector (IE)

3. An NSPC according to claim 2, where the PC emission spectrum and EI absorption spectrum are selected so that energy emitted by said PC particle is transferred to the EI.

4. An NSPC according to claim 3, wherein the transfer of energy from the PC to the EI causes the EI to inject an electron into the semiconducting particle.

5. An NSPC according to claim 1, where energy absorbed by said PC particle is re-emitted as at least one of FRET and radiative energy.

6. An NSPC according to claim 1, wherein said nano-sized semiconducting particle comprises a metal dioxide, optionally titanium dioxide.

7. An NSPC according to claim 1, wherein said insulating coating comprises at least two layers.

8. A method for producing a chemically protected PC comprising:
    a. providing isolated quantum dot photon collector particles (PC); and
    b. coating surfaces of said PC with a protective coating that gives lasting protection from the corrosive action of electrolytes.

9. A method according to claim 8, wherein said coating comprises at least one of:

(a) passivating, (b) modifying, (c) capping, (d) substituting, (e) electro-deposition and combinations thereof.

10. A method according to claim 8, wherein said coating comprises applying a layer of an oxide to said surfaces of said PC.

11. A method according to claim 8, wherein said oxide includes at least one of TiO2, SiO2 and Al2O3.

12. A method according to claim 8, wherein said layer comprises at least two layers.

13. A method for producing a nano-sized photon collector particle (NSPC) comprising:
    a. providing a nano-sized crystalline semiconducting particle;
    b. applying one or more non-injecting quantum dot photon collector particles (PC) to said nano-sized semiconducting particle; and
    c. coating at least a portion of said PC while leaving at least a portion of said nanosized semiconducting particle un-coated;

    so that a nano-sized photon collector particle (NSPC) is produced.

14. A method according to claim 13, wherein said coating occurs prior to said applying.

15. A method according to claim 13, wherein said PC are coated with silica prior to said applying.

16. A method according to claim 13, comprising coating at least a portion of said PC with silica.

17. A method for producing a nano-sized photon collector (NSPC). comprising:
    a. providing a nano-sized crystalline semiconducting particle;
    b. coating at least a portion of a surface of said crystalline particle with an amorphous semiconductor layer;
    c. forming at least one quantum dot photon collector particle (PC) on said coated portion of said surface;

d. applying an additional amorphous semiconductor layer to said PC; and
e. applying electron injector (EI) to an uncoated portion of said nano-sized crystalline semiconducting particle;

to produce said nano-sized photon collector (NSPC).

18. A method according to claim 17, wherein said coating and said applying each independently comprise at least one process selected from the group consisting of: crystallizing, chemically reducing, pH adjustment, precipitation, oxidation, condensation, polymerization, complexation and substitution.

19. A method for producing a nano-sized photon collector (NSPC).
comprising:
a. *providing quantum dot photon* collector particles (PC) with surfaces coated at least with a layer comprising silica, such that they gain lasting protection from the corrosive action of electrolytes ;
b. forming a nano-sized semiconducting particle on said PC; and
c. applying an electron injector (EI) to produce said nano-sized photon collector (NSPC).

20. A method according to claim 19, wherein said forming comprises at least one process selected from the group consisting of: crystallizing, chemical reduction, pH adjustment, precipitation, oxidation, condensation, polymerization, complexation and substitution.

21. A method according to claim 19, wherein said surface of said PC is also insulated with at least one layer not comprising silica.

22. A method for producing a nano-sized photon collector(NSPC) particle comprising:
a. providing a nano-sized crystalline semiconducting particle with an electron injector (EI) on at least a portion of its surface; and
b. applying one or more chemically protected, non-injecting quantum dot photon collector particles (PC) to said nano-sized semiconducting particle ;

so that said nano-sized photon collector(NSPC) particle is produced.

23. A method according to claim 22, wherein said applying includes attachment via a linker molecule.

24. A FRET enhanced dye-sensitized solar cell (FSC) comprising
    a. an electrolyte,
    b. a plurality of nano-sized photon collectors (NSPC) according to claim 1 arranged so that said protective coating on said PC blocks direct contact between said PC and said electrolyte; and
    c. at least one electron injector (EI).

25. An FSC according to claim 24, wherein at least some of said at least one EI is in direct contact with said nano-sized semiconducting particle.

26. An FSC according to claim 24, wherein at least some of said at least one EI is in contact with said nano-sized semiconducting particle via an electrically conductive protective coating on said PC.

27. An FSC according to claim 24, wherein at least some of said at least one EI is in direct contact with said electrolyte.

28. An FSC according to claim 24, wherein at least some of said at least one EI is in contact with said electrolyte via an electrically conductive protective coating.

Fig.1

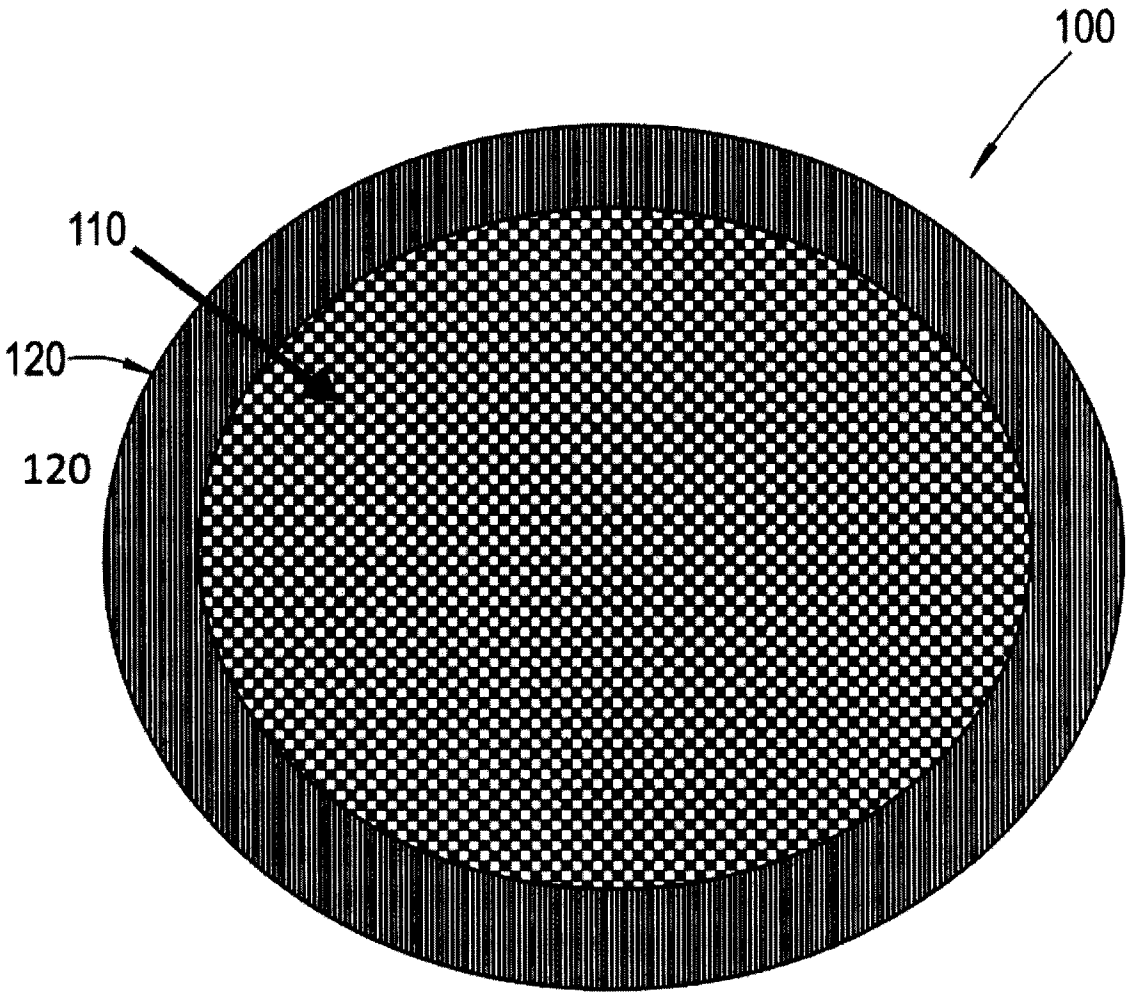


Fig.2

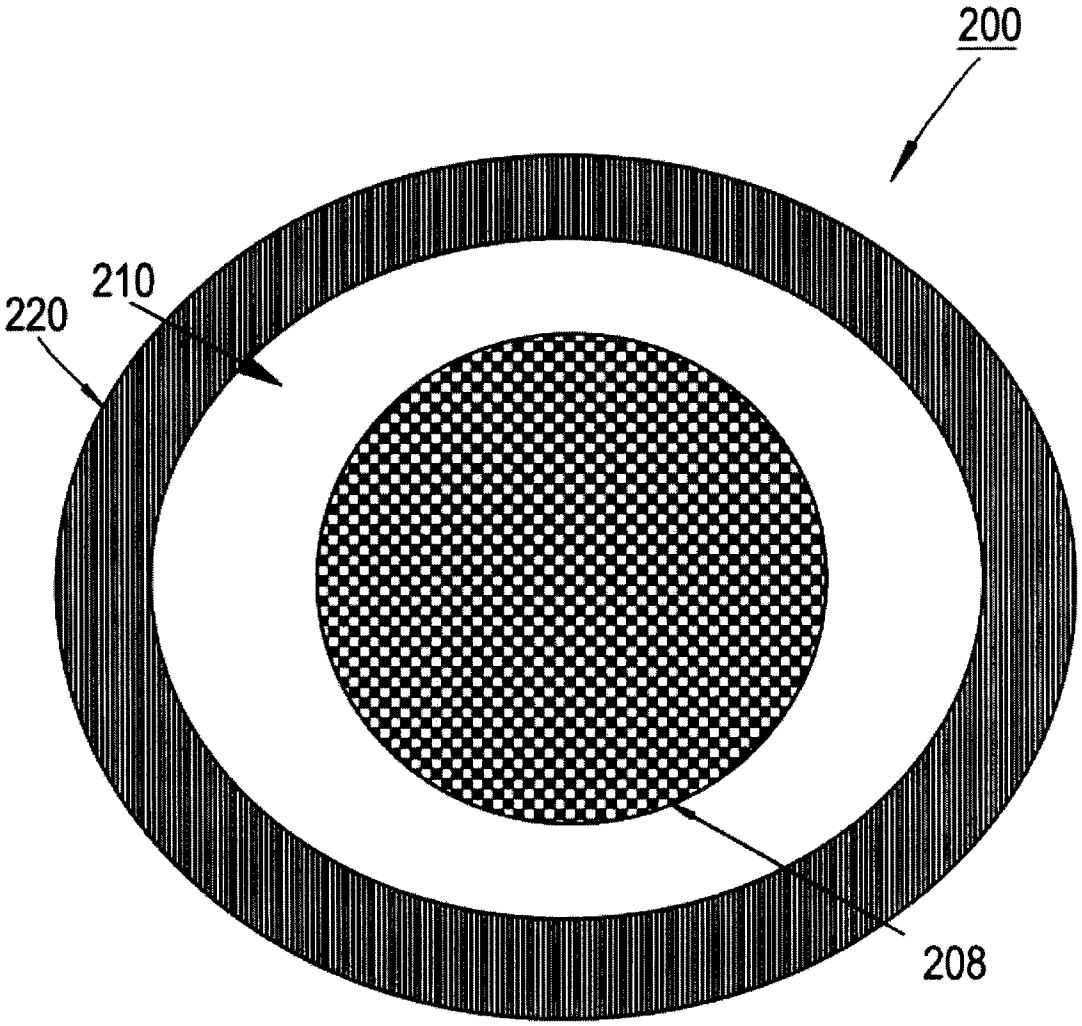


Fig.3

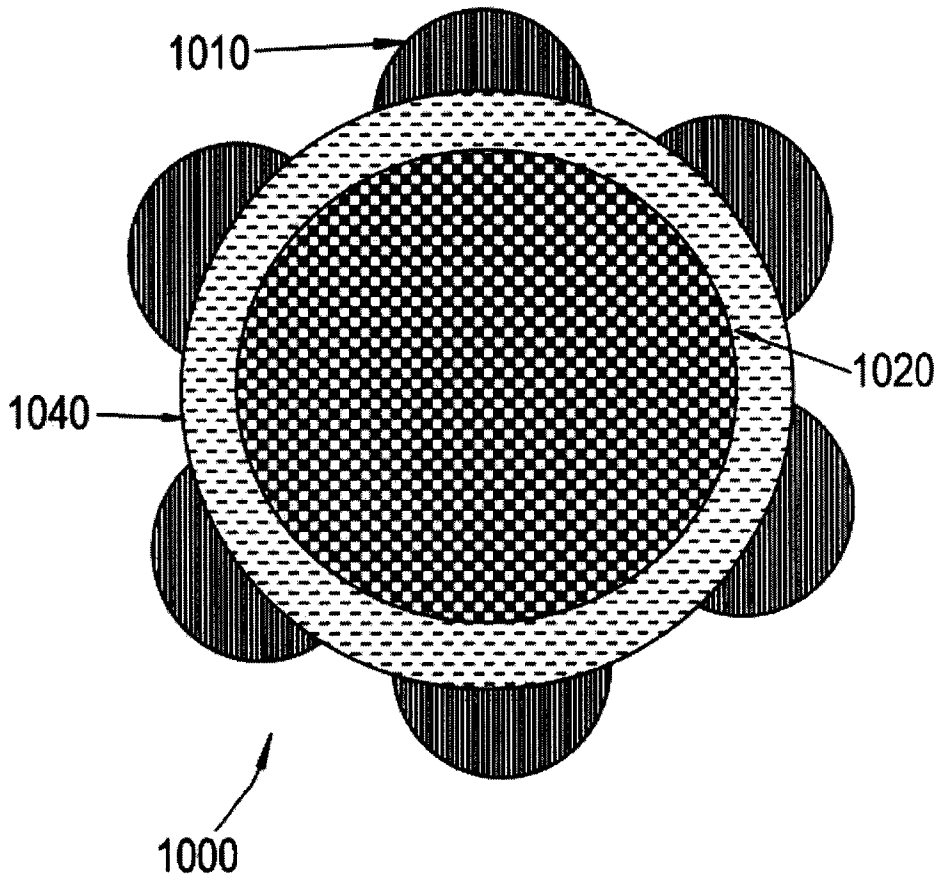


Fig.4

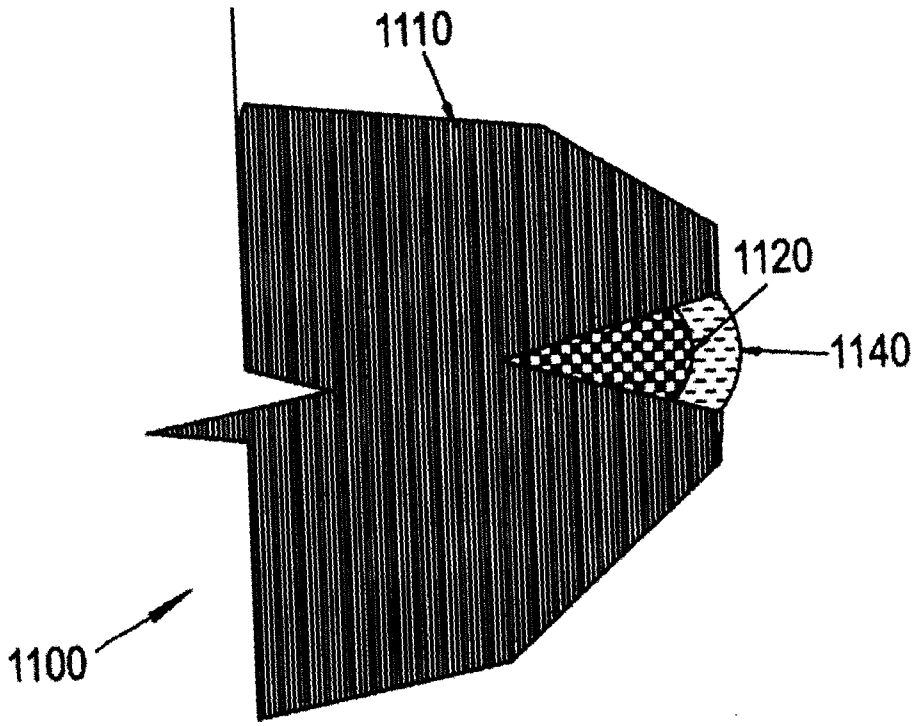


Fig.5

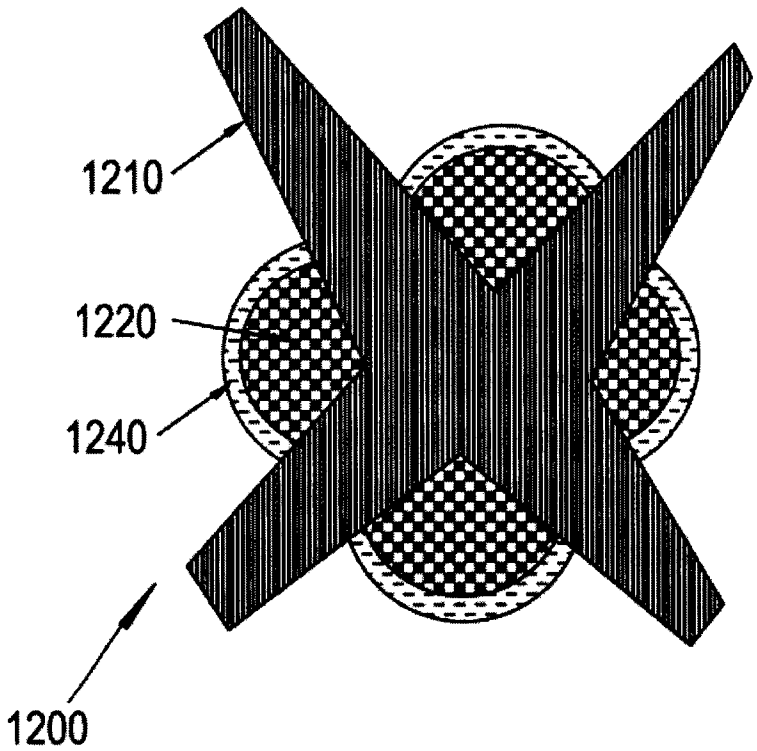
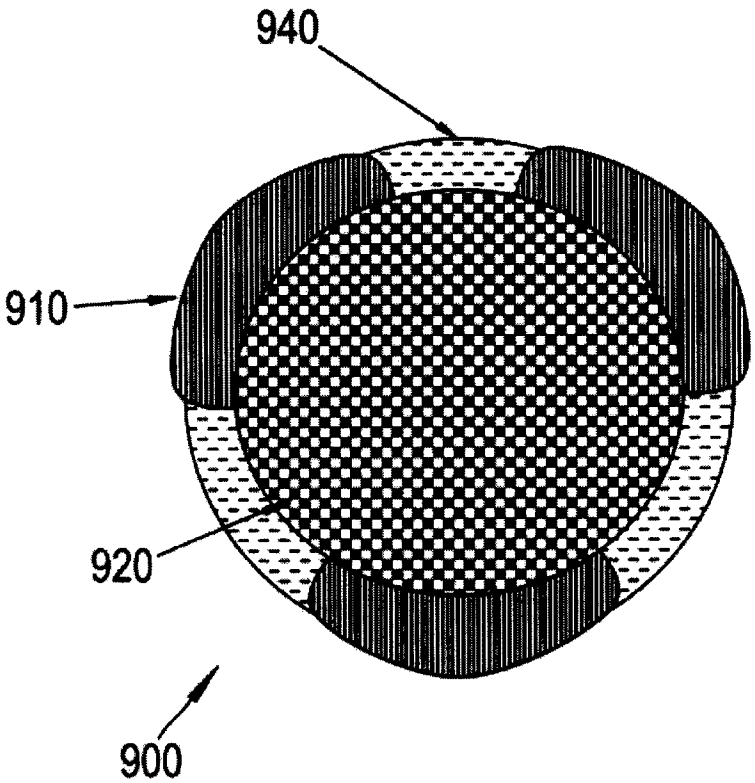


Fig.6



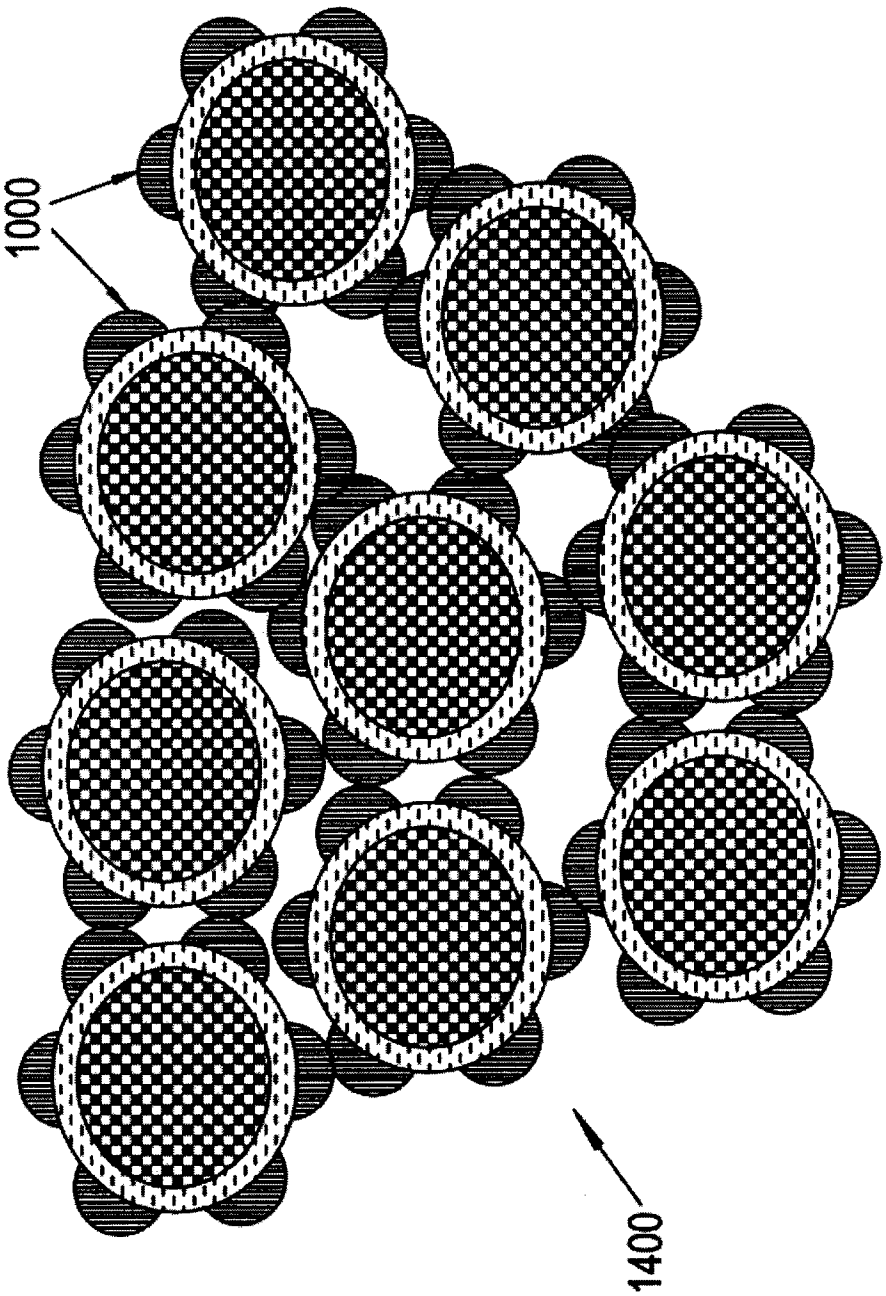
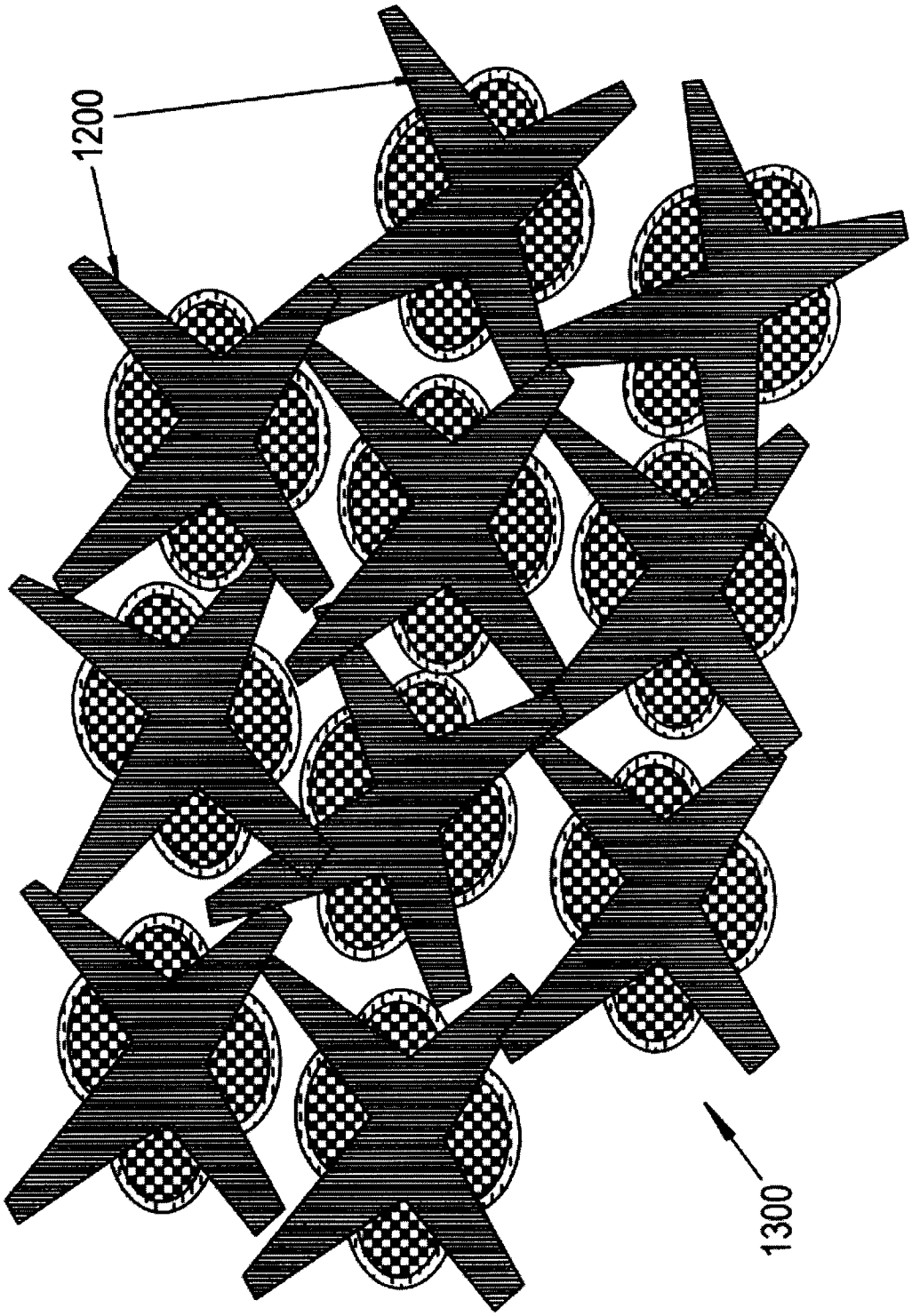


Fig.7

Fig.8



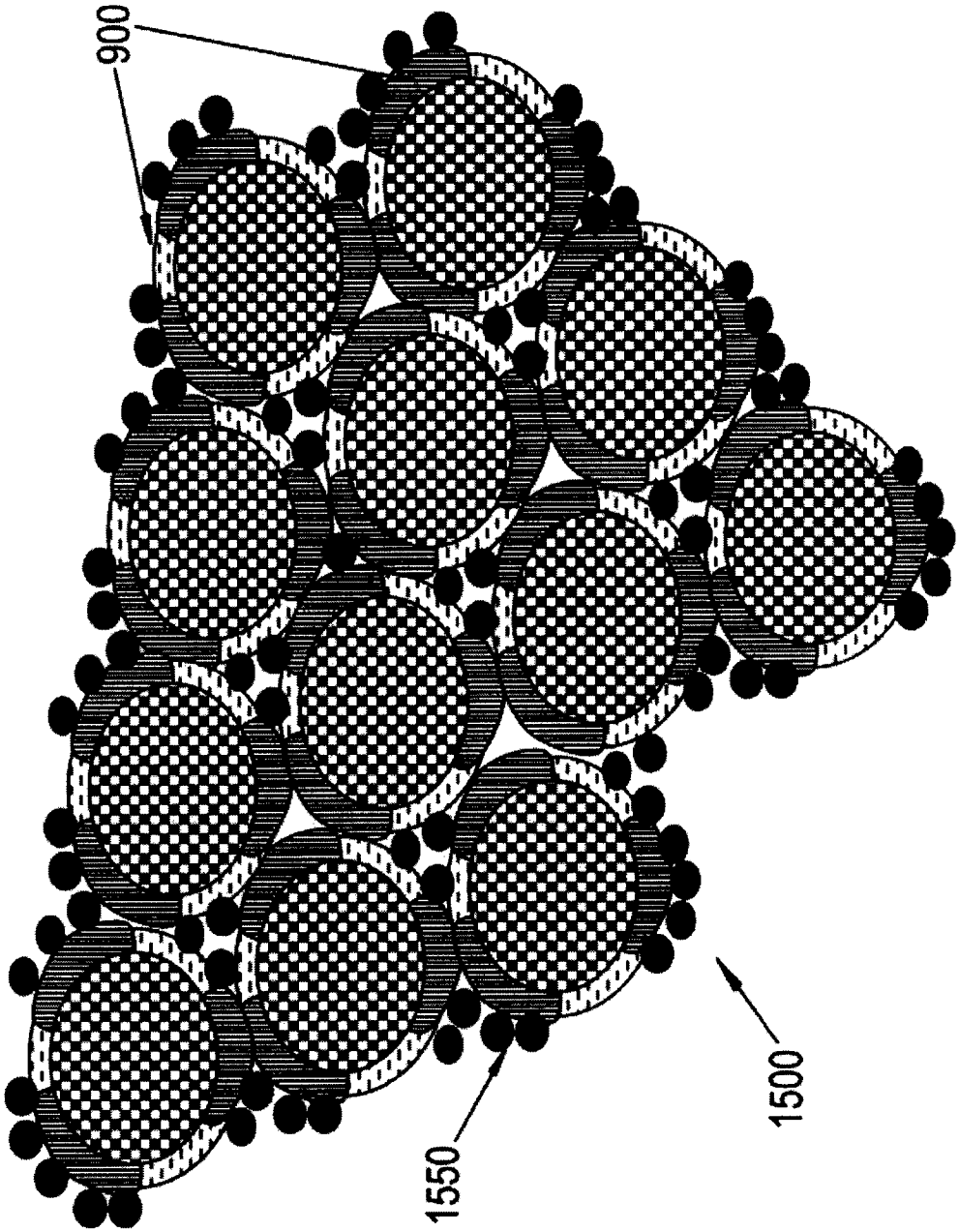


Fig.9

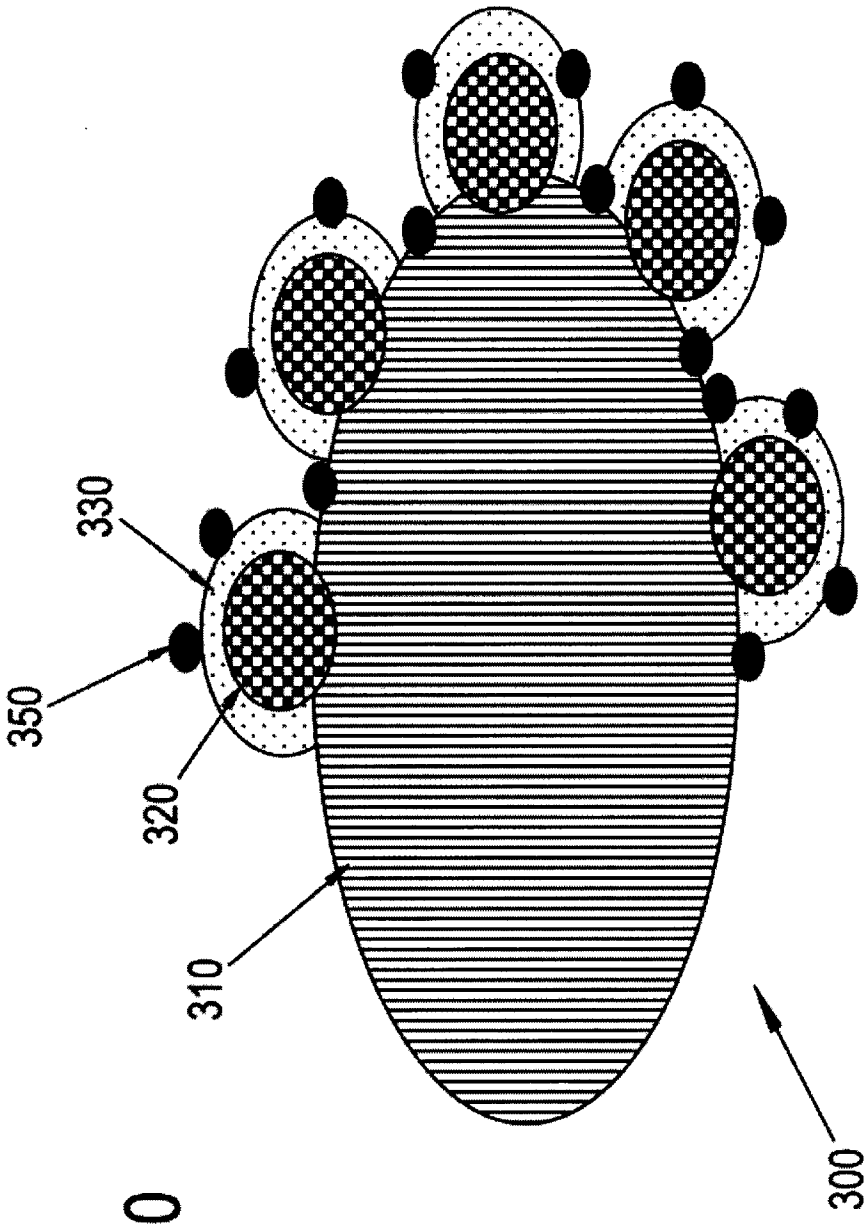


Fig.10

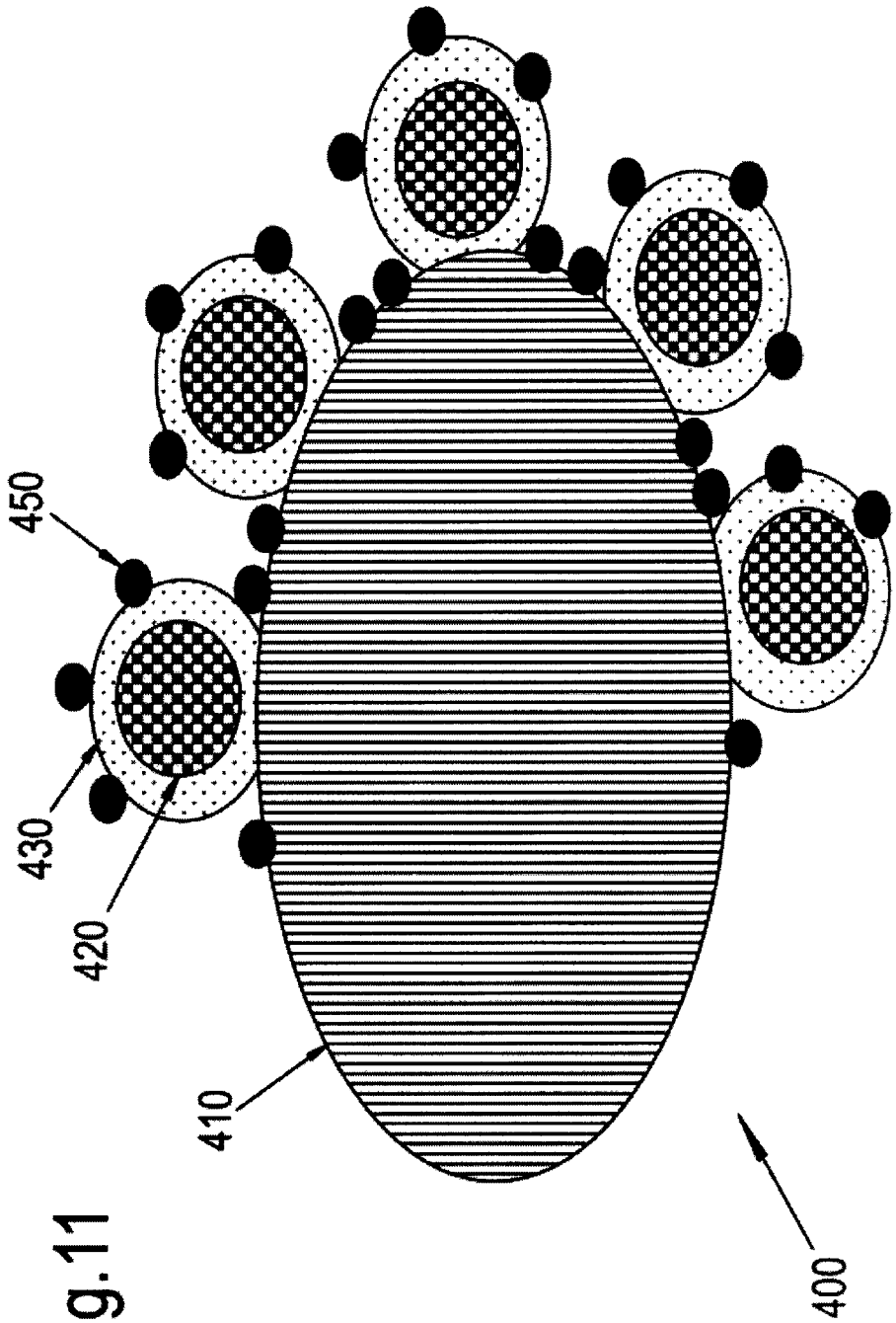


Fig.11

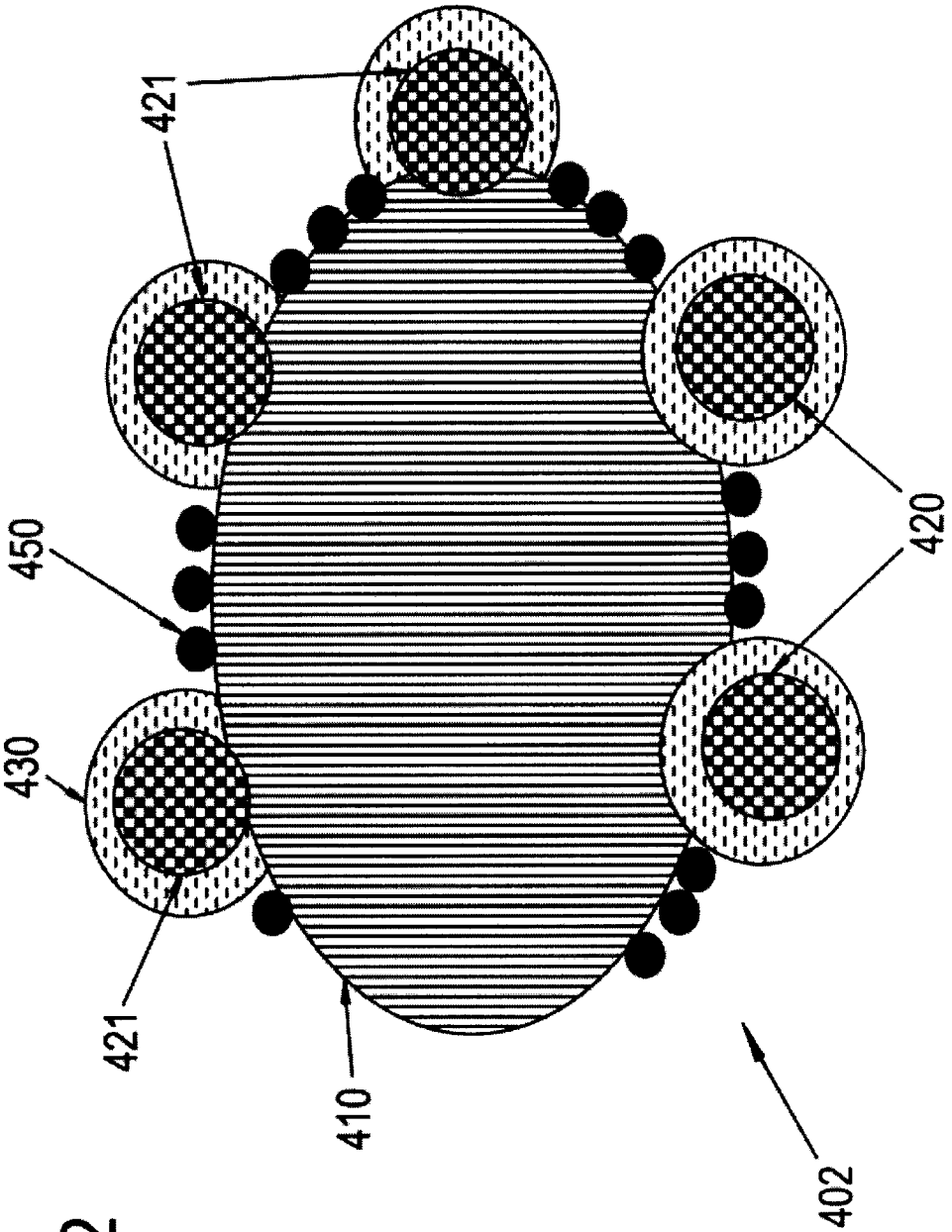


Fig.12

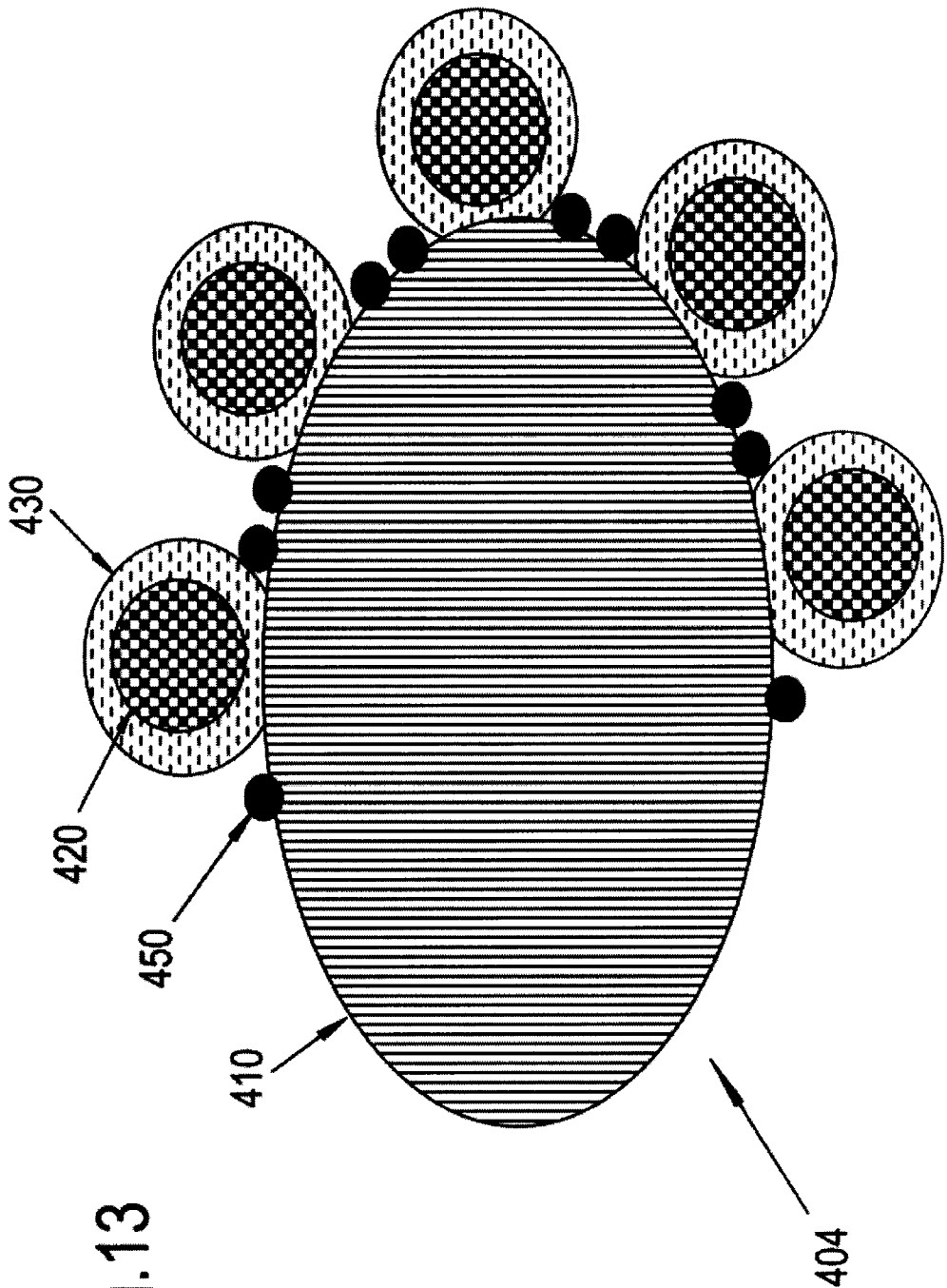


Fig.13

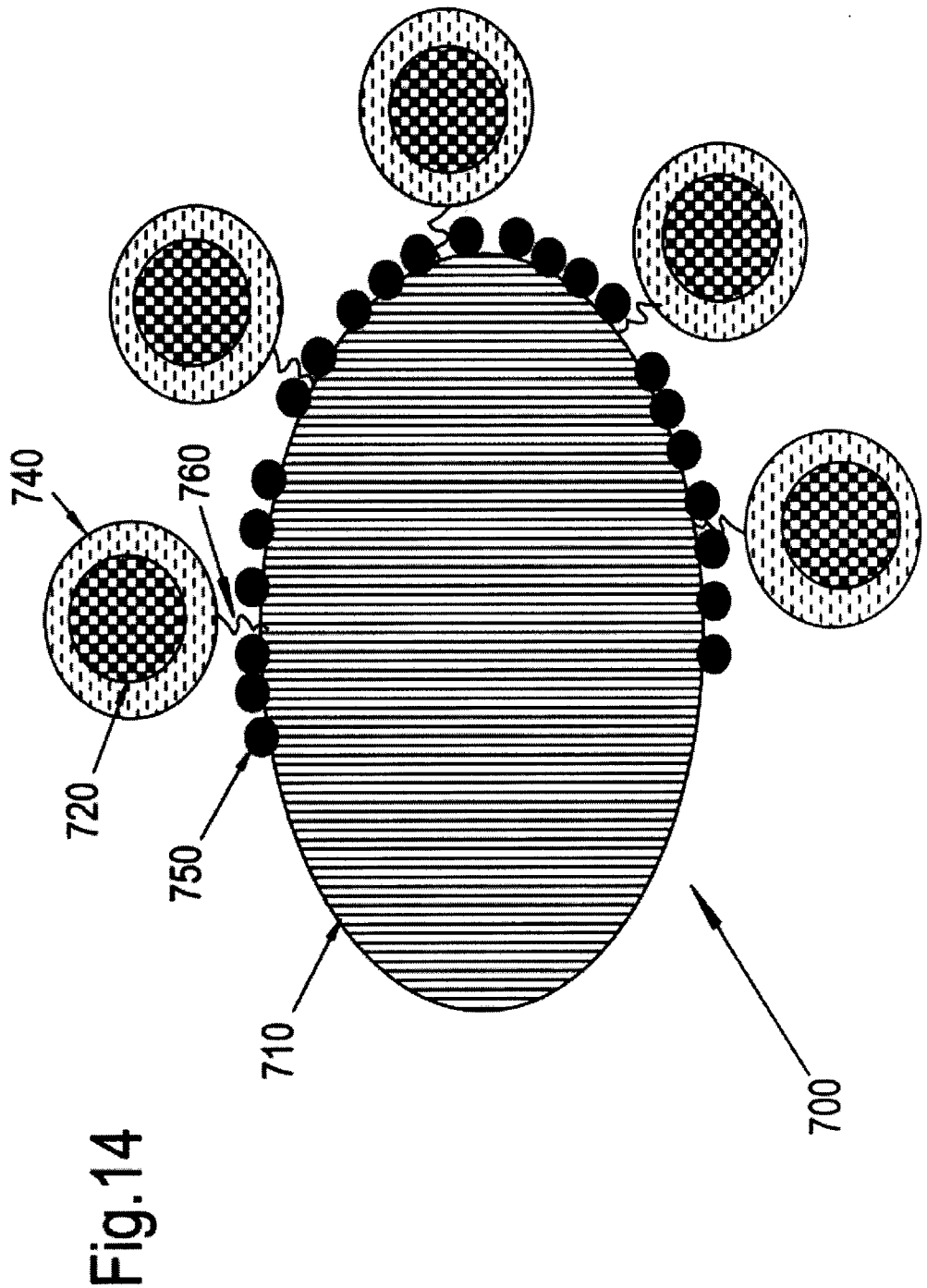


Fig.14

Fig.16

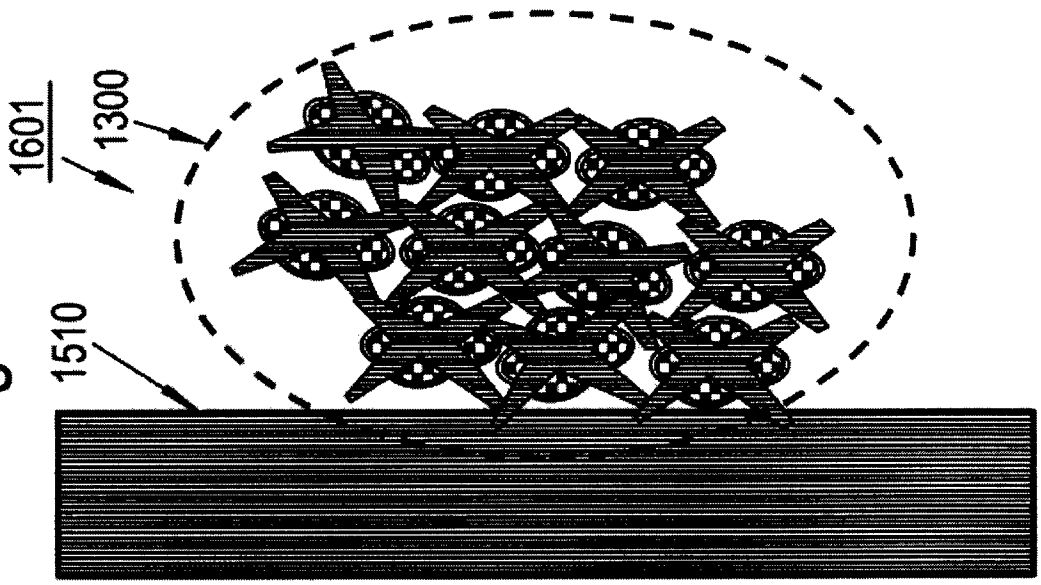
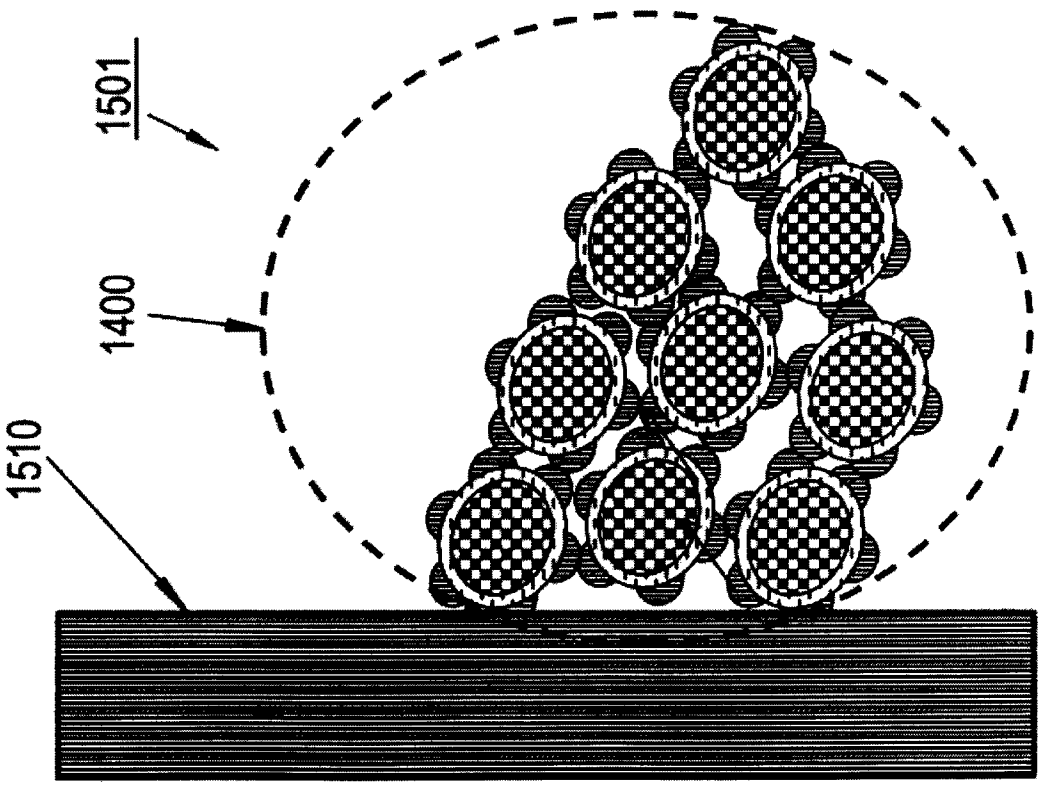


Fig.15



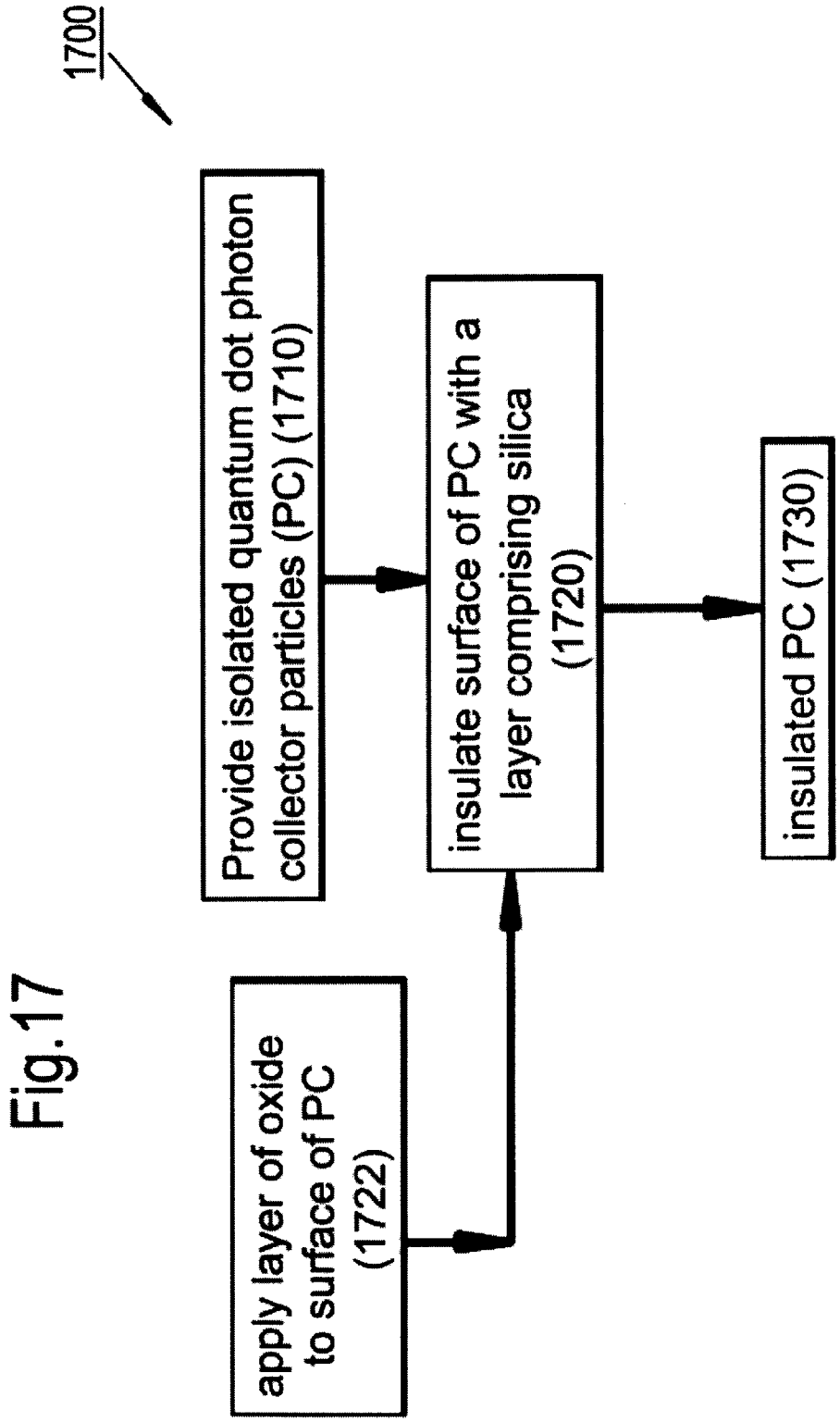

1700
Provide isolated quantum dot photon collector particles (PC) (1710)
insulate surface of PC with a layer comprising silica (1720)
insulated PC (1730)
apply layer of oxide to surface of PC (1722)

Fig.17

Fig.18

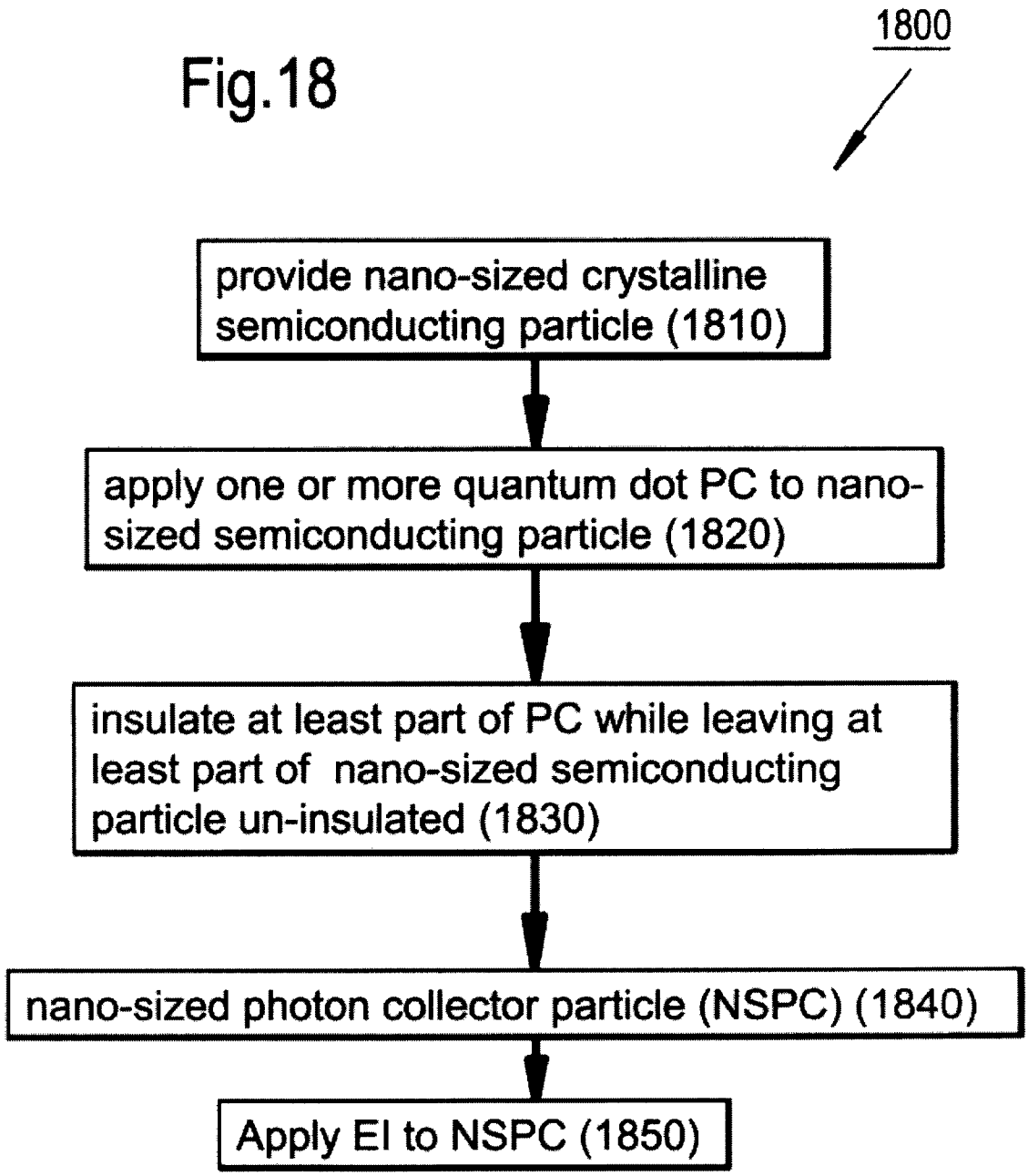

1800
provide nano-sized crystalline semiconducting particle (1810)
apply one or more quantum dot PC to nano-sized semiconducting particle (1820)
insulate at least part of PC while leaving at least part of nano-sized semiconducting particle un-insulated (1830)
nano-sized photon collector particle (NSPC) (1840)
Apply EI to NSPC (1850)

Fig.19

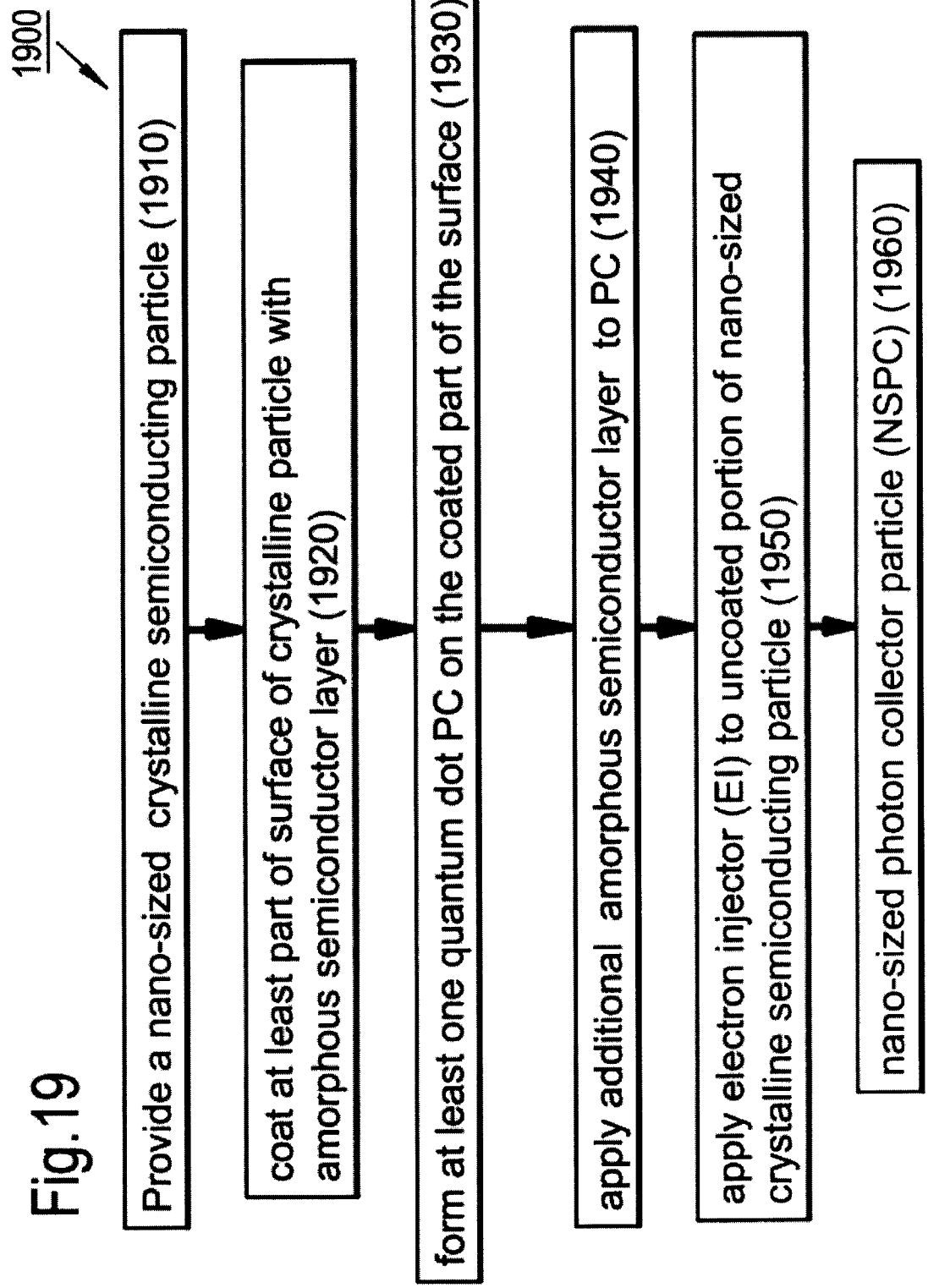

1900
Provide a nano-sized crystalline semiconducting particle (1910)
coat at least part of surface of crystalline particle with amorphous semiconductor layer (1920)
form at least one quantum dot PC on the coated part of the surface (1930)
apply additional amorphous semiconductor layer to PC (1940)
apply electron injector (EI) to uncoated portion of nano-sized crystalline semiconducting particle (1950)
nano-sized photon collector particle (NSPC) (1960)

Fig.20

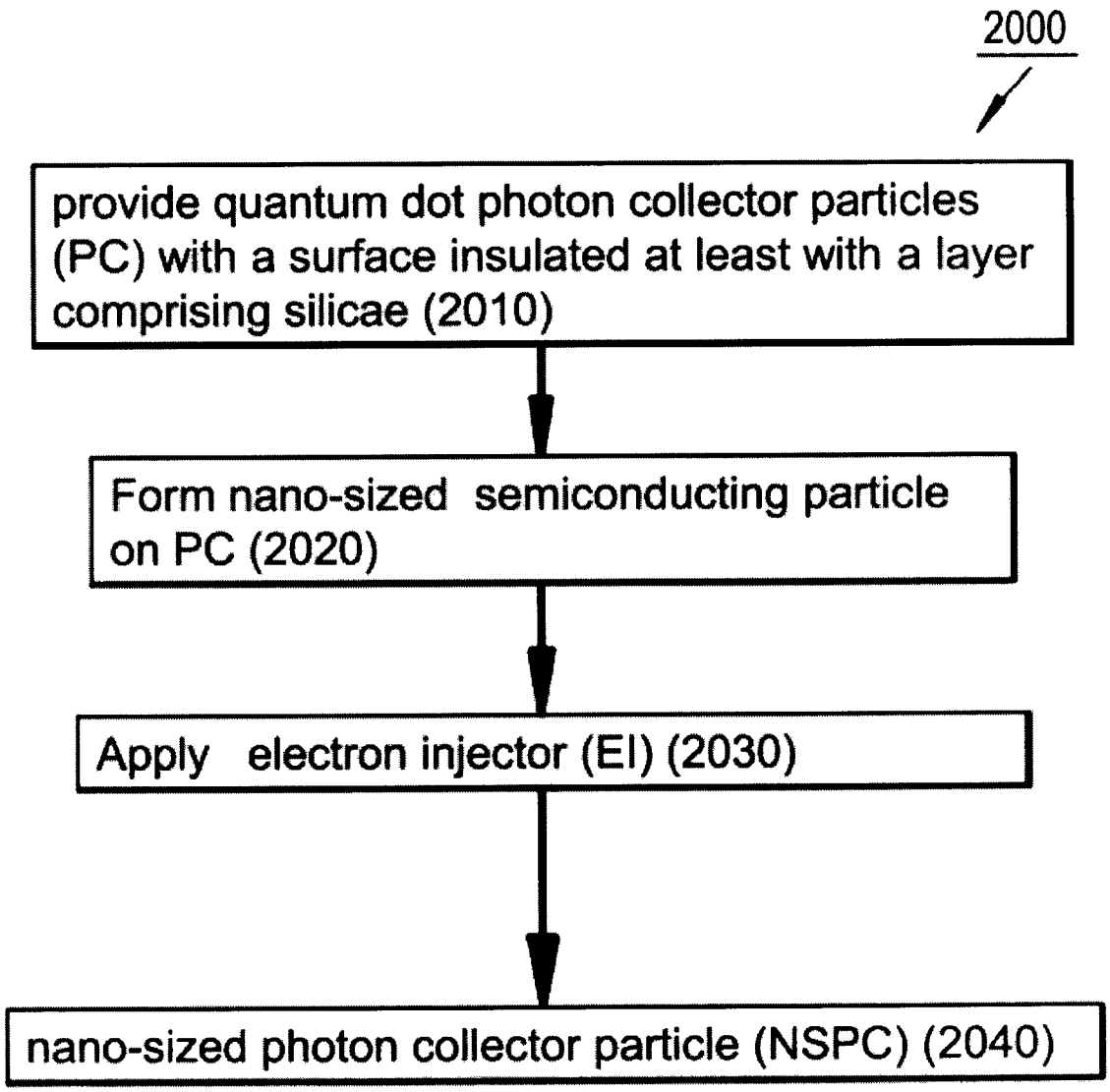

2000
provide quantum dot photon collector particles (PC) with a surface insulated at least with a layer comprising silicae (2010)
Form nano-sized semiconducting particle on PC (2020)
Apply electron injector (EI) (2030)
nano-sized photon collector particle (NSPC) (2040)

Fig.21

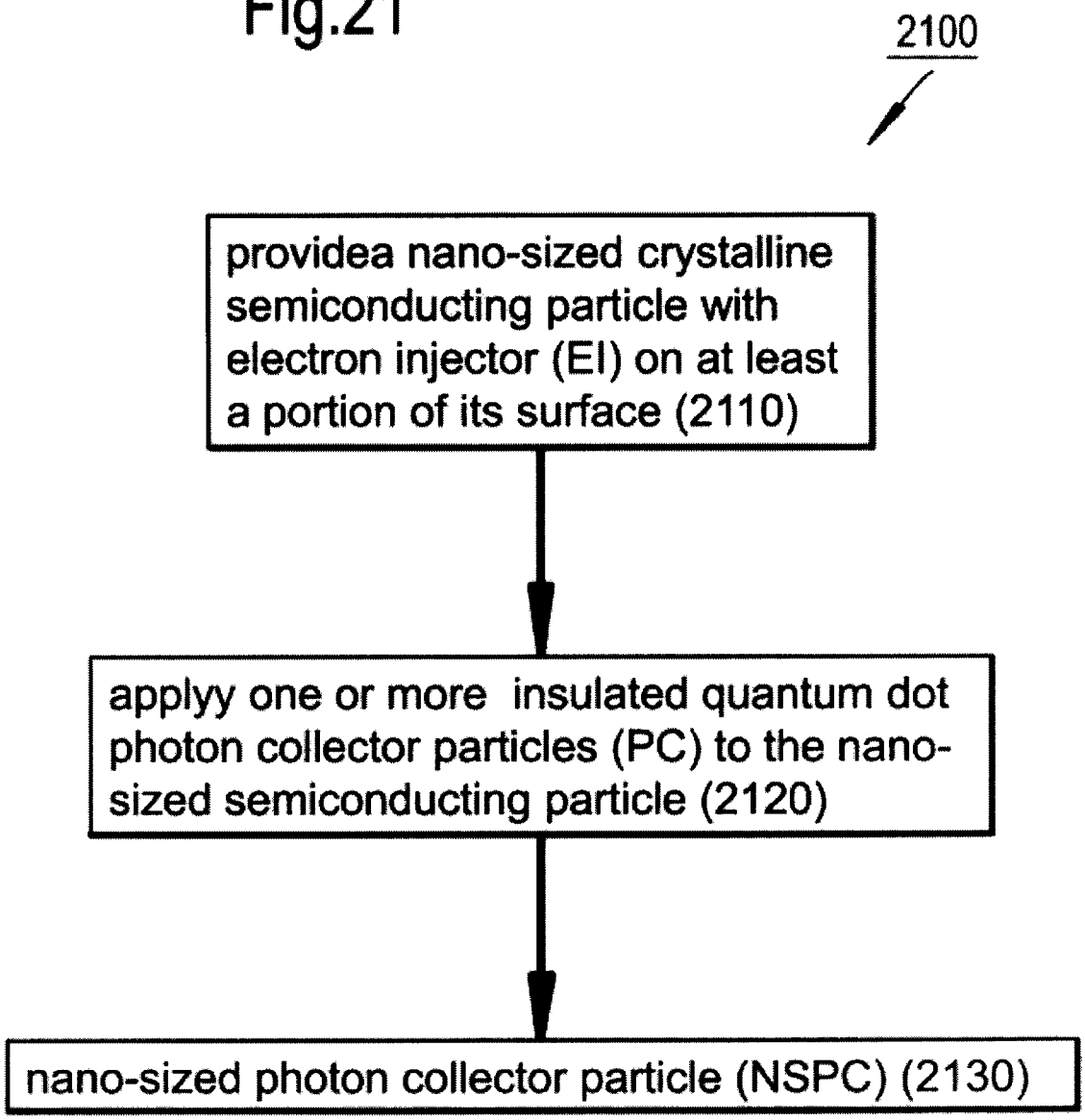
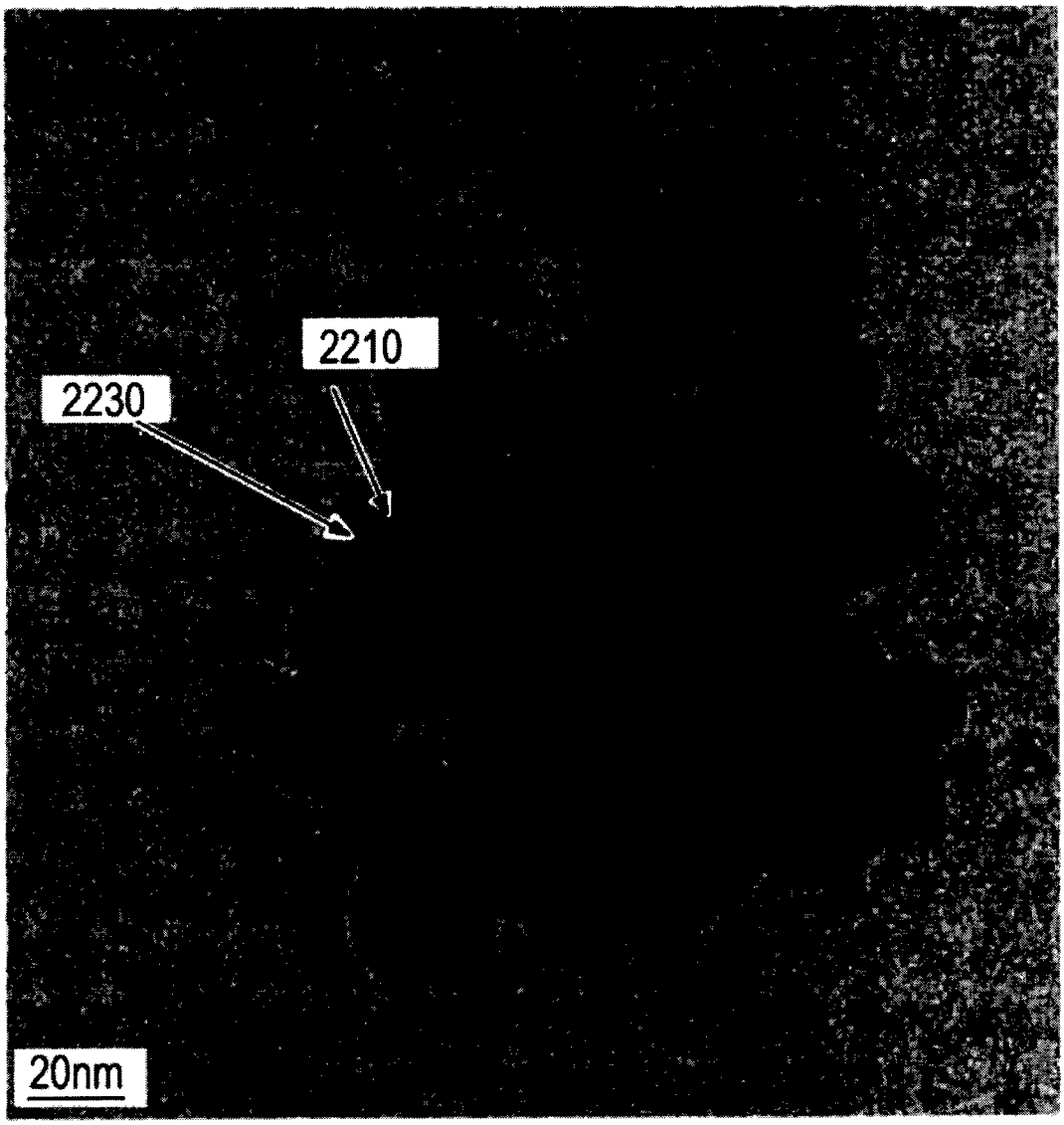

2100
providea nano-sized crystalline semiconducting particle with electron injector (EI) on at least a portion of its surface (2110)
applyy one or more insulated quantum dot photon collector particles (PC) to the nano-sized semiconducting particle (2120)
nano-sized photon collector particle (NSPC) (2130)

Fig.22



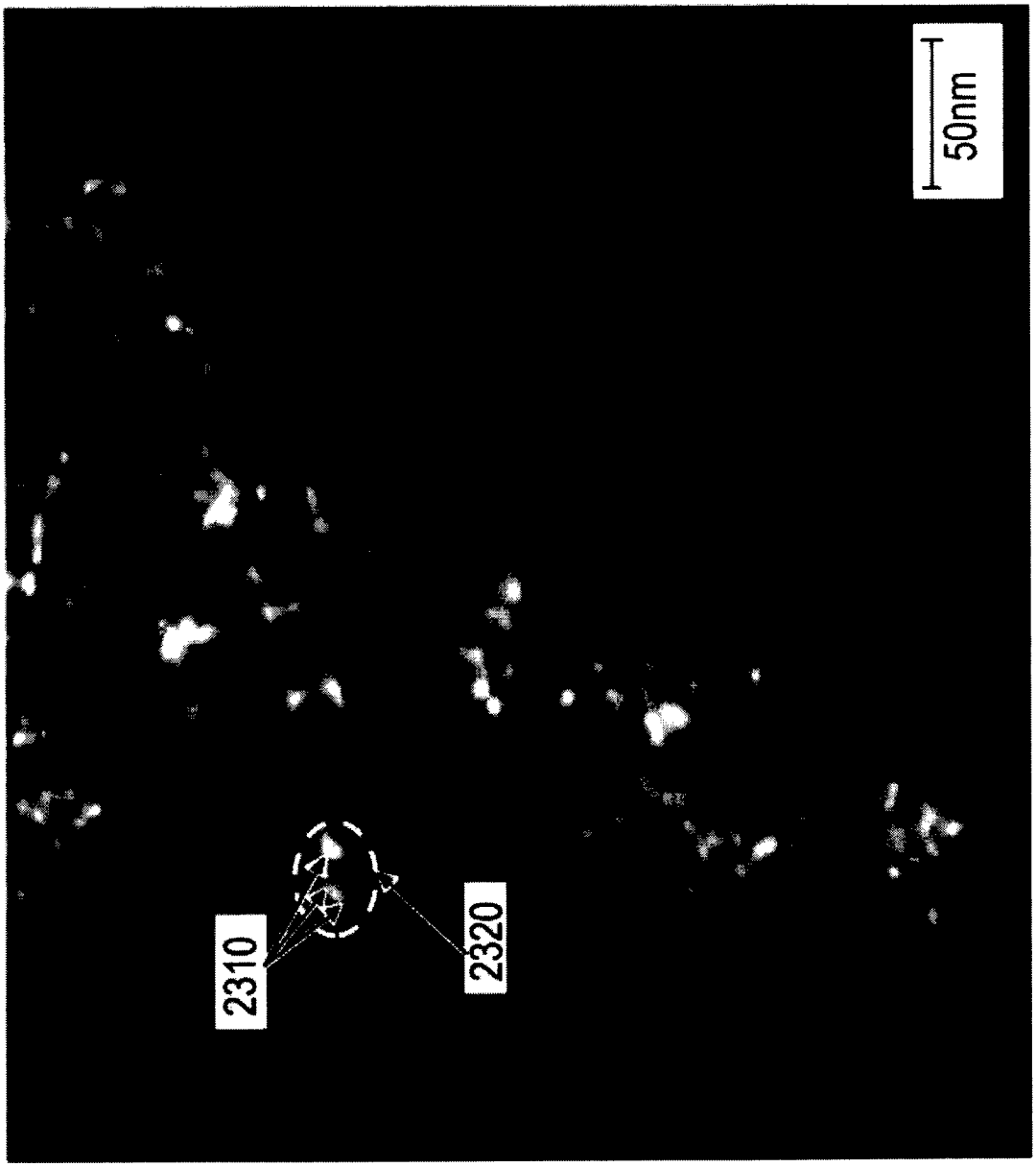


Fig.23

Fig.24

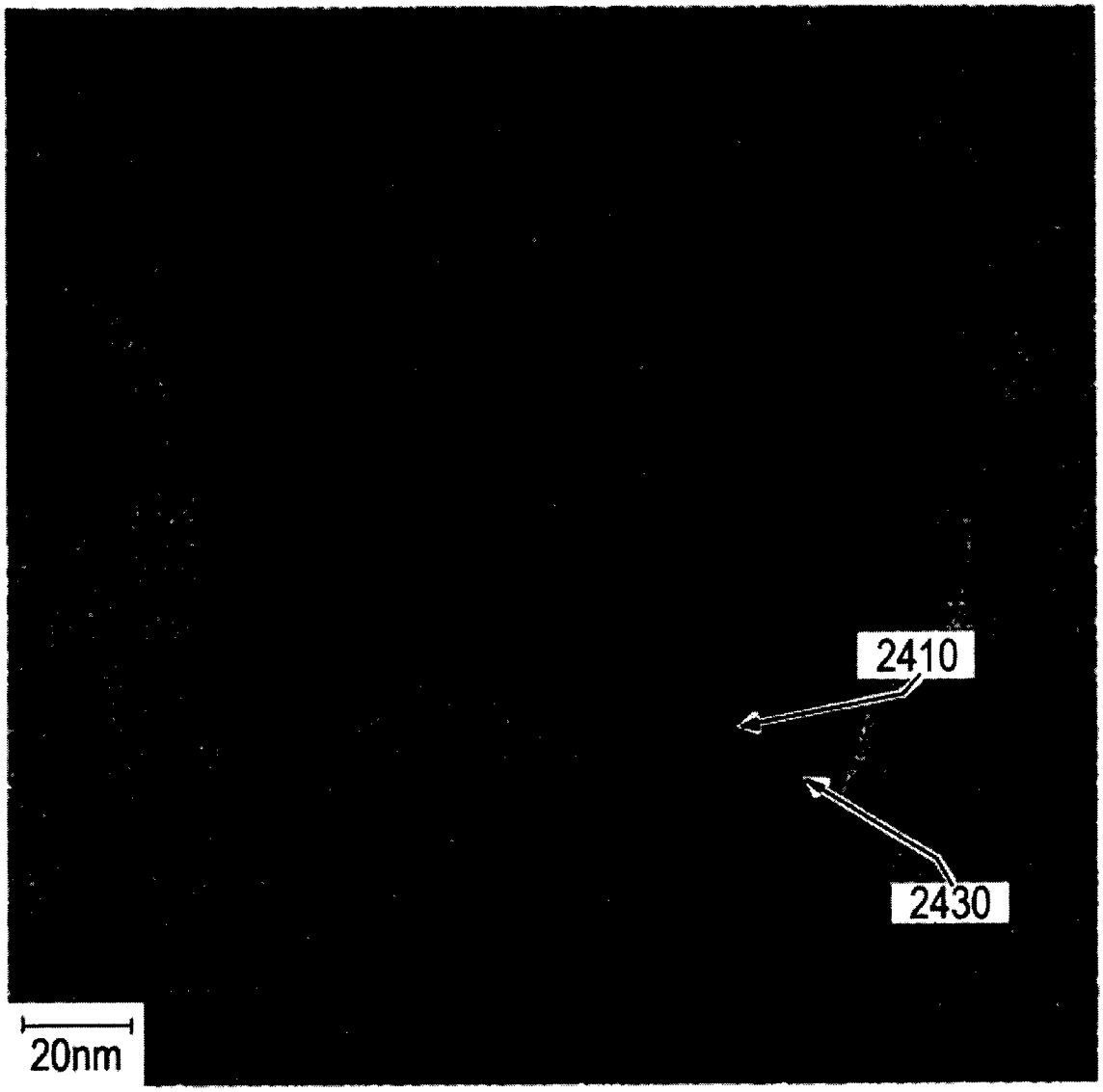


Fig.25

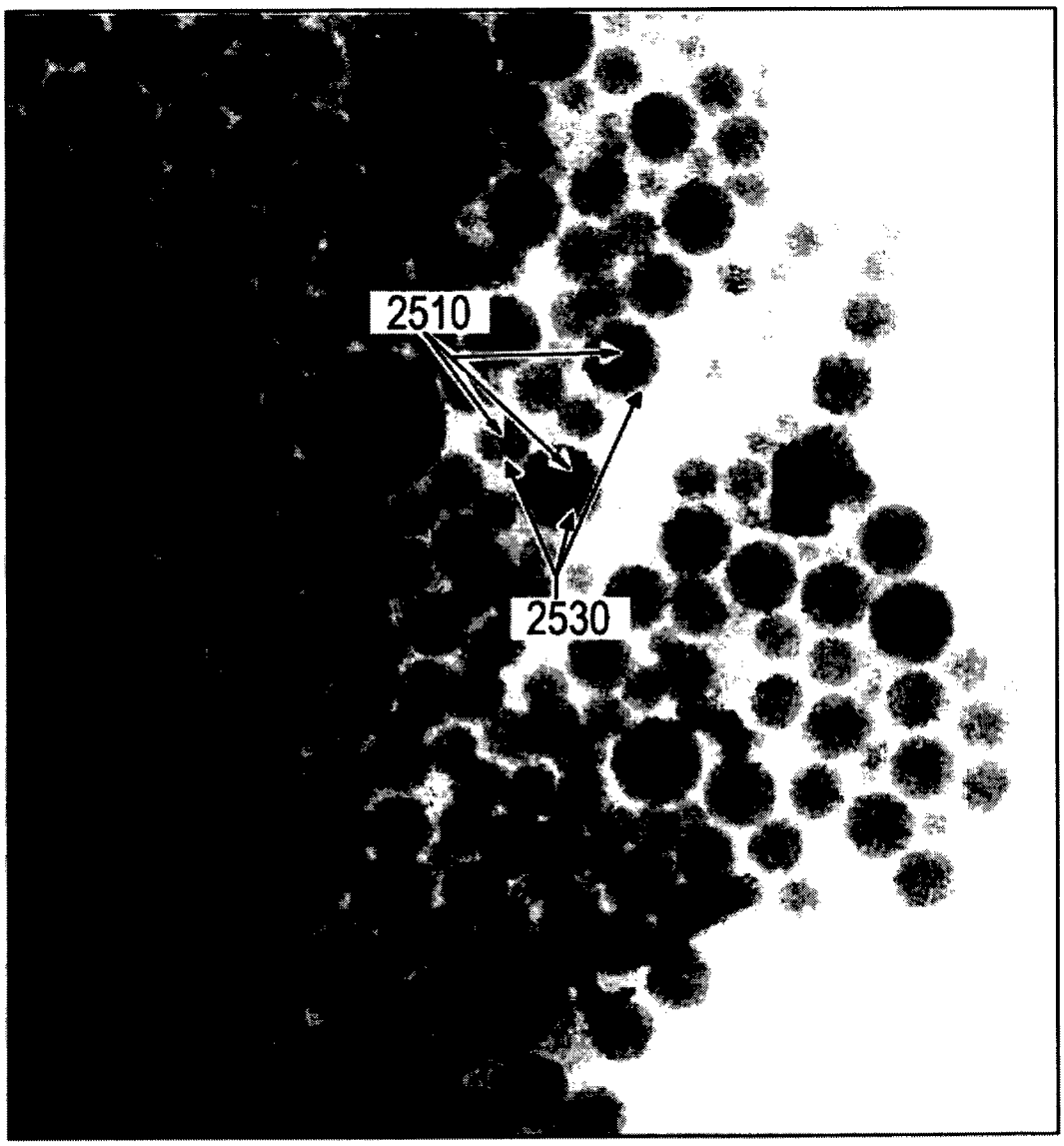
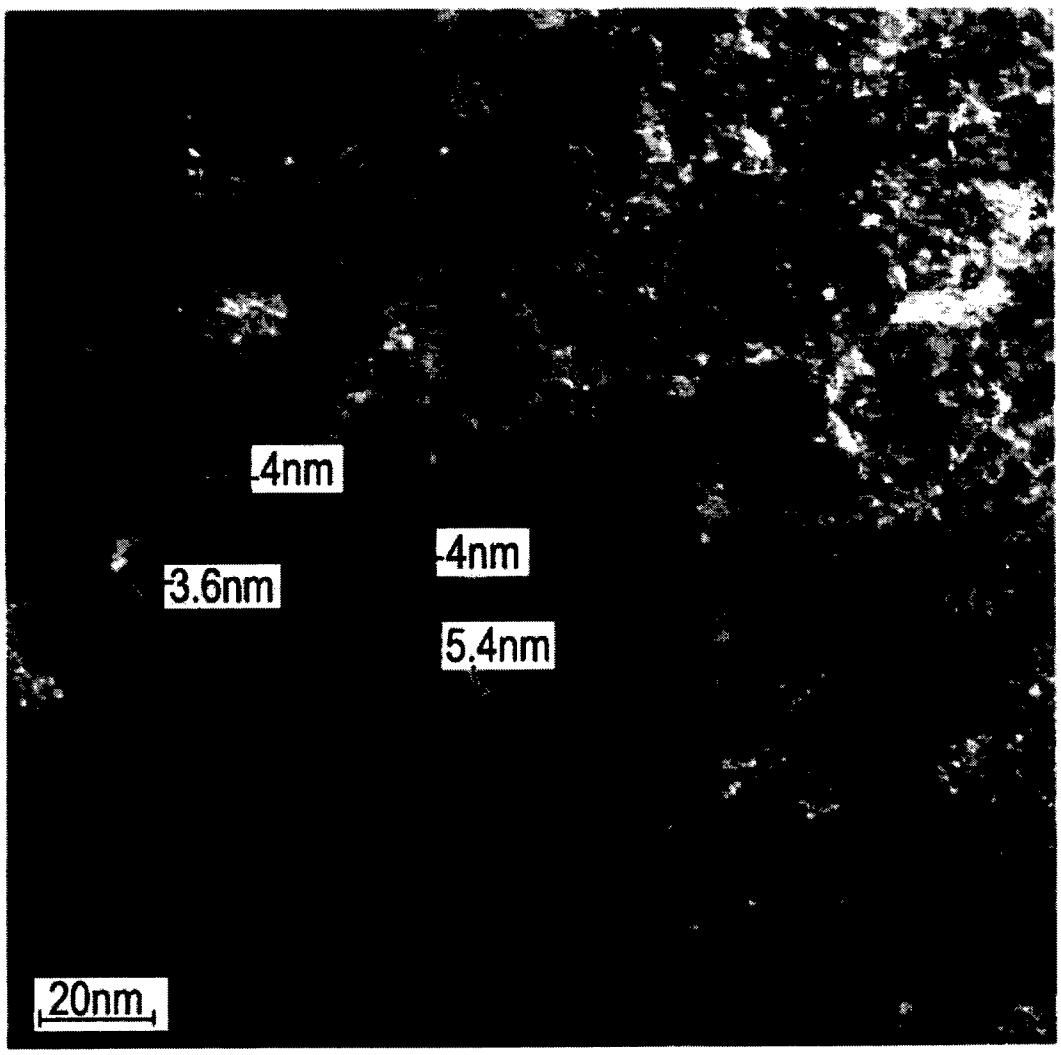


Fig.26



INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2011/000603

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01G9/20
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01G

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SOPHIA BUHBUT ET AL: "Built-in Quantum Dot Antennas in Dye-Sensitized Solar Cells", ACS NANO, AMERICAN CHEMICAL SOCIETY, UNITED STATES, vol. 4, no. 3, 23 March 2010 (2010-03-23), pages 1293-1298, XP002637326, ISSN: 1936-0851, DOI: 10.1021/NN100021B [retrieved on 2010-02-15] the whole document -----	1-13,17, 20-22
X	US 2006/165404 A1 (JUNG WON-CHEOL [KR] ET AL) 27 July 2006 (2006-07-27) paragraphs [0011], [0017], [0034] - [0037]; claims 5-8 -----	1-17, 20-29
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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
18 October 2011	25/10/2011

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Wolfbauer, Georg

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2011/000603

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KEVIN TVRDY ET AL: "Substrate Driven Photochemistry of CdSe Quantum Dot Films: Charge Injection and Irreversible Transformations on Oxide Surfaces +", THE JOURNAL OF PHYSICAL CHEMISTRY A, vol. 113, no. 16, 16 January 2009 (2009-01-16), pages 3765-3772, XP55009700, ISSN: 1089-5639, DOI: 10.1021/jp808562x	9-12
A	the whole document -----	1
A	MORA-SERO I ET AL: "Large improvement of electron extraction from CdSe quantum dots into a TiO2 thin layer by N3 dye coabsorption", THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 516, no. 20, 30 August 2008 (2008-08-30), pages 6994-6998, XP022777897, ISSN: 0040-6090, DOI: 10.1016/J.TSF.2007.12.110 [retrieved on 2007-12-23] the whole document -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IL2011/000603

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006165404 A1	27-07-2006	JP 2006202762 A	03-08-2006
		KR 20060085109 A	26-07-2006