ABSTRACT OF THE DISCLOSURE

A new generation solar cell is disclosed that absorbs radiated sunlight across a wide spectrum of wavelengths using a glass-metal twin tube assembly exhibiting photonic to electric conversion and thermal absorption simultaneously. More specifically, the twin tube solar cell assembly consists in a metallic tube inserted into a glass tube coated with a dye-sensitized semiconductor electrode and space between twin tubes filled with suitable electrolyte. Sunlight radiate through the glass tubes onto the dyed semiconductor which absorb the photonic and thermal energy. The photonic energy is converted to useful electric energy while the thermal energy is conducted through to the metal tube by heat transfer. The thermal energy is extracted by a fluid or gas circulating in the inner metal tube.

PHOTOSYNTHESIS TWIN TUBE SOLAR CELL AND COATING METHOD

The present invention relates to the art of methods for capturing solar radiated energy by means of a dye-sensitized semiconductor coating deposited into a glass-metal twin tube cell assembly for absorbing radiated sunlight and heat and converting sunlight photonic energy into electric energy and collecting thermal energy. The present invention also relates to the photonic to electronic conversion of high energy photons by mesoporous titanium dioxide (TiO_2) semiconductor impregnated with a organic anthocyanin pigments exhibiting higher absorption in the lower visible light spectrum.

BACKGROUND OF THE INVENTION

Devices for solar energy collection and conversion can be classified into concentrating types and non-concentrating types. Non-concentrating types of solar collectors capture heat from sunlight with a flat array composed of absorbing materials or devices such as photovoltaic cells or fluid conduit, for example. The output is a direct function of the area of the array. Concentrating type of solar collectors focuses the energy rays using a parabolic reflector or a lens system, concentrating the solar radiated light onto a focal point. The sunlight is concentrated to increase the intensity of conversion of solar radiation to higher photovoltaic outputs or to higher temperature of collected heat from the solar radiation to provide for higher temperature applications.

In current photovoltaic thermal (PVT) solar collectors, conventional radiation absorbing materials and photovoltaic cells are combined to convert solar radiated light into thermal and electrical energy. Other types of concentrating and non-concentrating solar energy collectors exist where the solar radiation is typically absorbed through a metallic conductive conduit or photovoltaic cell array. The solar radiation can be focused at a point from a circular reflector (e.g., a dish-shaped reflector) or along a focal line from a cylindrical shaped reflector. Such apparatus perform efficiently in ideal conditions and climates where a lower energy output less than 700 Wth/M^2 heat and 150 Wev/M^2 are sufficient throughput.

In the current dye-sensitized solar cell (DSSC), a dye pigment coats a semiconductor and is used to absorb incoming light and raise energy level of electrons. The dye sensitized solar cell (DSSC) generally includes two planar conducting electrodes arranged in a sandwich configuration. A dye-coated semiconductor film separates the two electrodes which may comprise glass coated with a transparent conducting oxide (TCO) film, for example. The semiconductor layer is porous and has a high surface area thereby allowing sufficient dye for efficient light absorption to be attached as a molecular monolayer on its surface. The remaining intervening space between the electrodes and the pores in the semiconductor film (which acts as a sponge) is filled with an electrolyte solution containing an oxidation/reduction couple such as triiodide/iodide, for example.

One exemplary technique for fabricating a dye-sensitized solar cell is to coat a conductive glass plate with a semiconductor film such as titanium dioxide (TiO_2) or zinc oxide (ZnO), for example. The semiconductor film is saturated with a dye and a single layer of dye molecules self-assembles on each of the particles in the semiconductor film, thereby "sensitizing" the film. A liquid electrolyte solution containing triiodide/iodide is introduced into the semiconductor film. The electrolyte fills the pores and openings left in the dye-sensitized semiconductor film. To complete the solar cell, a second planar electrode with a catalyst coating such as graphite is implemented to provide a cell structure having a dye-sensitized semiconductor and electrolyte composite sandwiched between two counter-electrodes.

However, conventional, concentrating and dye-sensitized solar energy receivers require improvement for many reasons. First, the solar radiated energy conversion in conventional systems occurs at the surface of an absorbing material which conducts thermal energy to a conduit which in turn conducts the thermal energy to a fluid being pumped through the conduit, creating numerous thermal resistances. Secondly, a large portion of the solar radiated energy absorbed initially by the absorbing material is reflected back to the atmosphere during its conductivity path to the conduit.

Thirdly, conventional solar collectors, photovoltaic solar cells and today's dye-sensitized solar cells do not allow the dual extraction of photonic and thermal forms of solar energy simultaneously. Moreover, the photovoltaic (PV) solar cells and the dye-sensitized solar cells (DSSC) exhibit lower performance at higher temperature as the sunlight radiated heat is accumulated into the solar cell and is not extracted in current apparatus. Furthermore, current dye-sensitized solar cells heat accumulation causes electrolyte to expand and leak. Additionally, dye pigment impregnation/porosity fill of the current dye-sensitized solar cell is inadequate due to its planar design concept.

There is a need for a new generation of solar cell that converts sunlight photonic and radiated heat energies simultaneously for the better use and application of solar energy in most applications. The present invention describes a new generation of solar cell exhibiting simultaneous conversion of sunlight energy into electronic and thermal energy efficiently and economically.

Some of the US patents related to the field of the invention are;

4293594	October, 1981	Yoldas, et al.
4732621	March, 1988	Murata, et al.
5084365	January, 1992	Gratzel, et al.
5728487	March, 1998	Gratzel, et al.
6057504	May, 2000	Izumi
6479745	November, 2002	Yamanaka, et al.
6861722	March, 2005	Graetzel, et al.
7118936	October, 2006	Kobayashi, et al.
7196264	March, 2007	Murai, et al.
7202412	April, 2007	Yamanaka, et al.
7312507	December, 2007	Tomita
7332785	February, 2008	Tomita

Other reference documents;

1. Spectral methods of characterizing anthocyanins (1957), J.B.Harborne.
2. Spectral signatures of photosynthesis, Kiang et al., Astrobiology, volume 7, number 1, 2007
3. A low-cost, high efficiency solar cell based on dye-sensitized colloidal TiO2 films, B O'Regan, M Gratzel, Nature (1991).

4. The production and evaluation of photocatalytic titanium dioxide coatings on glass tubes, H. Alsbury and A. Robertson, Loughborough University, UK.
5. Semiconductor materials for liquid electrolyte solar celld, Bruno Scrosati, University of Rome, Italy (1987).
6. Testing of dye sensitized TiO_2 solar cells, Greg smestad, Laboratory for Energy and Process Technology, Switzerland (1993).
7. Implications for a photoelectrochemical cell utilizing an anthocyanin dye-sensitized TiO_2 nanocrystalline electrode, Nerine Cherepy et al., Journal of Physics (1997).
8. Density, Viscosity and Thermal Conductivity of aqueous ethylene, dyethylene and triethylene glycol mixtures between 290K and 450K, Tongfan Sun and Amyn S. Teja, School of Chemical Engineering, Georgia Institute of Technology, USA (2002).
9. Sol-Gel TiO_2 thin films sensitized with the mulberry pigment cyanidin, Emerson Henrique de Faria et al., University de Franca, Brazil (2007).
10. Solar cell model for electron transfer in photosynthesis, Markvart and Landsberg, University of Southampton, UK.

Steadily, the sun delivers energy at the earth's surface at the average rate of 1,000 Watts/m^2 of thermal and photonic energy at sea level. This is enough energy to heat and light the whole world on a continuous basis. However, the efficiency of conventional solar collectors in converting radiated solar energy into heat and electricity has been limited. The flat plate solar collectors widely used at the present time provide applications heating dwelling spaces and hot water for domestic uses and photovoltaic panels to produce electricity. The present day technology for collecting electric and thermal solar energy (PVT) requires the packaging of two panels (flat plate and PV) into one at a significantly elevated cost, weight and size. Higher temperature is limited to parabolic reflectors and focusing lenses, which are expensive, complex and cumbersome technologies and are neither promising nor encouraging in terms of their present status and their future potential. One of the most typical examples of solar energy application is the use of solar energy for air conditioning in the tropical and subtropical regions where the expense of cooling in summer time is far greater than the expense of heating in winter time.

Solar photovoltaic cells are usually produced as small units, each capable of producing limited electric power in the range of a few watts. For large scale applications, it is necessary to integrate many cells to form a module that can produce larger electric output. Due to technology limitations, the photovoltaic technology only convert solar energy into electricity, the thermal solar energy is lost. To this day, no solar cells are known on the market to capture both electrical and thermal energy.

There is a need to improve and develop and manufacture new solar cell technology allowing the conversion of solar energy to both thermal and electrical energy efficiently in all climates to deliver heat and electric power reliably at a reasonable cost.

SUMMARY OF THE INVENTION

The primary object of the present invention is to provide a solar cell that absorbs radiated solar energy to produce thermal and electrical energy simultaneously at a higher efficiency for residential, industrial and commercial applications and into systems that are affordable.

Another object of the present invention is to provide a solar cell that absorbs radiated solar energy to produce thermal and electrical energy simultaneously by means of a photosynthesis twin tube solar cell assembly composed of a glass transparent electrode tube, dye-sensitized semiconductor coating, electrolytic fluid and a internal metal tube electrode.

A further object of the present invention is to provide a solar cell that absorbs radiated solar energy to produce thermal and electrical energy simultaneously employing a glass-metal twin tube assembly allowing solar radiated energy to be captured and thermally conducted to a coolant fluid circulating through the metal tube thereby allowing the control of the solar cell temperature.

Yet another object of the present invention is to provide a solar cell that absorbs radiated solar energy to produce thermal and electrical energy simultaneously whereas a organic dye of the anthocyanin group and more specially a cyanidin-3-glucoside dye molecule is employed to capture photons to raise energy levels for electron injections into the semiconductor conduction band to provide useful electrical energy.

Still another object of the present invention is to provide a solar cell that absorbs radiated solar energy to produce thermal and electrical energy simultaneously whereas an electrolyte consisting of a reduction/oxidation couple and ethylene glycol fluid is encapsulated between the glass-metal electrodes whereas the reduction/oxidation couple allows the regeneration of the dye molecules.

Still a further object of the present invention is to provide a method of manufacturing the photosynthesis twin tube solar cell assembly comprising steps of: (a) preparing a semiconductor colloidal solution composed of (TiO_2), acetic acid, deionized water, acetylacetone and citric acid; (b) applying a thin uniform coat of the semiconductor mixture into a glass tube employing a spinning apparatus to create centrifugal force and heat to achieve coating uniformity, adherence and density; (c) preparing a organic dye and impregnating the semiconductor coating employing a vacuum apparatus to achieve optimal dye molecule chelation onto the titanium dioxide (TiO_2) semiconductor.

These and other objects of the present invention will become clear as the description thereof proceeds.

There is disclosed herein a photosynthesis twin tube solar cell comprising a outer tube made of glass and a inner tube made of metal where said inner tube serve as coolant conduit and electrical cathode. The solar cell outer glass tube is first coated with a transparent conductive coating serving as electrical anode and further coated with a nanocrystalline titanium dioxide (TiO_2) semiconductor coating and dyed using a high energy photon absorption organic pigment. The photosynthesis twin tube solar cell assembly outer tube is sealed to the inner tube at both ends. A specially prepared electrolyte fluid fills the cavity between the glass and metal tubes assembly.

The photosynthesis twin tube solar cell is exposed to sunlight allowing solar radiated energy to penetrate the twin tube cell outer glass tube and dyed semiconductor. A fraction of the solar energy captured is converted to electronic energy and a fraction as thermal energy. The electronic energy is produced from photon absorption contributing energy to the organic dye molecule which then contributes an electron to the conduction band of the semiconductor coating. The solar thermal energy is conducted to the electrolyte which in turn is extracted by a coolant fluid or refrigerant gas circulating through the inner metal tube. The electrolyte allows the absorption of solar heat and its transfer to the inner metal tube. The electrolyte also contains a reduction/oxidation couple ex., iodide and triiodide allowing the electron displacement from the cathode to the dye molecule. The electron transfer reduce triiodide to iodide ions which travel from the cathode to the dye-sensitized semiconductor layer where they regenerate the dye molecule by electron transfer while the iodide is oxidized back to iodine.

Two embodiments (figure 2 and figure 3) are proposed whereas the inner metal tube is used to conduct heat from the solar cell and thereby allowing control of the temperature and performance of the solar cell while extracting said heat to provide useful energy. In the preferred embodiment (figure 2) a coolant fluid flows through the inner metal tube and extracts the heat. The inner metal tube can be of many possible diameters but the preferred embodiment employs a 12,7 mm O.D. (outside diameter) which is a widely used metal tubing diameter and allows adequate thermodynamics performance. The preferred embodiment inner metal tube is matched with a outer glass tube of 16 mm O.D. and 13,6 mm I.D. (internal diameter) leaving a clearance gap of ,4-,5 mm +/- ,05 mm between the metal and glass tube to allow for the dyed semiconductor coating, the electrolyte and the metal tube graphite coating.

In the alternative embodiment (figure 3) the inner metal tube is employed as in the principle of the heat pipe. The two ends of the inner metal tube are sealed, a wick is inserted and used as a capillary liquid conductor and a refrigerant gas such as R134, CO_2 or Amonia is charged inside the inner metal tube at predetermined pressure and temperature values. The inner metal tube heat pipe operates as a typical thermodynamic process containing an evaporation phase and a condensation phase where the heat accumulated in the solar cell evaporates the refrigerant gas which boils and move to the upper condensing manifold where it gives the heat back, condenses and returns through the wick to the evaporator end.

Electrically, the photosynthesis twin tube solar cell outer tube “Anode” and twin tube cell inner tube “cathode” have electrical connections to provide the electrical energy.

It is therefore a broad object of the present invention to ameliorate the disadvantages of the prior art solar cells.

It is a further broad object of the present invention to provide a solar cell capable of absorbing radiated solar energy for conversion to thermal energy and electric energy to supply heat and electricity for a wide range of applications.

In accordance with the present invention, there is therefore provided a high efficiency photosynthesis twin tube solar cell and method of making same, said photosynthesis twin tube solar cell being made of an outer glass tube, dye-sensitized semiconductor coating, inner metal tube and electrolyte fluid being made of reduction/oxidation couples, wherein said photosynthesis twin tube solar cell converts sunlight energy to electricity and wherein electrolytic fluid indirectly absorb and conduct solar thermal energy and wherein said thermal energy is recuperated through said inner tube by a coolant fluid or refrigerant gas.

The present invention was accomplished on the basis of the above discussed recognition and further experimentation which presentation and discussion follows:

A brief review of photosynthetic organisms reveals close similarities with the photosynthesis twin tube solar cell showed in figure 1. In photosynthesis, photosystems coordinate the spectral selection of light energy and conversion to electrochemical energy for reduction-oxidation (redox) reactions. The excitation of light harvesting pigments by a photon of light causes an electron to be transferred along biochemical pathways that lead to the reduction of carbon dioxide (CO_2). The photon must be of sufficient energy to generate a voltage potential difference that is great enough to oxidize the reductant as well as afford the electron transfer for reduction of the relevant systems.

In the present invention, the light energy harvesting is achieved by the dye molecule which is attached to a porous titanium dioxide (TiO_2) semiconductor coating. The photon must be of sufficient energy to allow the electron transfer to the conduction band of the titanium dioxide (TiO_2) semiconductor. Titanium dioxide (TiO_2) is preferred because of its wide band gap and its transparency to visible light at the coated thickness. This ensures that maximum light energy is absorbed by the organic dye molecules.

A class of flavonoid known as anthocyanin is responsible for the red and purple colors of many fruits and berries. The most common anthocyanin dye, cyanidin-3-glucoside, colors blueberries and blackberries. In acidic solution pH less than 3, the acid donates a hydrogen nucleus and the cyanidin-3-glucoside molecule becomes positive, appears red and absorbs blue and green light with a strong peak absorbance at ~530 nm. A similar reaction takes place when the cyanidin-3-glucoside is impregnated to the porous nanocrystalline titanium dioxide (TiO_2) coating. The complexion of the molecule with metal ions shifts the pigment color to red and the molecule absorption towards green light. In the present invention cyanidin-3-glucoside is used as the dye pigment but other organic dye pigments naturally found in small fruits and flowers can be used. Delphinidin and pelargonidin groups are two alternative and naturally occurring pigments that can be used in the dye-sensitized solar cell. Synthetic forms of cyanidin and delphinidin are commercially available as pure pigments and constitute stable options for full scale manufacturing. In the present invention, anthocyanin pigment material was extracted from 1 kg of blueberries described in recent literature to possess high concentrations of anthocyanins and more specially the cyanidin-3-glucoside group. Other fruits and quantities can provide acceptable results. 1 kilogram of fresh blueberries are put in a stainless steel jar and placed in nitrogen. The blueberries are rapidly ground using a mortar and pestle to fine particles and extracted in 5 liters of methanol-formic acid (9:1) at room temperature for 24 hours. The extraction is evaporated into syrup. The syrup is dissolved in 1 liter of purified water-.01 M HCl. The solution is filtered and evaporated into syrup. The dye pigment material obtained is stored at 4°C in a dark refrigerator until used. At the time of use, the solution is diluted with methanol (concentration 3:1) and used to dye the nanoporous semiconductor coating.

The nanoporous semiconductor coating is deposited on the internal surface of a glass tube prepared with a transparent conductive electrode exhibiting an electrical resistance of 5 to 30 ohms/cm. The method to prepare the transparent conductive electrode can be performed by spin-deposit of a tin solution into the glass tube installed into an apparatus similar to that shown in figure 6 and baked during concurrent spin at 500-600 RPM. The glass tubes can be procured with the transparent conductive coating or obtained from specialized laboratories. The transparent coating regulates the sunlight transmission through the outer glass tube. A thick conductive electrode increases conductivity but reduces light transmission. A thin conductive electrode increases resistivity but augments light transmission. An option proposed in the present invention is to deposit a thin electrode of conductivity = 5 to 8 ohms/cm to allow a high transparent index and to perform a second deposit of a 2-5 μm thick linear narrow (2 mm) conductive pad across the entire length of the glass tube (achieved without spin).

The following process allows to spin-deposit a coat of nanoporous semiconductor coating. Titanium dioxide (TiO_2) or indium oxide (In_2O_3) or dicadmium stannate ($Cd_2 SnO_4$) can be used for the semiconductor coating with titanium dioxide (TiO_2) being the preferred material exhibiting high photon to electron conversion and is a mesoporous wide band gap semiconductor offering excellent impregnation with the organic dye pigment. The optimal titanium dioxide (TiO_2) semiconductor coating is achieved by sol-gel method and requires grinding using a mortar and pestle and mixing of nanocrystalline titanium dioxide (TiO_2) powder and acetylacetone (aa) as particle stabilizer and proper quantities of diluted acetic acid (,05M) with deionized water until a fluid colloidal suspension is achieved. A detergent such as Triton X-100 is added to reduce the colloid surface tension and improve spreading. Citric acid (,05M) with deionized water is added to further liquefy the coating mixture as necessary prior to injecting the mixture into the glass tube so that the liquid mixture will spread easily. Sufficient (TiO_2) coating mixture must be prepared and injected into the glass tube to achieve a uniform coating thickness of 10 to 20 microns covering the entire internal surface of the glass tube after spin and bake processes are complete. The spin-bake schedule of figure 5 will ensure that the colloid mixture is spread evenly, that the organic binders and surfactants are decomposed and that the TiO_2 nanoparticles adhere to the transparent conductive coating. Prior and after the spin-bake process, the glass tube must be washed with isopropanol, rinsed with deionized water and dryed properly.

The volumetric fractions for the preparation of the semiconductor mixture are obtained by calculating the volume created by the coating thickness;

Glass Tube		Typical mixtures			
I.D.(mm)	Length (mm)	TiO_2(gr)	aa (ml)	Diluted acetic acid(ml)	
11,0	1,500	4,4	4,0	4,0	increments
14,0	1,500	5,6	5,0	5,0	
17,0	1,500	6.8	6,0	6,0	
20,0	1,500	8,0	7,0	7,0	
23,0	1,500	9,2	8,0	8,0	

Spinning of the tube is performed in a oven with a holding apparatus (refer to figure 6) allowing to spin the glass tube at various speeds from 100 to 3600 rpm with preferred initial rotation speed of 2400 rpm for 2-6 minutes depending of mixture viscosity followed by 600 rpm during baking. It is critical to achieve a uniform coating thickness which depends on the mixture viscosity and initial spinning speed. The oven apparatus must allow for the simultaneous baking schedule varying from 250°C to 450°C as shown in figure 5 during the 600 rpm spin. During high speed spin, the coating mixture spreads evenly and during the baking schedule the mixture bonds to the internal conductive coating of the glass tube, the citric and acetic acids as well as water evaporates and other organics decomposed leaving a nanoporous titanium dioxide (TiO^2) semiconductor coating. The coating density and resulting volumetric porosity is a direct function of the initial mixture preparation (grinding), spinning speed (during the baking process) and added citric acid to the mixture. The decomposition of citric acid and other organic components at temperatures over 200ºC contributes to the porous aspect of the semiconductor coating.

In the present invention, one single coat of the nanoporous semiconductor was disclosed achieving superior performance dimensionally, electrically and thermally compared to commercially available products. However, multiple coats of semiconductor and dye pigment impregnation can be applied using new process conditions for second layer, generally reducing the spin-bake process to mid-spin/mid-temp phase attempts to optimize the photon to electron conversion rate (IPCE). Multiple coats of nanoporous semiconductor and dye pigment can be performed at varying thickness and porosity percentages as shown in the graphical representation of figure 4 and disclosed mixture preparation method.

The following step consists in impregnating the nanoporous semiconductor coating with a sufficient quantity of the dye pigment mixed with acetylethanol (concentration 5:1). This operation is achieved under vacuum to optimize the dye penetration into the porous semiconductor material. The apparatus shown in figure 7 can be employed to inject the dye pigment into the coated glass tubes. With a cap at one end and a vacuum pump adapter at the other end of the glass tube, the internal pressure of the glass tube is reduced between 100 and 150 torr and then the suction valve is closed. The dye pigment is then injected by opening the reservoir valve sharply to let the dye pigment spread all over and into the porous semiconductor material. Optimal impregnation of the semiconductor coating provides a total density coating and higher cell performance. Excess dye is recuperated and dyed tubes are placed in the spin-baking apparatus at 600 RPM and 200°C for 30 minutes. The nanoporous semiconductor impregnation with the dye pigment under vacuum was found to be the most efficient method to ensure the greatest percentage of dye molecule chelation onto and into the porous semiconductor.

The inner metal tube is made of copper but other materials such as steel or aluminum or other types on material exhibiting good thermal and electrical conductivity could be used. Optimal thermal and electrical conductivity is achieved with copper. The inner metal tube is cut to exceed the coated glass tubes of the preferred embodiment by minimum 5 cm at each end totaling 1,600 mm to allow for later installation to solar panel headers by end users. The inner metal tube is coated with graphite to allow for the catalytic process to take place between the coating, electrons and the electrolyte. The graphite coating optimal thickness is 40-60 μm thick and is applied on a tube length of 1,500 mm leaving 50 mm at each end to allow for the metal tubes later installation in a solar panel.

A connector allows the electrical connection to the glass tube anode for useful application of the solar cell. The connector includes a solder pad allowing multiple photosynthesis twin tube solar cells to be mounted in arrays and panels for solar energy projects and positive wires to be soldered to each solar cell. The negative electrical connection is provided by the inner metal tubes.

The electrolyte fills the space between the coated glass tube and the inner metal tube. The electrolyte is obtained by mixing .5 M potassium iodide and .05 M iodine with ethylene glycol or propylene glycol.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention and the advantages thereof, reference is now made to the following description taken in conjunction with the accompanying Drawings in which:

FIGURE 1, illustrates the operation principles of the photosynthesis twin tube solar cell comprising the coated transparent glass tube, semiconductor and dye molecule coating, electrolyte and carbon coated metal tube electrode.

FIGURE 1A, is a schematic representation of the photonic to electronic operating principles and semiconductor bandgap.

FIGURE 2, illustrates a cross sectional view of photosynthesis twin tube solar cell preferred embodiment.

FIGURE 2A, is a cross sectional view of connector end cap seal.

FIGURE 3 illustrates a cross sectional view of photosynthesis twin tube solar cell alternative embodiment.

FIGURE 4 is a graphical representation of the relation between the TiO_2 coating density and volumetric porosity versus the spinning speed.

FIGURE 5 is a graphical representation of the TiO_2 coating spin-bake schedule.

FIGURE 6 is a schematic representation of the spin-bake apparatus.

FIGURE 7 is a schematic representation of the TiO_2 coating impregnation fixture.

While the principles of the present invention have now been made clear by the illustrative embodiments, it will be immediately obvious to those skilled in the art that many modifications of the structure, arrangements, elements, proportions and materials which are particularly adapted to a certain working environment and operating condition in the practice of the invention are possible without departing from those principles of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIGURE 1 and 1A, there is illustrated the operating principles of the photosynthesis twin tube solar cell 1 according to the present invention and consisting of four critical layers. The solar light 2 irradiates the twin tube solar cell 1 directly or indirectly using a reflector or lenses or other reflective apparatus to concentrate solar radiated energy onto the photosynthesis twin tube solar cell 1. The glass tube layer incorporate a transparent conductive coating 3 allowing solar radiated photons to penetrate the solar cell. The semiconductor coating layer with impregnated dye molecule absorbs photons and releases electrons. The coated inner metal tube layer 6 receives electrons after useful work is performed. The electrolyte layer 5 performs a regenerative process through an ionic exchange to fill the electron hole of the dye molecule.

The semiconductor coating 4 is impregnated with a dye molecule that absorbs solar radiated energy 2 composed of photons. Said photons excite the dye molecule and in doing so raises the dye molecule energy level from the HOMO (highest occupied molecular orbital) level to the LUMO (lowest unoccupied molecular orbital) level. The LUMO level energy state is higher than the semiconductor conduction band allowing the excited electrons to jump to the semiconductor coating 4 conduction band CB. The excited electrons released to the conduction band of the semiconductor coating 4 migrate to the glass tube transparent conductive electrode 3 to exit the solar cell at 7. The electrons travel to the load 8 where they provide useful work and return to the solar cell inner metal tube 6. A portion of the photon energy absorbed by the electrons is converted to heat and accumulate into the twin tube solar cell 1. The thermal energy accumulated into the photosynthesis twin tube solar cell 1 is extracted through the inner metal tube 6 using a coolant fluid or refrigerant gas. The electrons reenter the solar cell after giving useful work through the inner metal tube 6. A graphite catalyst 9 donates the electrons to the electrolyte 5. Said electrolyte 5 is composed of a reduction/oxidation couple such as iodide/triiodide and glycol allowing the conduction of the electrons to the dye molecule in a regeneration process.

Referring now to FIGURE 2, there is illustrated a cross sectional view of the photosynthesis twin tube solar cell preferred embodiment 10 according to the present disclosure, comprising a outer glass tube 11 having internal diameter generally between 11 and 165 mm, preferably between 11 and 23 mm. The outer glass tube 11 is coated internally with a transparent conductive oxide coating 12 generally made of metal oxide such as tin oxide (SnO_2) or tin tetrachloride ($SnCl_4$) or aluminum oxide (Al_2O_3) but preferably made of tin oxide (SnO_2). The outer glass tube 11 transparent conductive oxide coating is generally of thickness between 100 and 500 nm, preferably 300 to 450 nm and is applied usually by spin-bake (Alsbury and Robertson) or gas deposition or pyrolysis (Yoldas et al.) or chemical vapor deposition APCVD. The outer glass tube 11 is generally of wall thickness 1 to 5 mm but preferably 1 mm. The outer glass tube 11 is made of borosilicate glass with preferably low iron content and is available commercially according to the preferred embodiment from Richland Glass Inc. or Specialty Glass products or Pegasus glass products or other quality specialty glass producers. The preferred transparent conductive coating can be performed by the glass manufacturer or can be sourced with specialized laboratories.

The outer glass tube 11 with inside transparent conductive coating 12 is further coated with a semiconductor coating 14 such as titanium dioxide (TiO_2) or indium oxide (In_2O_3) or dicadmium stannate ($Cd_2 SnO_4$) but preferably titanium dioxide (TiO_2). The semiconductor coating 14 is generally of thickness 10 to 30 µm, preferably 20 µm. The semiconductor coating 14 is deposited using a concurrent spin-bake method in accordance with the present invention to obtain a volumetric porosity generally between 2% and 30%, preferably 15% to 27%. The semiconductor coating 14 is mixed according to the present invention and deposited according to the present invention and spin-bake schedule of figure 5 and extends entire length of outer glass tube 11 less 2 cm at each end to allow for electrical contact between connector insert 17 and transparent conductive oxide coating 12. The preferred method for applying the semiconductor coating 14 onto the transparent conductive coating 12 inside the outer glass tube 11 will now be described with reference to optimal semiconductor coating of figure 4 and density/porosity 35 and in accordance with figure 5 and spin-bake schedule 40 and with reference to figure 6 and apparatus 50;

1. Determine the quantity of semiconductor mixture (titanium dioxide) needed for each tube to be coated using the calculation that follows for tube length of 1500mm ;

   TiO_2 mass = tube id x 3.1416 x tube length x coating thickness x TiO_2 density

   $$TiO_2 \text{ mass} = \frac{\text{id mm} \times 3.1416 \times 1500 \text{ mm} \times .025 \text{ mm} \times 4.04 \text{ g/cm}^3 \, *}{1000 \text{ mm}^3/\text{cm}^3}$$

   *Density will vary according to the percentage of each rutile and anatase forms of titanium dioxide present in the TiO_2 powder. Rutile TiO_2 has a density of 4,25 g/cm³ and the anatase form of TiO_2 has a density of 3,9 g/cm³.

2. Mix the quantities of titanium dioxide, acetic acid and acetylacetone (aa) as per the table below into a mortar and grind using a pestle while adding the acetic acid in increments until a fine milky like colloidal fluid is obtained.

Glass Tube		Typical mixtures		
I.D.(mm)	Length (mm)	TiO_2(gr)	aa (ml)**	Diluted acetic acid (ml)* Increments of;
11,0	1,500	4,38	4,0	4,0
14,0	1,500	5,58	5,0	5,0
17,0	1,500	6.77	6,0	6,0
20,0	1,500	7,97	7,0	7,0
23,0	1,500	9,16	8,0	8,0

*Add sufficient diluted acetic acid by increments as shown in the table above to ensure the colloidal mixture flows from one end to the other end of the glass tube. Diluted acetic acid ,05M and deionized water.

** Further liquefy the semiconductor mixture with shown amount of acetylacetone and (,05M) citric acid.

3. The semiconductor mixture is introduced into the outer glass tube 11 having transparent conductive oxide coating 12 and end cap 13 placed at each end to prevent mixture from spilling out of the tube. End cap 13 is used in final assembly to provide seal between outer glass tube 11 and inner metal tube 18 and has opening in the center allowing evaporation of organics during the spin-bake schedule 40.
4. The outer glass tube 11 or bundle of tubes is placed into apparatus 50 shown in figure 6 and apparatus 50 is placed into oven 51 as shown. Align and insert motor 52 shaft into spline 53 properly to ensure connection during entire process.
5. The outer glass tube 11 is processed according to spin-bake schedule 40 of figure 5. Initial spin 44 at 2400 rpm for time=6 minutes allows to spread the TiO_2 coating evenly.

Spin is reduced to 600 rpm and heat is set at 250 °C until time=45 minutes.

Spin is reduced to 200 rpm and heat is set at 450 °C until time=90 minutes.

Upon completion of the 450 °C baking cycle 42 the tubes are let to cool 43 within the oven 51 during the remaining 30 minutes. The cooling time is necessary to avoid cracks of the outer glass tube or coatings or both. The end caps 13 are not removed at this operation.

The semiconductor coating 14 is further dyed using a generally available dye pigment, usually an organic dye pigment of the anthocyanin group usually cyanidin or delphinidin, preferably a cyanidin-3-glucoside dye pigment 20 obtained by extraction from small fruits such as wildberries, blackberries or blueberries, preferably blueberries (J.B. Harborne). The dye pigment molecule 20 is obtained by extraction or procured from commercially viable sources. Synthetic molecules identical to organic cyanidin-3-glucoside is available from Biolink. The dye pigment molecule 20 is injected into the outer glass tube 11 to impregnate the semiconductor coating 14 and fill the volumetric porosities according to the present method with reference to impregnation fixture 60 and figure 7.

1. Install hard rubber cap 61 on one end of the outer glass tube 11.
2. Ensure the valve 64 is closed and valve 65 is open and pour approximately 20 ml of dye pigment 20 into pigment reservoir 63 and install cover 62.
3. Insert impregnation fixture taper end 66 into outer glass tube end cap 13 firmly and activate vacuum pump.
4. Pump until a vacuum pressure of 100 to 150 Torr is reached.
5. Close valve 65 and stop vacuum pump.
6. Open valve 64 sharply ½ to ¾ turn to allow the dye pigment to flow into the outer glass tube 11 and rotate tube slightly to allow the dye pigment to reach the entire surface.
7. Recuperate excess dye pigment.
8. Install dyed outer glass tube 11 into apparatus 50 and install apparatus 50 into oven 51.
9. Rotate dyed outer glass tubes at 200 rpm and set temperature to 200ºC for 30 minutes.
10. Allow dyed outer glass tubes to cool within the oven 51 with temperature turned off.
11. Wash the dyed outer glass tubes with ethanol and remove one of the two end cap 13.

A inner metal tube 18 usually copper or aluminum, preferably copper coated with graphite 19 and used as the electrical cathode of the photosynthesis twin tube solar cell. The inner metal tube 18 diameter is selected to leave a gap of ,4-,5 mm between the inner metal tube 18 and the internal diameter of the outer glass tube 11. Note that this gap clearance is sufficient to allow assembly of cells with multiple semiconductor coatings. Final assembly of the twin tube solar cell 10 can proceed with the insertion of the inner metal tube 18 into the outer glass tube 11. It is recommended to cover the inner metal tube with a thin plastic sheet that can be pulled out after the insertion of the inner metal tube 18. The gap between the outer glass tube 11 and inner metal tube 18 is filled with the electrolyte 15.

During operation, the thermal energy accumulated into the photosynthesis twin tube solar cell 10 is extracted using a coolant fluid and appropriate pumping and regulating components to allow for the thermal energy recuperation and control of the photosynthesis twin tube solar cell temperature. It will be obvious to those skilled in the art that the twin tube solar cell can be employed in arrays and thereby forming solar panels that produce electricity and collect heat from solar radiation.

While referring now to FIGURE 2A, there is illustrated a cross sectional view of connector end cap seal 16 composed of connector pin 17 and Teflon sealing diameters 21 and 22. Connector pin 17 extends out of sealing diameter 21by approximately ,2 mm thereby making contact with the glass tube transparent conductive electrode 12.

While referring now to FIGURE 3, there is illustrated an alternative embodiment photosynthesis twin tube solar cell 30 composed of outer glass tube 11 and inner metal tube 31. The thermal energy transferred to the inner metal tube 31 is extracted employing a method commonly referred to by those skilled in the art as a heat pipe. The inner metal tube 31 is used as the heat absorption body of the heat pipe cooling method. The outer glass tube 11 of the alternative embodiment is identical to the disclosure given of the preferred embodiment 10 in figure 2. The inner metal tube 31 is partially filled with a refrigerant such as the commonly used R134a or CO_2 or ammonia but preferably R134a. The inner metal tube 31 is sealed at one end by a metal cap 23 and at the other end by heat transfer reservoir 34 both secured in place by brazing. A wick 25 is placed inside the inner metal tube allowing the refrigerant to flow by capillary action. The thermodynamic process allowing heat to be moved from the lower end of the inner tube 24 to the higher end 26 is described now:

1. The radiated solar heat 28 is absorbed by the inner metal tube 31 and forces the liquid refrigerant at the bottom of the tube to boil and evaporate 24.
2. The refrigerant gas expands under the effect of boiling, evaporates and moves up the tube.
3. The heat 29 that was contained in the boiling refrigerant gas is transferred through the walls of the condenser cavity 26 and the refrigerant condenses and returns as a liquid.
4. The liquid refrigerant 27 returns to the wick 25 and flows to the bottom end of the tube.

The condenser cavity 26 is designed to fit into standard solar panels utilizing the heat pipe method.

The inner metal tube 31 is preferably made of copper and coated with graphite 33 and used as the electrical cathode of the photosynthesis twin tube solar cell. The inner metal tube 31 diameter is selected to leave a gap of .5 mm between the inner metal tube 31 and the internal diameter of the outer glass tube 11. Note that this gap clearance is sufficient to allow assembly of cells with multiple semiconductor coatings. Final assembly of the photosynthesis twin tube solar cell alternative embodiment 30 can proceed with the insertion of the inner metal tube 31 into the outer glass tube 11. It is recommended to cover the inner metal tube with a thin plastic sheet that can be pulled out after the insertion of the inner metal tube 31. The end cap 16 is installed at the condenser end of the inner metal tube 31. The gap between the outer glass tube 11 and inner metal tube 31 is filled with the electrolyte 15. The end cap 32 seals the photosynthesis twin tube solar cell 30.

Referring now to FIGURE 4, there is illustrated a graphical representation of the spin parameter needed to achieve the optimal nanoporous semiconductor coating 14 during the initial baking phase at 250°C. Semiconductor material density 37 is composed of approximately 60% anatase and 40% rutile form Titanium dioxide. The optimal combination identified by area 35 is achieved by setting spin rpm 36. Resulting density leads to porosity 38 for ideal impregnation of dye pigment.

Referring now to FIGURE 5, there is illustrated the spin-bake schedule 40 composed of spin curve 41 and bake curve 42. Spin curve 41 has high-spin/low-temp phase 44 allowing the semiconductor colloid mixture to spread evenly, mid-spin/mid-temp phase 45 allowing the decomposition of organic components and low-spin/high-temp phase 46 allowing the binding of the nanoporous semiconductor to the electrode coating. Cooling zone 43 is reached at power off, leaving the oven 51 to cool without additional support. The cooling zone 43 enables slower material retractions avoiding thermal shocks and potential cracks of the glass or coating or both.

Referring now to FIGURE 6, there is illustrated the spin-bake apparatus 50 and oven 51 needed to perform the spin-bake schedule illustrated in figure 5. The spin-bake apparatus 50 consist of ceramic wheels 54 and wheel support 55 forming racks of ceramic wheels secured with metal springs 56 to retain the glass tubes 11 stable during the spin-bake process. The spin-bake apparatus can be installed into oven 51 with motor 52 shaft is inserted into spline 53 to allow tube rotation.

Referring now to FIGURE 7, there is illustrated a typical spray gun 60 used to inject the dye pigment into the coated glass tube 11 by means of negative pressure with a vacuum pump to impregnate the semiconductor coating porosity with the dye pigment molecules. Container 63 is used to stock sufficient dye pigment and valve 65 to apply the negative pressure to the tube. Valve 64 is used to inject the dye pigment.

It will be obvious to those skilled in the art that different versions of the photosynthesis twin tube solar cell can be constructed without departing from the principles of operation disclosed by the present invention and achieve similar performance. Materials and processes needed to construct the photosynthesis twin tube solar cell may vary without departing from the disclosed invention and coating method.

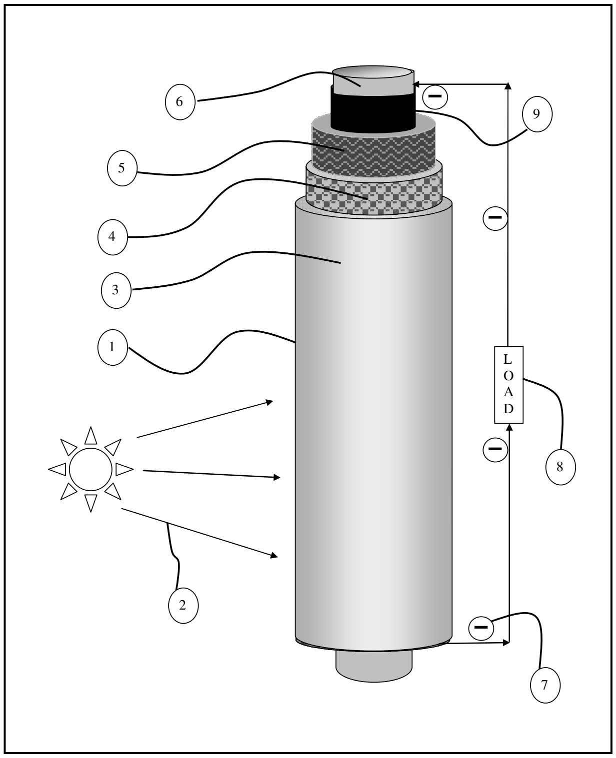

Figure 1, Schematic representation of the operating principles of the photosynthesis twin tube solar cell.

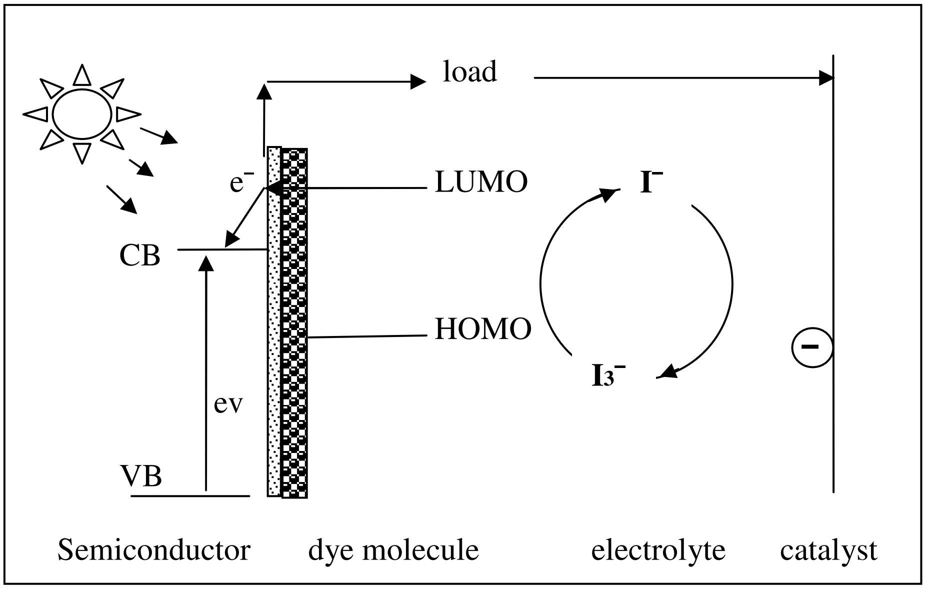

Figure 1A, Schematic representation of electronic operating principles

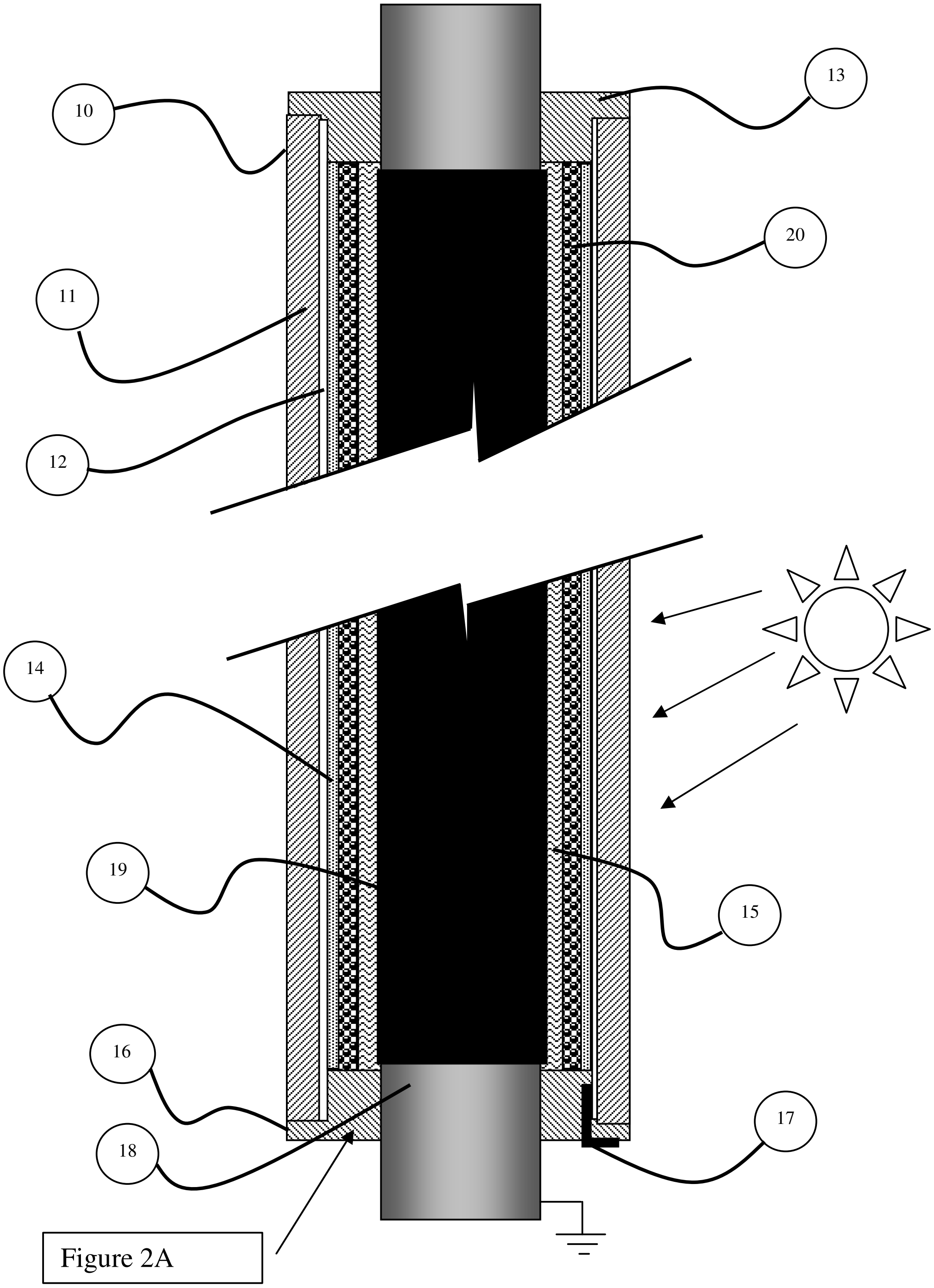

Figure 2, Cross sectional view of dye-sensitized twin tube solar cell preferred embodiment

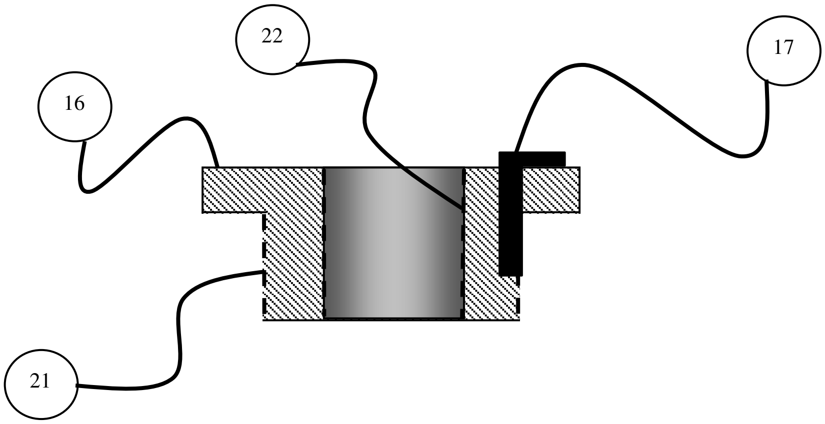

Figure 2A, Cross sectional view of connector end cap seal

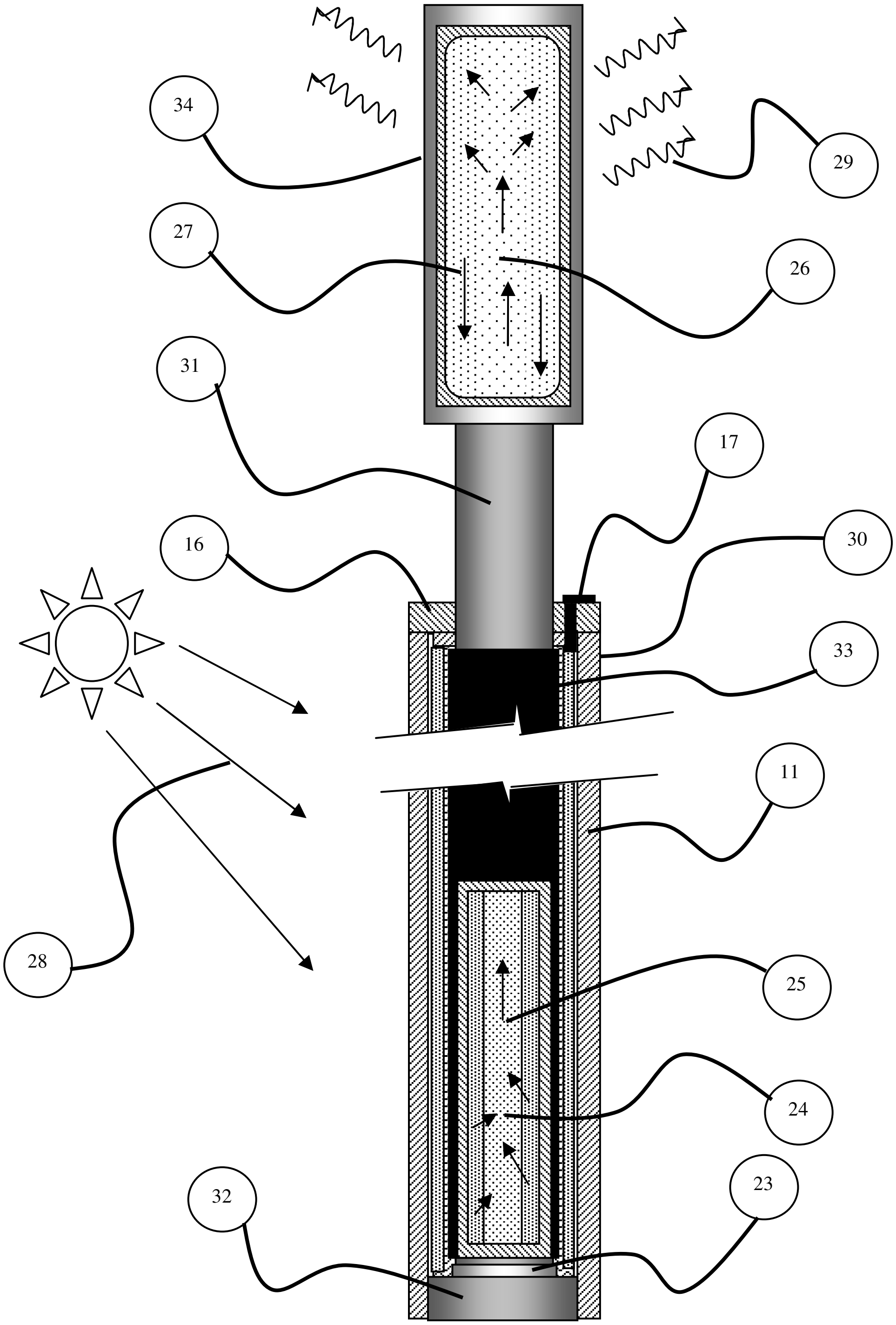

Figure 3, Cross sectional view of photosynthesis twin tube solar cell alternative embodiment

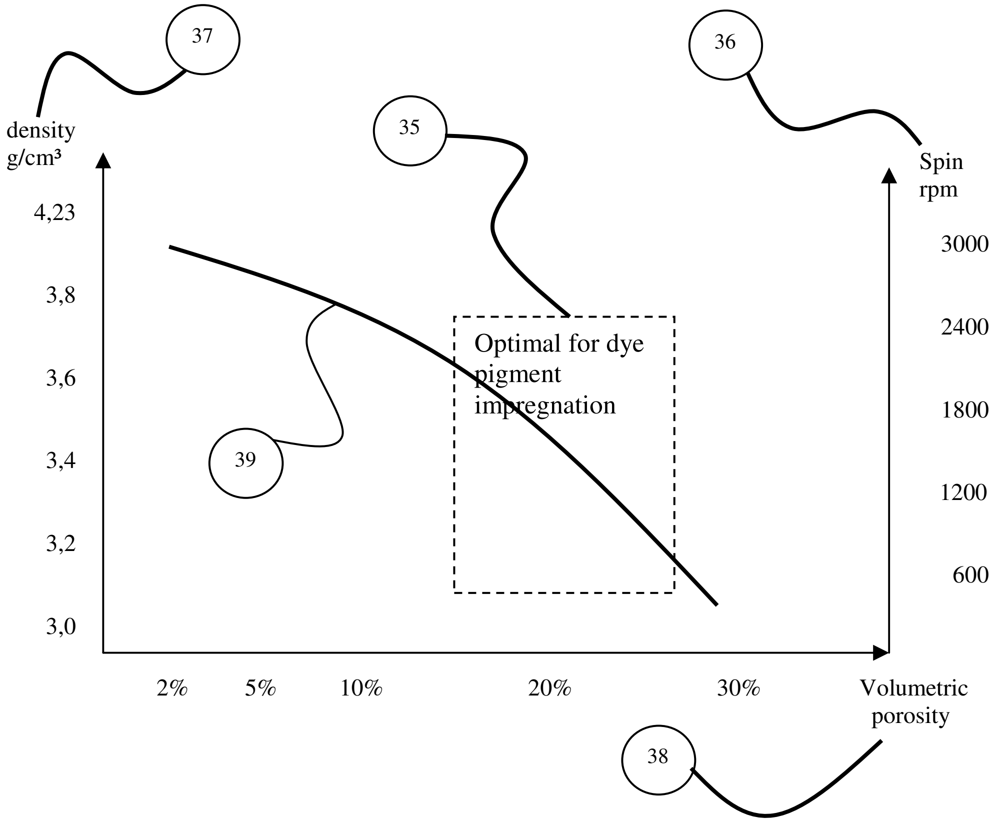

Figure 4, Semiconductor coating density & porosity vs spin relation achieved at mid-spin/mid-temp phase

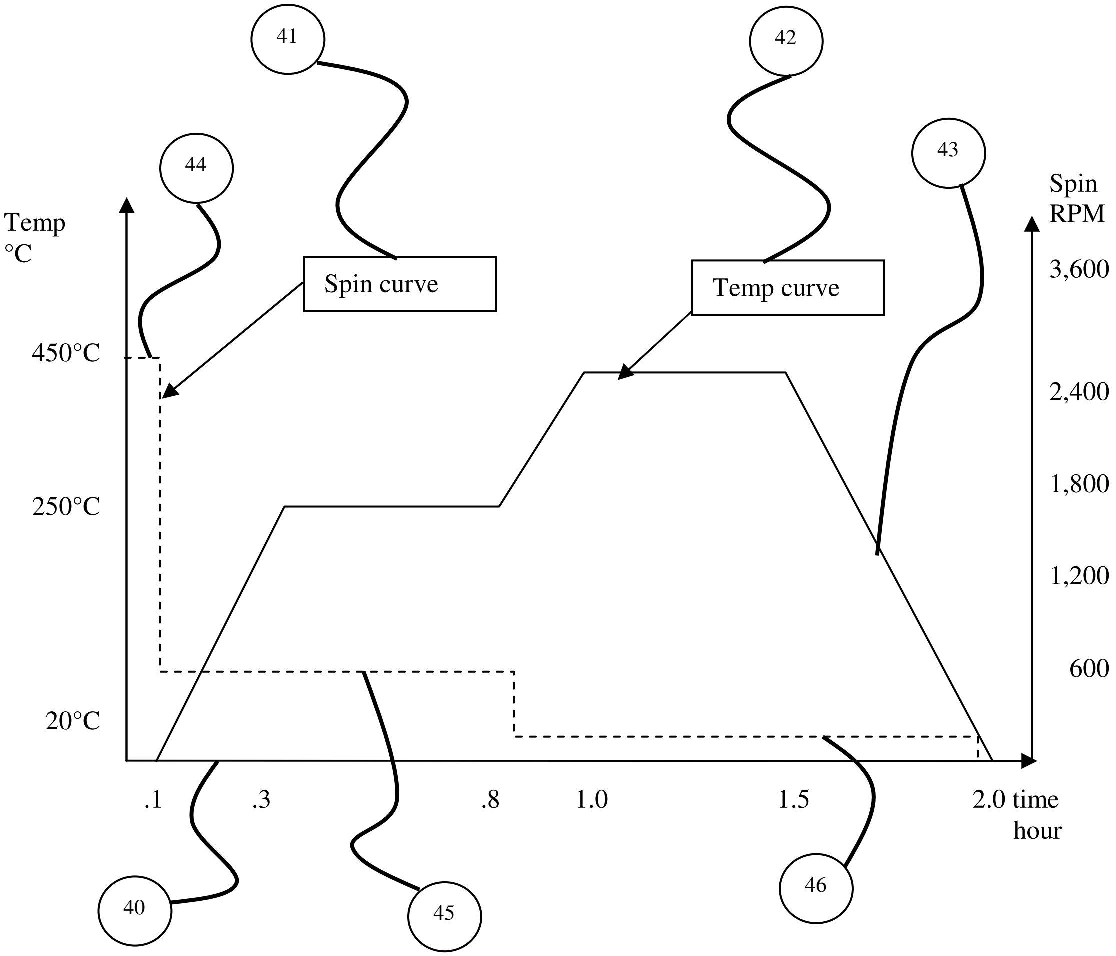

Figure 5, TiO2 coating spin-bake schedule

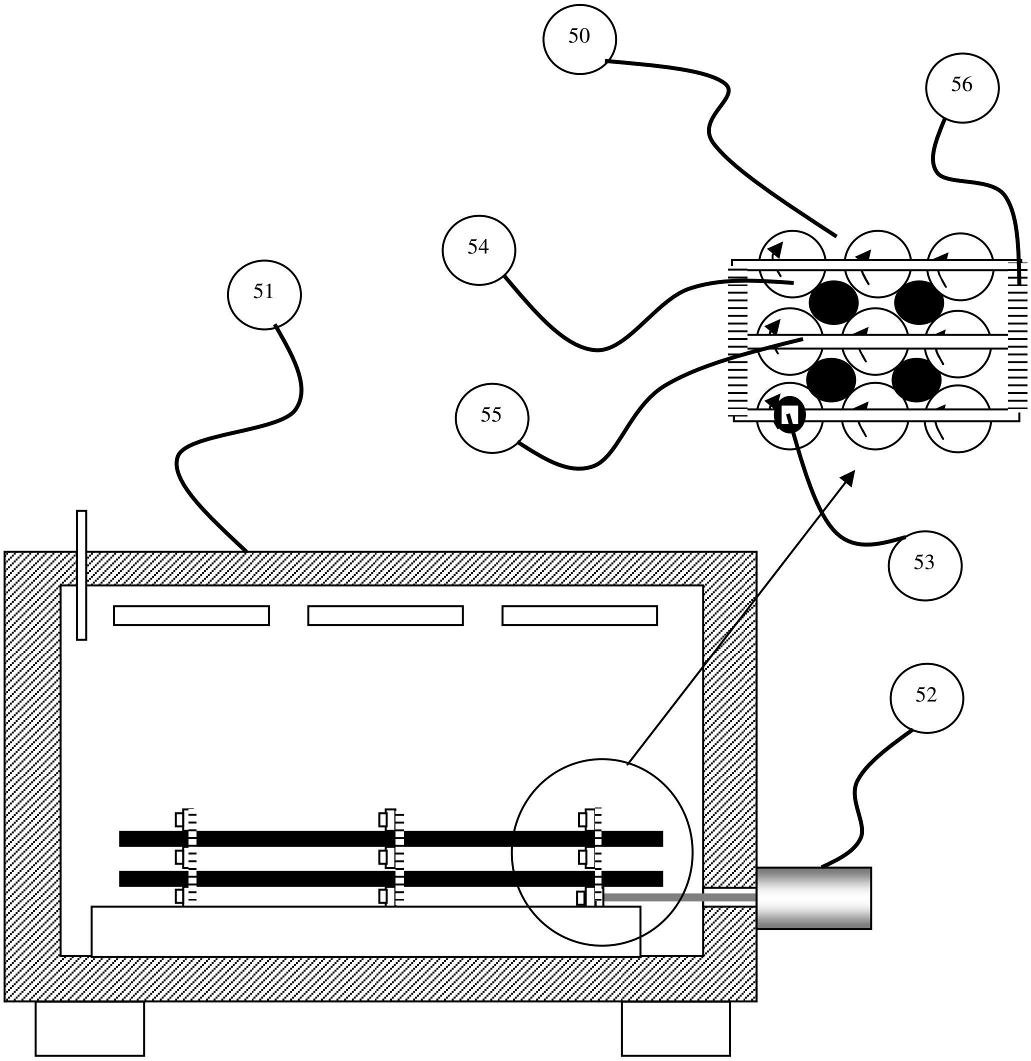

Figure 6, Spin-bake apparatus

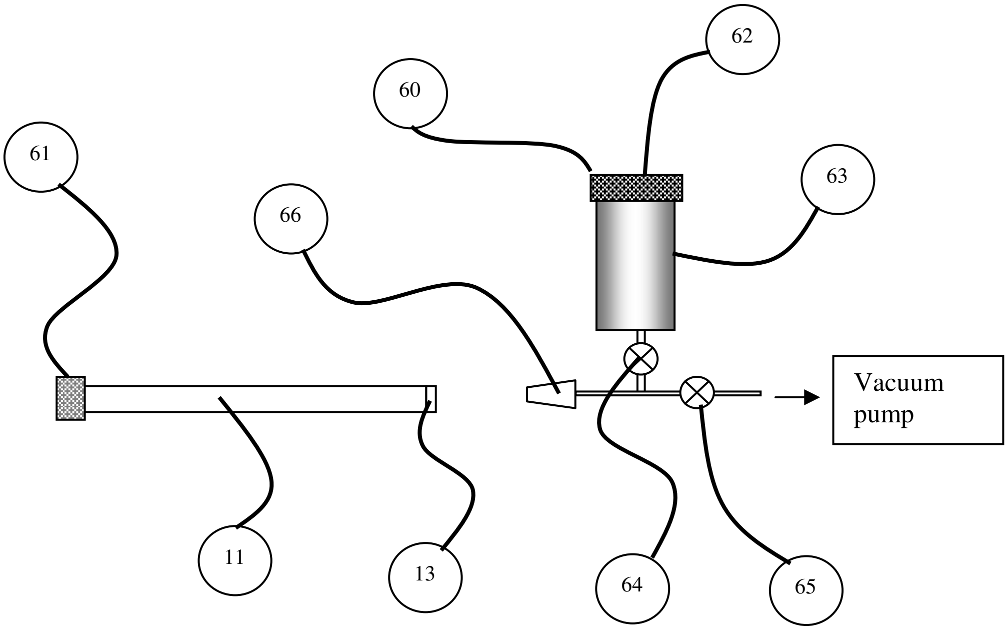

Figure 7, TiO_2 coating impregnation fixture