(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 394 084 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
03.07.2024 Bulletin 2024/27

(21) Application number: **23203871.1**

(22) Date of filing: **16.10.2023**

(51) International Patent Classification (IPC):
C25B 1/04 $^{(2021.01)}$ ***C25B 3/26*** $^{(2021.01)}$
C25B 9/19 $^{(2021.01)}$ ***C25B 9/50*** $^{(2021.01)}$
C25B 11/052 $^{(2021.01)}$

(52) Cooperative Patent Classification (CPC):
C25B 1/04; C25B 3/26; C25B 9/19; C25B 9/50; C25B 11/052

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **28.12.2022 JP 2022212561**

(71) Applicant: **Hitachi, Ltd.**
Tokyo 100-8280 (JP)

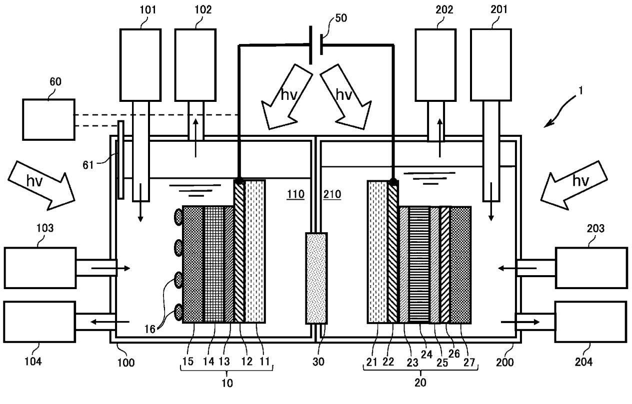
(72) Inventors:
- **TAKAHASHI, Hiromasa**
  Tokyo, 100-8280 (JP)
- **FUKATANI, Naoto**
  Tokyo, 100-8280 (JP)
- **TAKAMATSU, Daiko**
  Tokyo, 100-8280 (JP)
- **YABUUCHI, Shin**
  Tokyo, 100-8280 (JP)
- **HAYAKAWA, Jun**
  Tokyo, 100-8280 (JP)

(74) Representative: **Strehl Schübel-Hopf & Partner**
Maximilianstrasse 54
80538 München (DE)

(54) PHOTOCATALYTIC APPARATUS

(57) A photocatalytic apparatus is provided that uses a photovoltaic action for both electrodes and conjugates a photocatalytic action with the photovoltaic action to efficiently perform material transformation on the basis of a redox reaction on the electrodes using light energy. A photocatalytic apparatus includes a first electrode (10) functioning as an anode and a second electrode functioning as a cathode. The first electrode (10) includes a first transparent conductive substrate (11) having light transmittivity and electrical conductivity, a first light power generation layer (14) that is disposed on the first transparent conductive substrate (11) and absorbs light to generate electrons and holes, and a photocatalytic layer (15) that is disposed on the first light power generation layer (14) and catalyzes an oxidation reaction when being irradiated with light. The second electrode includes a second transparent conductive substrate (21) having light transmittivity and electrical conductivity, a second light power generation layer (24) that is disposed on the second transparent conductive substrate (21) and absorbs light to generate electrons and holes, and a catalytic layer (27) that is disposed on the second light power generation layer (24) and catalyzes a reduction reaction.

FIG. 1



Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a photocatalytic apparatus that performs material transformation using an electrical redox reaction caused by conjugation of a photocatalytic action and a photovoltaic action.

2. Description of the Related Art

[0002] In recent years, attention has been paid to a technology for performing material transformation using light energy. As such a technology, photocatalysts are known that exhibit a catalytic action under light irradiation. Photocatalysts have been mainly used for coating for the purpose of contamination prevention, sterilization, or the like. However, studies have been conducted about application of photocatalysts to purification of air or water quality.

Additionally, much effort has been made to develop photoelectrodes using water splitting or a photovoltaic action and artificial photosynthesis devices that reduce carbon dioxide using light energy.

[0003] Use of the photovoltaic action allows electrons and holes to be separately extracted at electrodes. This can be used for an electrical redox reaction using electrodes, enabling material transformation to be performed using light energy. The technology for performing material transformation using light energy involves no discharge of carbon dioxide and allows the use of sunlight or the like that is natural energy. The technology is thus expected to be applied in the fields of energy, environments, and the like. Studies have been conducted about merger of a photoelectric conversion mechanism and a catalytic technology for purifying contaminants and producing valuables, realizing a sound material-cycle society system.

[0004] For example, a redox reaction enables electrolyzation of seawater and the like, purification of carbon dioxide, methane, NOx, and the like in the air, and purification of nitrogen components and the like that contaminate aqueous environments. Hydrogen resulting from water decomposition may be an inexpensive accumulable energy carrier. Additionally, reduction of carbon dioxide enables valuables such as carbon monoxide, alcohol, formic acid, and the like to be produced. The technology for providing photovoltaic power using light energy and performing material transformation using photovoltaic power is expected to contribute to spread of hydrogen energy and reduction of carbon dioxide.

[0005] Japanese Patent No. 6774165 describes a photochemical reaction device that reduces carbon dioxide using water as an electron source to synthesize carbon compounds. An electrolysis cell of a photochemical reaction device houses an electrode for oxidation reaction that selectively oxidizes water to generate oxygen and an electrode for reduction reaction that selectively reduces carbon dioxide under the presence of oxygen. The electrolysis cell is connected to a light absorber and configured to reduce carbon dioxide using light energy.

[0006] Japanese Patent No. 6316436 describes a hydrogen generating electrode for an artificial photosynthesis module. The hydrogen generating electrode includes a conductive layer, an inorganic semiconductor layer having a pn junction, and a functional layer. The functional layer supports a promotor for generating hydrogen. The hydrogen generating electrode is configured to use a photovoltaic action of the inorganic semiconductor layer.

[0007] In general, a photoelectrode exhibiting a photovoltaic action includes a power generation layer on a transparent conductive substrate. The power generation layer is a layer that absorbs light to generate electrons and holes and that is formed of an oxide semiconductor or the like. A counter electrode generally used is a metal electrode such as platinum. In the power generation layer, light energy causes electrons to be excited by a conductance band, and band bending separates electrons from holes. Accordingly, the electrons and holes can be extracted at the electrodes, forming redox reaction fields. Typically, an external power supply is connected between the electrodes to apply auxiliary power required for a redox reaction.

SUMMARY OF THE INVENTION

[0008] A system that performs material transformation using light energy has a problem in material transformation efficiency. Light energy conversion efficiency achieved by the photoelectrodes remains approximately several percents or lower due to a large bandgap of the material and the like. In a case where the known photoelectrodes are used for material transformation, auxiliary power needs to be applied using the external power supply. For such systems, there has been a demand to increase the material transformation efficiency in order to enable a reduction in auxiliary voltage and abolition of the external power supply.

[0009] Additionally, the photoelectric conversion mechanism using the photovoltaic action has a problem in power and reaction efficiency that decrease over time. Peel-off may occur at an interface of the power generation layer exhibiting the photovoltaic action, due to a continued electrochemical reaction or dynamic or thermal environmental effects. Additionally, continued operation of a catalytic electrode immersed in an electrolytic solution may causes a redox reaction to generate gas, leading to accumulated bubbles inside the electrode or at the interface. A problem with such peel-off and bubbles is a failure to maintain electrode output and material transformation efficiency.

[0010] In the known art, a water electrolysis system using solar cells has also been developed as a system that performs material transformation using light energy. However, a problem with solar cells is also the likelihood of being degraded in an electrolytic solution. On the other hand, installation of solar cells outside the electrolytic solution leads to a power transmission loss. Simple use of solar cells increases material transformation costs. Under such a situation, there has been a desire for a technology for increasing the utilization rate of light energy and improving the material transformation efficiency.

[0011] In Japanese Patent No. 6774165, a photoelectrode is used as a reduction reaction electrode that is a cathode, and IrOx or $WO_3/BiVO_4$ is used as an electrode for oxidation rection that is an anode. In Japanese Patent No. 6316436, a photoelectrode is used as a hydrogen generating electrode that is a cathode, and a conductive layer formed of metal is used as an oxygen gas generating section that is an anode. In Japanese Patent Nos. 6774165 and 6316436, only one of the electrodes uses the photovoltaic action, and the utilization rate of light energy and the material transformation efficiency have limitations.

[0012] Accordingly, an object of the present invention is to provide a photocatalytic apparatus that allows both electrodes to use the photovoltaic action and conjugate the photocatalytic action with the photovoltaic action to efficiently perform material transformation on the basis of the redox reaction on the electrodes using light energy.

[0013] In order to achieve the object, a photocatalytic apparatus according to the present invention includes a first electrode disposed in an electrolytic solution or in steam and functioning as an anode, and a second electrode electrically connected to the first electrode and disposed in an electrolytic solution or in steam, the second electrode functioning as a cathode. The first electrode includes a first transparent conductive substrate having light transmittivity and electrical conductivity, a first light power generation layer that is disposed on the first transparent conductive substrate and absorbs light to generate electrons and holes, and a photocatalytic layer that is disposed on the first light power generation layer and catalyzes an oxidation reaction when being irradiated with light. The second electrode includes a second transparent conductive substrate having light transmittivity and electrical conductivity, a second light power generation layer that is disposed on the second transparent conductive substrate and absorbs light to generate electrons and holes, and a catalytic layer that is disposed on the second light power generation layer and catalyzes a reduction reaction.

[0014] According to the present invention, a photocatalytic apparatus can be provided that allows both electrodes to use the photovoltaic action and conjugate the photocatalytic action with the photovoltaic action to efficiently perform material transformation on the basis of the redox reaction on the electrodes using light energy.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

FIG. 1 is a diagram schematically depicting a photocatalytic apparatus according to a first embodiment of the present invention;

FIG. 2 is a diagram schematically depicting a photocatalytic apparatus according to a second embodiment of the present invention;

FIG. 3 is a diagram schematically depicting a photocatalytic apparatus according to a third embodiment of the present invention;

FIG. 4 is a diagram schematically depicting a photocatalytic apparatus according to a fourth embodiment of the present invention;

FIG. 5 is a diagram schematically depicting a photocatalytic apparatus according to a fifth embodiment of the present invention;

FIG. 6 is a diagram depicting an example of a relation between an electrode potential and a current density of a known photocatalytic electrode;

FIG. 7 is a diagram depicting an example of a relation between an output time and the current density of the known photocatalytic electrode;

FIG. 8 is a diagram depicting an example of a relation between an electrode potential and a current density of a photocatalytic electrode; and

FIG. 9 is a diagram depicting an example of a relation between an output time and the current density of the photocatalytic electrode per electrode area.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] A photocatalytic apparatus according to an embodiment of the present invention will be described below with reference to the drawings. Note that, in the figures below, common configurations are denoted by the same reference signs, and duplicate descriptions are omitted.

<First Embodiment>

[0017] FIG. 1 is a diagram schematically depicting a photocatalytic apparatus according to a first embodiment of the present invention.

[0018] As depicted in FIG. 1, a photocatalytic apparatus 1 according to the first embodiment includes a first electrode 10 functioning as an anode, a second electrode 20 functioning as a cathode, electrolysis cells 100 and 200, and the like.

[0019] The photocatalytic apparatus 1 according to the present embodiment is an apparatus that performs material transformation on the basis of a redox reaction on the electrode caused by conjugation of a photocatalytic action and a photovoltaic action. In the photocatalytic apparatus 1, both the anode- and cathode-side electrodes perform material transformation on the basis of an electric redox reaction using the electrodes. In the photocatalytic apparatus 1, the both anode- and cathode-side electrodes are configured to use the photovoltaic action, whereas the anode side is configured to use the photocatalytic action and the photovoltaic action.

[0020] The first electrode 10 and the second electrode 20 are disposed inside the electrolysis cells 100 and 200. The electrolysis cells 100 and 200 accommodate a conductive electrolytic medium that can transport ions. The first electrode 10 and the second electrode 20 are held immersed in the electrolytic medium. The electrolytic medium is provided with a predetermined reductant or oxidant subjected to material transformation on each electrode by the redox reaction.

[0021] The first electrode 10 is an electrode functioning as an anode, and performs photovoltaic generation to separate electrons from holes due to the photovoltaic action, and performs an oxidation reaction catalyzed by a photocatalyst. The first electrode 10 uses the photovoltaic action and the photocatalytic action catalyzed by the photocatalyst to oxidize a reductant contained in the electrolytic medium to perform material transformation of the reductant into a predetermined product.

[0022] The second electrode 20 is an electrode functioning as a cathode, and performs photovoltaic generation to separate electrons from holes on the basis of the photovoltaic action, and performs a reduction reaction catalyzed by an intended electrode catalyst. The second electrode 20 uses the photovoltaic action and the catalytic action catalyzed by the electrode catalyst to reduce an oxidant contained in the electrolytic medium to perform material transformation of the oxidant into a predetermined product.

[0023] In FIG. 1, the electrolysis cells 100 and 200 are an anode-side first electrolysis cell 100 and a cathode-side second electrolysis cell 200, which are partitioned as two chambers. The first electrolysis cell 100 is separated from the second electrolysis cell 200 by a diaphragm 30. The first electrolysis cell 100 accommodates a first electrolytic solution 110 as an anode-side electrolytic medium. The second electrolysis cell 200 accommodates a second electrolytic solution 210 as a cathode-side electrolytic medium.

[0024] The first electrolytic solution 110 used can be conductive liquid containing an appropriate reductant according to an application or a purpose of the photocatalytic apparatus 1. Specific examples of the reductant include water used to generate oxygen, ammoniacal nitrogen, reducing sulfur, and ions generated by the ammoniacal nitrogen or reducing sulfur. As the reductant, water is particularly preferable in terms of resource availability. The first electrode 10 preferably oxidizes water to generate oxygen.

[0025] The second electrolytic solution 210 used can be conductive liquid containing an appropriate oxidant according to the application or the purpose of the photocatalytic apparatus 1. Specific examples of the oxidant include water used to generate hydrogen, carbon dioxide, nitrate nitrogen, oxidizing sulfur, and ions generated by carbon dioxide, nitrate nitrogen, or oxidizing sulfur. As the reductant, carbon dioxide is particularly preferable in terms of resource availability. The second electrode 20 preferably reduces carbon dioxide to generate carbon monoxide or a carbon compound.

[0026] Specific examples of the first electrolytic solution 110 and the second electrolytic solution 210 include seawater, lake water, river water, domestic wastewater, factory wastewater, treated water thereof, tap water, industrial water, special wastewater with a carbon content, a nitrogen content, a sulfur content, or the like, and the like.

[0027] The diaphragm 30 polarizes the electrolytic medium between the anode side and the cathode side. The diaphragm 30 is formed of a material that blocks transmission of gas while permitting transmission of ions such as hydrogen ions. The diaphragm 30 used may be a semipermeable membrane, an ion-exchange membrane, a porous resin filter, a porous ceramic filter, or the like.

[0028] In FIG. 1, the first electrolysis cell 100 connects to a first gas feeding apparatus 101, a first gas discharge apparatus 102, a first electrolytic solution feeding apparatus 103, and a first electrolytic solution discharge apparatus 104 each via piping. The second electrolysis cell 200 connects to a second gas feeding apparatus 201, a second gas discharge apparatus 202, a second electrolytic solution feeding apparatus 203, and a second electrolytic solution discharge apparatus 204 each via piping.

[0029] The first gas feeding apparatus 101 is an apparatus that feeds gas to the first electrolysis cell 100. The first gas discharge apparatus 102 is an apparatus that discharges gas from the first electrolysis cell 100. The first gas discharge apparatus 102 is connected to an upper side of the first electrolysis cell 100, corresponding to a gas phase portion.

[0030] The first electrolytic solution feeding apparatus 103 is an apparatus that feeds an electrolytic solution to the first electrolysis cell 100. The first electrolytic solution feeding apparatus 103 can function as a feeding mechanism that feeds the first electrode 10 with a reactant of an oxidation reaction. The first electrolytic solution discharge apparatus 104 is an apparatus that discharges an electrolytic solution from the first electrolysis cell 100. The first electrolytic solution discharge apparatus 104 is connected to a lower side of the first electrolysis cell 100, corresponding to a liquid phase portion. The first electrolytic solution discharge apparatus 104 can function as a recovery mechanism that recovers a product generated by the first electrode 10.

[0031] The first electrolytic solution feeding apparatus 103 feeds the first electrolysis cell 100 with the first electrolytic solution 110 containing a predetermined reductant. Additionally, the first electrolytic solution discharge apparatus 104 discharges, from the first electrolysis cell 100, the first electrolytic solution 110 containing a product generated by oxidation of the reductant, with the first electrolytic solution 110 recovered.

[0032] A pump, a tank, or the like constitutes each of the first gas feeding apparatus 101, the first gas discharge apparatus 102, the first electrolytic solution feeding apparatus 103, and the first electrolytic solution discharge apparatus 104. These apparatuses can be continuously or intermittently operated. Additionally, the first gas feeding apparatus 101 and the first gas discharge apparatus 102 can adjust the concentration of dissolved gas in the first electrolytic solution 110, feed a gaseous reductant, and recover a gaseous product.

[0033] The second gas feeding apparatus 201 is an apparatus that feeds gas to the second electrolysis cell 200. The second gas discharge apparatus 202 is an apparatus that discharges gas from the second electrolysis cell 200. The second gas discharge apparatus 202 is connected to an upper side of the second electrolysis cell 200, corresponding to a gas phase portion.

[0034] The second electrolytic solution feeding apparatus 203 is an apparatus that feeds an electrolytic solution to the second electrolysis cell 200. The second electrolytic solution feeding apparatus 203 can function as a feeding mechanism that feeds a reactant of a reduction reaction to the second electrode 20. The second electrolytic solution discharge apparatus 204 is an apparatus that discharges the electrolytic solution from the second electrolysis cell 200. The second electrolytic solution discharge apparatus 204 is connected to a lower side of the second electrolysis cell 200, corresponding to a liquid phase portion. The second electrolytic solution discharge apparatus 204 can function as a recovery mechanism that recovers a product generated by the second electrode 20.

[0035] The second electrolytic solution feeding apparatus 203 feeds the second electrolysis cell 200 with the second electrolytic solution 210 containing a predetermined oxidant. Additionally, the second electrolytic solution discharge apparatus 204 discharges, from the second electrolysis cell 200, the second electrolytic solution 210 containing a product generated by reduction of the oxidant, with the second electrolytic solution 210 recovered.

[0036] A pump, a tank, or the like constitutes each of the second gas feeding apparatus 201, the second gas discharge apparatus 202, the second electrolytic solution feeding apparatus 203, and the second electrolytic solution discharge apparatus 204. These apparatuses can be continuously or intermittently operated. Additionally, the second gas feeding apparatus 201 and the second gas discharge apparatus 202 can adjust the concentration of dissolved gas in the second electrolytic solution 210, feed a gaseous oxidant, and recover a gaseous product.

[0037] The first electrode 10 and the second electrode 20 are irradiated with visible light, ultraviolet light, or the like, as depicted by blank arrows in FIG. 1. Irradiation light has light energy larger than the bandgap of a material using light energy. The irradiation light may be natural light such as sunlight or may be artificial light.

[0038] An appropriate artificial light source can be used as a light source that radiates artificial light. Examples of the artificial light source include a fluorescent light, an incandescent lamp, a light emitting diode (LED), an organic electroluminescence (EL) light source, a laser light source, a cold-cathode tube, and discharge lamps such as a mercury lamp, a xenon lamp, and a sodium lamp.

[0039] Each of the electrolysis cells 100 and 200 can be at least partly provided in a light transmissive structure. For example, for each of the electrolysis cells 100 and 200, a part or all of a ceiling portion or a side surface portion can be formed of a transparent material such as glass. The artificial light source may be installed inside or outside each of the electrolysis cells 100 and 200.

[0040] The first electrode 10 and the second electrode 20 are electrically connected via external wiring. In FIG. 1, an external power supply 50 is electrically connected between the first electrode 10 and the second electrode 20. The external power supply 50 is a power supply for applying an auxiliary potential. In the photocatalytic apparatus 1, in a case where a potential difference required for material transformation cannot be obtained only by light irradiation, the external power supply 50 can be used to apply the auxiliary potential.

[0041] In FIG. 1, a voltmeter 60 is installed in the photocatalytic apparatus 1. The voltmeter 60 is electrically connected in parallel to external wiring and a reference electrode 61. The reference electrode 61 is installed inside the first electrolysis cell 100 and immersed in the first electrolytic solution 110.

[0042] In the photocatalytic apparatus 1, the electrode potential of the first electrode 10 can be measured in real time using the voltmeter 60. The measured electrode potential of the first electrode 10 allows monitoring of usage of light energy and the degradation state of a layer using light energy. When the result of the measurement determines that the electrode potential of the first electrode 10 does not reach a reaction potential in consideration of overvoltage required for material transformation, the external power supply 50 can be activated.

[0043] The first electrode 10 includes a first transparent substrate 11, a first conductive layer 12, a first electron transport layer 13, a first light power generation layer 14, and a photocatalytic layer 15. The first transparent substrate 11 and the first conductive layer 12 constitute a first transparent conductive substrate having light transmittivity and electrical conductivity. The photocatalytic layer 15 carries a promotor 16.

[0044] The first conductive layer 12 is disposed on a front surface of the first transparent substrate 11. The first electron transport layer 13 is disposed on a front surface of the first conductive layer 12. The first light power generation layer 14 is disposed on a front surface of the first electron transport layer 13. The photocatalytic layer 15 is disposed on a front surface of the first light power generation layer 14. The promotor 16 is supported on a front surface of the photocatalytic layer 15 on the electrolytic solution side.

[0045] The first electrode 10 can be provided as a structure in which a sealing material not illustrated seals functional layers such as the first conductive layer 12, the first electron transport layer 13, and the first light power generation layer 14. The photocatalytic layer 15 and the promotor 16 are provided in such a manner that at least one surface of each of the photocatalytic layer 15 and the promotor 16 is in contact with the first electrolytic solution 110.

[0046] The first transparent substrate 11 permits external light to be transmitted to the first light power generation layer 14 and the photocatalytic layer 15, and mechanically supports electrode elements of the first electrode 10. The first transparent substrate 11 can be provided in an appropriate form such as a plate, film, or a sheet. The first transparent substrate 11 is formed of a material exhibiting light transmittivity for the irradiation light and having mechanical strength. A single-layer or multilayer antireflection film may be formed on the front surface of the first transparent substrate 11 on which the irradiation light is incident.

[0047] Examples of a material for the first transparent substrate 11 include glass materials such as soda lime glass, silica glass, and borosilicate glass, polyesters such as polyethylene terephthalate and polyethylene naphthalate, polyolefins such as polyethylene and polypropylene, and resin materials such as polystyrene, polycarbonate, cellulose ester, polyamide, and acrylic resin. Examples of a material for the antireflection film include titania, zirconia, and silica.

[0048] The first conductive layer 12 permits external light to be transmitted to the first light power generation layer 14 and the photocatalytic layer 15 and functions as a current collector for the first electrode 10. The first conductive layer 12 is electrically connected to the second electrode 20 via external wiring. The first conductive layer 12 is formed of a material exhibiting light transmittivity for the irradiation light and having high electrical conductivity.

[0049] Examples of a material for the first conductive layer 12 include indium tin oxide (ITO), a fluorine-doped tin oxide (FTO), indium oxide zinc oxide (IZO), gallium oxide zinc oxide (GZO), aluminum-doped zinc oxide (AZO), zinc oxide (ZnO), tin oxide (SnOz), and the like.

[0050] The first electron transport layer 13 is interposed at an interface of the first light power generation layer 14 as a buffer layer, and selectively transports electrons from the first light power generation layer 14 toward the first conductive layer 12. The first electron transport layer 13 preferably has a thickness that permits light to be transmitted to the first light power generation layer 14 and the photocatalytic layer 15. The first electron transport layer 13 is formed of a material such as an n-type semiconductor that has high electron transportability.

[0051] Examples of a material for the first electron transport layer 13 include oxide semiconductors such as titanium oxide (TiOz), zinc oxide (ZnO), tin oxide (SnOz), magnesium oxide (MgO), molybdenum trioxide (MoOs), and niobium oxide (NbO), which are metal excessive, and the oxide semiconductors doped with Cr, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, In, Sn, Sb, and the like, metal complexes, and organic materials such as fluorene derivative, oxadiazole derivative, and benzodiazole derivative.

[0052] Provision of the first electron transport layer 13 enables a reduction in loss of charge at the interface between the first light power generation layer 14 and another layer. Additionally, electrons in the first light power generation layer 14 can be selectively transported toward the first conductive layer 12, while migration of holes is inhibited. When electrons generated in the first light power generation layer 14 are separated by band bending, the electrons are difficult to recouple to holes generated in the first light power generation layer 14. The first light power generation layer 14 increases light energy conversion efficiency, thus enabling an increase in the efficiency of material transformation by the first electrode 10.

[0053] The first light power generation layer 14 is a layer using light energy and absorbs light to generate electrons and holes. Electrons generated in the first light power generation layer 14 are transported to the first conductive layer 12 side. Holes generated in the first light power generation layer 14 are transported to the photocatalytic layer 15 side. The first light power generation layer 14 is formed of a material exhibiting a photovoltaic action and absorbing light to generate electrons and holes. The material causes band bending toward the interface to separate the electrons from the holes.

[0054] A material for the first light power generation layer 14 includes a valence band having an energy level higher than that of a redox potential of a predetermined reductant contained in the first electrolytic solution 110. Examples of the material for the first light power generation layer 14 include bismuth oxyiodide (BiOI), bismuth oxybromide (BiOBr), bismuth oxychloride (BiOCl), a composite material of any of the above-listed materials and an electron mediator, a semiconductor composite material of pn joined semiconductors or pin joined semiconductors, and the like.

[0055] Examples of the semiconductor include oxide semiconductors such as titanium oxide, zinc oxide, tin oxide, molybdenum trioxide, gallium oxide, nickel oxide (II), copper oxide (I), bismuth tungstate, bismuth vanadium oxide, tin niobate, strontium titanate, and iridium oxide zinc oxide doped with Cr, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, In, Sn, or Sb, sulfides such as cadmium sulfide, copper indium sulfide, and copper zinc tin sulfide, selenides such as cadmium selenium, copper indium selenide, and copper gallium selenide, tellurides such as copper gallium telluride and cadmium tellurium, nitrides such as niobium nitride and tantalum nitride, amorphous silicon, crystal silicon, and the like, germanium, impurity semiconductors such as a two-element mixed crystal doped with phosphor, arsenic, antimony, boron, aluminum, gallium, indium, or the like.

[0056] The material of the first light power generation layer 14 preferably includes a band gap smaller than that of the material of the photocatalytic layer 15 in view of conjugation of the photovoltaic action of the first light power generation layer 14 with the photocatalytic action of the photocatalytic layer 15. Additionally, the material for the first light power generation layer 14 preferably includes a valence band having an energy level lower than that of a valence band of the material for the photocatalytic layer 15 in view of separation of electrons. In addition, the material for the first light power generation layer 14 preferably includes a conduction band having an energy level higher than that of a conduction band of the material for the photocatalytic layer 15 in view of separation of holes.

[0057] With the first light power generation layer 14 provided, light radiated to the first electrode 10 causes a photovoltaic action to generate electrons and holes, and band bending allows the electrons generated to be separated from the holes generated, with the electrons migrated to the internal layer side and the holes migrated to the interface side. The electrons and the holes separated from one another can be used for a redox reaction at the respective electrodes, allowing material transformation to be achieved with high energy efficiency.

[0058] The photocatalytic layer 15 is a layer using light energy and catalyzes a predetermined oxidation reaction when being irradiated with light. The photocatalytic layer 15 may be either porous or non-porous. The photocatalytic layer 15 is preferably porous in view of reaction efficiency. The photocatalytic layer 15 is formed of a material exhibiting a photocatalytic action and absorbing light to generate electrons and holes in the material.

[0059] Examples of a material for the photocatalytic layer 15 include bismuth vanadium oxide ($BiVO_4$), bismuth tungstate (Bi_2WO_6), bismuth ferrate ($BiFeO_3$), tantalum oxynitride (TaON), tungsten trioxide (WO_3), titanium oxide (TiOz), and the like.

[0060] The promotor 16 assists a catalytic action performed by the photocatalytic layer 15. The promotor 16 used may be of a type providing a reaction field for the oxidation reaction by the photocatalytic layer 15, a type promoting generation of predetermined gas, a type adjusting optical responsivity for visible light, or the like.

[0061] Examples of the promotor 16 include metal nanoparticles such as copper, nickel, cobalt, manganese, silver, gold, platinum, palladium, rhodium, ruthenium, and iridium, and metal oxide nanoparticles such as chromium oxide, copper oxide, ferroxide, nickel oxide, manganese oxide, cobalt oxide, platinum oxide, and chromium oxide.

[0062] With the photocatalytic layer 15 provided, light radiated to the first electrode 10 causes a photocatalytic action to allow a predetermined oxidation reaction to be promoted. A reductant contained in the first electrolytic solution 110 can be efficiently oxidized using light energy, thus allowing a predetermined product to be generated with high material transformation efficiency. Additionally, the photocatalytic layer 15 carrying the promotor 16 increases the efficiency of material transformation performed by the photocatalytic layer 15. Accordingly, a large amount of product can be generated in a short time.

[0063] The second electrode 20 includes a second transparent substrate 21, a second conductive layer 22, a charge transport layer 23, a second light power generation layer 24, a second electron transport layer 25, a conductive reflection layer 26, and a catalytic layer 27. The second transparent substrate 21 and the second conductive layer 22 form a second transparent conductive substrate having light transmittivity and electrical conductivity.

[0064] The second conductive layer 22 is disposed on a front surface of the second transparent substrate 21. The charge transport layer 23 is disposed on a front surface of the second conductive layer 22. The second light power generation layer 24 is disposed on a front surface of the second electron transport layer 25. The second electron transport layer 25 is disposed on a front surface of the second light power generation layer 24. The conductive reflection layer 26 is disposed on a front surface of the second electron transport layer 25. The catalytic layer 27 is disposed on a front surface of the conductive reflection layer 26.

[0065] The second electrode 20 can be provided as a structure in which a sealing material not illustrated seals functional layers such as the second conductive layer 22, the charge transport layer 23, the second light power generation layer 24, the second electron transport layer 25, the conductive reflection layer 26, and the like. The catalytic layer 27 is provided in such a manner that at least one surface of the catalytic layer 27 is in contact with the second electrolytic solution 210.

[0066] The second transparent substrate 21 permits external light to be transmitted to the second light power generation layer 24, and mechanically supports electrode elements of the second electrode 20. The second transparent substrate 21 can be provided in an appropriate form such as a plate, film, or a sheet. The second transparent substrate 21 is formed of a material exhibiting light transmittivity for the irradiation light and having mechanical strength. A single-layer or multilayer antireflection film may be formed on the front surface of the second transparent substrate 21 on which the irradiation light is incident.

[0067] Examples of a material for the second transparent substrate 21 include glass materials such as soda lime glass, silica glass, and borosilicate glass, polyesters such as polyethylene terephthalate and polyethylene naphthalate, polyolefins such as polyethylene and polypropylene, and resin materials such as polystyrene, polycarbonate, cellulose ester, polyamide, and acrylic resin. Examples of a material for the antireflection film include titania, zirconia, and silica.

[0068] The second conductive layer 22 permits external light to be transmitted to the second light power generation layer 24 and functions as a current collector for the second electrode 20. The second conductive layer

22 is electrically connected to the first electrode 10 via external wiring. The second conductive layer 22 is formed of a material exhibiting light transmittivity for the irradiation light and having high electrical conductivity.

[0069] Examples of a material for the second conductive layer 22 include indium tin oxide (ITO), a fluorine-doped tin oxide (FTO), indium oxide zinc oxide (IZO), gallium oxide zinc oxide (GZO), aluminum-doped zinc oxide (AZO), zinc oxide (ZnO), tin oxide (SnOz), and the like.

[0070] The charge transport layer 23 is interposed at an interface of the second light power generation layer 24 as a buffer layer, and transports charge with high conductivity. The charge transport layer 23 can be provided as an electron transport layer that selectively transports electrons, as a hole transport layer that selectively transports holes, or as an intermediate layer that transports electrons and holes and causes recoupling of them. The charge transport layer 23 preferably has a thickness that permits light to be transmitted to the second light power generation layer 24. The charge transport layer 23 is formed of a material such as a p-type semiconductor or an n-type semiconductor that has high charge transportability.

[0071] Examples of a material for the charge transport layer 23 include, as materials having high hole transportability, nickel oxide (II) (NiO), ferroxide (II) (FeO), copper oxide (I) (CuzO), copper oxide (II) (CuO), and the like, oxide semiconductors including the above-listed materials doped with heterogenous elements, compound semiconductors such as copper iodide (CuI) and copper thiocyanate (I) (CuSCN), metal complexes, and organic materials such as triaryl amine derivative, phthalocyanine derivative, and oxazole derivative. Additionally, examples of a material for the charge transport layer 23 include, as materials having high electron transportability, oxide semiconductors such as titanium oxide (TiOz), zinc oxide (ZnO), tin oxide (SnO_2), magnesium oxide (MgO), and niobium oxide (NbO), which are metal excessive, and these oxide semiconductors doped with heterogeneous elements, metal complexes, and organic materials such as fluorene derivative, oxadiazole derivative, and benzodiazole derivative.

[0072] Provision of the charge transport layer 23 enables a reduction in loss of charge at the interface between the second light power generation layer 24 and another layer. Additionally, with the use of a material with high hole transportability, holes in the second light power generation layer 24 can be selectively transported toward the second conductive layer 22, while migration of electrons is inhibited. Holes generated in the second light power generation layer 24 can be inhibited from recoupling to electrons generated in the second light power generation layer 24. With the use of a material with high electron transportability, electrons in the second conductive layer 22 can be selectively transported toward the second light power generation layer 24. Holes generated in the second light power generation layer 24 can be recoupled to the electrons transported from the second conductive layer 22. The second light power generation layer 24 increases light energy conversion efficiency, thus enabling an increase in the efficiency of material transformation by the second electrode 20.

[0073] The second light power generation layer 24 is a layer using light energy and absorbs light to generate electrons and holes. Electrons generated in the second light power generation layer 24 are transported to the catalytic layer 27 side. Holes generated in the second light power generation layer 24 recouple to the electrons transported from the first electrode 10. The second light power generation layer 24 is formed of a material exhibiting a photovoltaic action and absorbing light to generate electrons and holes. The material causes band bending toward the interface to separate the electrons from the holes.

[0074] A material for the second light power generation layer 24 includes a conduction band having an energy level lower than that of a redox potential of a predetermined oxidant contained in the second electrolytic solution 210. Examples of the material for the second light power generation layer 24 include bismuth oxyiodide (BiOI), bismuth oxybromide (BiOBr), bismuth oxychloride (BiOCl), a composite material of any of the above-listed materials and an electron mediator, a semiconductor composite material of pn joined semiconductors or pin joined semiconductors, and the like.

[0075] With the second light power generation layer 24 provided, light radiated to the second electrode 20 causes a photovoltaic action to generate electrons and holes, and band bending allows the electrons generated to be separated from the holes generated, with the electrons migrated to the internal layer side and the holes migrated to the interface side. The electrons and the holes separated from one another can be used for a redox reaction at the respective electrodes, allowing material transformation to be achieved with high energy efficiency.

[0076] The second electron transport layer 25 is interposed at the interface of the second light power generation layer 24 as a buffer layer, and selectively transports electrons from the second light power generation layer 24 toward the catalytic layer 27. The second electron transport layer 25 is formed of a material such as an n-type semiconductor that has high electron transportability and that exhibits an electron injection capability based on a tunnel effect.

[0077] Examples of a material for the second electron transport layer 25 include oxide semiconductors such as titanium oxide (TiOz), zinc oxide (ZnO), tin oxide (SnO_2), magnesium oxide (MgO), and niobium oxide (NbO), which are metal excessive, and these oxide semiconductors doped with Cr, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, In, Sn, Sb, and the like, lithium fluorine (LiF), fluorocarbon, metal complexes, and organic materials such as fluorene derivative, oxadiazole derivative, and benzodiazole derivative.

[0078] Provision of the second electron transport layer

25 enables a reduction in loss of charge at the interface between the second light power generation layer 24 and another layer. Additionally, electrons in the second light power generation layer 24 can be selectively transported toward the catalytic layer 27, while migration of holes is inhibited. Electrons generated in the second light power generation layer 24 and electrons transported from the first electrode 10 are difficult to recouple to holes generated in the second light power generation layer 24. The second light power generation layer 24 increases light energy conversion efficiency, thus enabling an increase in the efficiency of material transformation by the second electrode 20.

[0079] The conductive reflection layer 26 has electrical conductivity and transports electrons from the second light power generation layer 24 side toward the catalytic layer 27 side. The conductive reflection layer 26 controls the conduction of charge at the interface between the second light power generation layer 24 side and the catalytic layer 27 side, and reflects irradiation light toward the second light power generation layer 24 side. The conductive reflection layer 26 is formed of a material having a high reflectance for visible light, ultraviolet light, and the like, a small work function, and high electron conductivity.

[0080] Examples of a material for the conductive reflection layer 26 include silver, chromium, aluminum, gold, platinum, and alloys thereof. The preferred materials for the conductive reflection layer 26 are silver, chromium, and alloys thereof in view of the small work functions thereof.

[0081] Provision of the conductive reflection layer 26 enables irradiation light to be reflected and radiated to the second light power generation layer 24 side. Additionally, provision of the conductive reflection layer 26 reduces a junction barrier at the interface between the second light power generation layer 24 side and the catalytic layer 27 side, allowing electron conduction and rectification at the interface to be improved. In a case where the catalytic layer 27 side is directly deposited on the front surface of the second electron transport layer 25, the interface is nonuniform, and conduction paths of electrons locally concentrate in the plane, leading to variation in potential difference. In contract, provision of the conductive reflection layer 26 reduces variation in conduction resistance, allowing electrons to be transported uniformly in an edgewise direction orthogonal to the lamination direction of the electrode elements.

[0082] The catalytic layer 27 receives electrons generated by the second light power generation layer 24 and catalyzes a predetermined reduction reaction. The catalytic layer 27 may be either porous or non-porous. The catalytic layer 27 is preferably porous in view of reaction efficiency. The catalytic layer 27 is formed of a material exhibiting an appropriate catalytic action according to the application or purpose of the photocatalytic apparatus 1.

[0083] The catalytic layer 27 used can be a reducing catalyst that reduces, for example, carbon dioxide, nitrate nitrogen, oxidizing sulfur compounds, and the like. Examples of a material for the catalytic layer 27 include copper, silver, gold, platinum, palladium, nickel, cobalt, zinc, tin, molybdenum, tungsten, vanadium, iridium, alloys thereof such as a copper-palladium alloy catalyst, oxides thereof such as copper oxide (I) (Cu_2O) and copper oxide (II) (CuO), molybdenum sulfide, tungsten sulfide, zinc sulfide, and the like.

[0084] Provision of the catalytic layer 27 enables a predetermined reduction reaction to be promoted by a catalytic action using electrons generated by the second light power generation layer 24. An oxidant contained in the second electrolytic solution 210 can be efficiently reduced using charge generated by light power generation, thus allowing a predetermined product to be generated with high material transformation efficiency. For example, reducing carbon dioxide allows carbon monoxide to be generated. Additionally, with reaction gas fed by the second gas feeding apparatus 201, reducing carbon dioxide allows generation of methanol, ethanol, ethylene, formic acid, or the like.

[0085] Each of the layers constituting the first electrode 10 and the second electrode 20 can be formed by an appropriate deposition method depending on the material. Examples of the deposition method include physical vapor deposition (PVD) such as vacuum deposition, sputtering, or ion plating, chemical vapor deposition (CVD) such as plasma CVD or organic metal CVD, chemical solution deposition (CSD) including application of a solution with precursors dispersed and firing.

[0086] Materials for each of the layers constituting the first electrode 10 and the second electrode 20 can be synthesized using an appropriate synthesis method such as metal organic decomposition (MOD), hydrothermal synthesis, solution phase synthesis, or sol-gel synthesis. The promotor 16 can be supported using PVD such as vacuum deposition or sputtering, electrodeposition, chemical deposition, adsorption, or the like.

[0087] The material transformation by the photocatalytic apparatus 1 is performed using the following method. First, the first electrolytic solution 110 containing a predetermined reductant is prepared in the first electrolysis cell 100. Additionally, the second electrolytic solution 210 containing a predetermined oxidant is prepared in the second electrolysis cell 200. Then, the first electrode 10 and the second electrode 20 are irradiated with irradiation light such as visible light, ultraviolet light, or the like.

[0088] When the irradiation light is incident on the first light power generation layer 14, electrons in the first light power generation layer 14 are excited by the conduction band and separated from holes. The electrons generated in the first light power generation layer 14 are transported to the first conductive layer 12 via the first electron transport layer 13. The electrons transported to the first conductive layer 12 are transported to the second conductive layer 22 via external wiring. The holes generated in the first light power generation layer 14 are transported to the photocatalytic layer 15.

[0089] Additionally, when the irradiation light is incident on the photocatalytic layer 15, the electrons in the photocatalytic layer 15 are excited by the conduction band to generate electrons and holes in the material. The reductant contained in the first electrolytic solution 110 receives, due to the oxidation reaction by the photocatalytic layer 15, holes generated by the photocatalytic layer 15 and the first light power generation layer 14, and is transformed into a predetermined product. Some or all of the electrons generated in the photocatalytic layer 15 recouple to the holes generated in the first light power generation layer 14, with the remaining electrons transported to the first conductive layer 12. The product resulting from the oxidation reaction is recovered by the first electrolytic solution discharge apparatus 104.

[0090] Additionally, when the irradiation light is incident on the second light power generation layer 24, the electrons in the second light power generation layer 24 are excited by the conduction band and separated from the holes. Holes generated in the second light power generation layer 24 are transported toward the charge transport layer 23. Electrons generated in the second light power generation layer 24 are transported to the catalytic layer 27 via the second electron transport layer 25 and the like.

[0091] When the electrons are transported to the catalytic layer 27, the electrical reduction reaction by the catalytic layer 27 is promoted. Some or all of the electrons generated in the first light power generation layer 14 recouple to the holes generated in the second light power generation layer 24, with the remaining electrons transported to the catalytic layer 27. The oxidant contained in the second electrolytic solution 210 receives, due to the reduction reaction by the catalytic layer 27, the electrons generated by the second light power generation layer 24 and the first light power generation layer 14, and is transformed into a predetermined product. The product resulting from the reduction reaction is recovered by the second electrolytic solution discharge apparatus 204.

[0092] In the photocatalytic apparatus 1 described above, the anode side uses the photocatalytic action to allow material transformation to be inexpensively performed on the basis of oxidation power using light energy. Additionally, both the anode-side electrode and the cathode-side electrode use the photovoltaic action, and thus the utilization rate of the light energy can be increased to improve the material transformation efficiency based on the electrode reaction. Light power generation performed at both electrodes allows reduction of the auxiliary potential or abolishment of the external power supply with a potential difference ensured that is required for the redox reaction, enabling a reduction in the material transformation cost as a whole. Additionally, conjugation of the photocatalyst with the light power generation layer makes mutual migration and mutual use of charge efficient to allow the utilization rate of the light energy to be increased. Accordingly, with the photovoltaic action used at both the anode- and cathode-side electrodes and conjugation of the photocatalytic action with the photovoltaic action, efficient material transformation can be performed on the basis of the redox reaction on the electrodes using light energy.

[0093] Additionally, in the photocatalytic apparatus 1 described above, the buffer layer is formed at the interface of each of the first light power generation layer 14 and the second light power generation layer 24, which perform light power generation, enabling a reduction in scattering loss and recoupling loss of charge at the interface. The charge generated in the first light power generation layer 14 and the second light power generation layer 24 is stabilized and has extended lifetime, allowing the material transformation efficiency to be improved at both electrodes. Further, improved transportability of charge allows the conduction paths of charge to be prevented from being locally concentrated in the plane of the interface. This makes the conduction paths less likely to have locally low voltages at the interface, allowing prevention of a decrease in electrode output during light irradiation.

<Second Embodiment>

[0094] FIG. 2 is a diagram schematically depicting a photocatalytic apparatus according to a second embodiment of the present invention.

[0095] As depicted in FIG. 2, a photocatalytic apparatus 2 according to the second embodiment includes the first electrode 10 functioning as an anode, the second electrode 20 functioning as a cathode, the electrolysis cells 100 and 200, and the like as with the photocatalytic apparatus 1 described above.

[0096] The photocatalytic apparatus 2 according to the present embodiment differs from the photocatalytic apparatus 1 described above in that, instead of the promotor 16, a promotor layer 17 is formed on the front surface of the photocatalytic layer 15 of the first electrode 10. The other main configuration of the photocatalytic apparatus 2 is similar to that of the photocatalytic apparatus 1 described above.

[0097] The promotor layer 17 is a layer that assists the catalytic action by the photocatalytic layer 15. The promotor layer 17 used may be of a type providing a reaction field for the oxidation reaction by the photocatalytic layer 15, a type promoting generation of predetermined gas, a type adjusting optical responsivity for visible light, or the like. The promotor layer 17 may be either porous or non-porous. The promotor layer 17 is preferably porous in view of reaction efficiency.

[0098] Examples of a material for the promotor layer 17 include metals such as copper, silver, gold, platinum, palladium, rhodium, and ruthenium, and metal oxides such as chromium oxide, copper oxide, ferroxide, nickel oxide, manganese oxide, cobalt oxide, platinum oxide, and chromium oxide, and the like.

[0099] Examples of the deposition method for forming the promotor layer 17 include PVD such as vacuum deposition or sputtering, CVD such as plasma CVD or organic metal CVD, CSD, and the like. The promotor layer 17 can be patterned in any shape on the front surface of the photocatalytic layer 15.

[0100] The photocatalytic apparatus 2 produces effects similar to those of the photocatalytic apparatus 1 described above. Additionally, the formation of the promotor layer 17 on the front surface of the photocatalytic layer 15 allows possible drop-off or elution of the promotor to be prevented, compared to the support of promotor particles on the front surface. Additionally, the promotor can be uniformly disposed on the front surface of the photocatalytic layer 15, thus enabling a reduction in variation in migration of charge to the promotor in the edgewise direction orthogonal to the lamination direction of the electrode elements.

<Third Embodiment>

[0101] FIG. 3 is a diagram schematically depicting a photocatalytic apparatus according to a third embodiment of the present invention.

[0102] As depicted in FIG. 3, a photocatalytic apparatus 3 according to the third embodiment includes the first electrode 10 functioning as an anode, the second electrode 20 functioning as a cathode, the electrolysis cells 100 and 200, and the like as with the photocatalytic apparatus 1 described above.

[0103] The photocatalytic apparatus 3 according to the present embodiment differs from the photocatalytic apparatus 1 described above in that an insulator is embedded in the first electrode 10, and that the electrode elements of the first electrode 10 are divided into cell structures by the insulator 18. The other main configuration of the photocatalytic apparatus 3 is similar to that of the photocatalytic apparatus 1 described above.

[0104] The insulator 18 divides the electrode elements of the first electrode 10 into cell structures to electrically insulate the partitioned cell units from one another. The insulator 18 is formed like a lattice as viewed in the lamination direction of the electrode elements of the first electrode 10. The electrode elements of the first electrode 10 are divided into the cell units in the edgewise direction orthogonal to the lamination direction of the electrode elements, the cell units being bounded by the insulator 18. The insulator 18 is formed of an electric insulating material having low electron conductivity.

[0105] Examples of a material for the insulator 18 include inorganic insulating materials such as alumina, magnesia, silica, zirconia, ceria, barium titanate, strontium titanate, silicon nitride, and aluminum nitride, and organic insulating materials such as epoxy resin, silicone resin, polyimide, and the like.

[0106] The insulator 18 can be provided in an appropriate shape as viewed in the lamination direction of the electrode elements. Examples of the shape of the cell units into which the electrode elements are partitioned by the insulator 18 include polygons such as a rectangle, a rhombus, and a hexagon. The insulator 18 can be provided as slits, squares, or the like as viewed in the lamination direction of the electrode elements.

[0107] Note that, in FIG. 3, the insulator 18 is formed to penetrate the first electron transport layer 13, the first light power generation layer 14, and the photocatalytic layer 15 in the lamination direction of the electrode elements. However, the insulator 18 can be formed to penetrate one or more of the first electron transport layer 13, the first light power generation layer 14, and the photocatalytic layer 15. The insulator 18 is preferably formed to penetrate at least the first electron transport layer 13.

[0108] Examples of the deposition method for depositing the insulator 18 include PVD such as vacuum deposition or sputtering, CVD such as plasma CVD or organic metal CVD, CSD, and the like. The insulator 18 can be formed by a method of patterning using a mask, a method of combining etching with deposition, or a method of combining with potting of an insulating material like fluid.

[0109] The photocatalytic apparatus 3 produces effects similar to those of the photocatalytic apparatus 1 described above. Additionally, the insulator 18 is embedded in the first electrode 10, and the electrode elements of the first electrode 10 are divided into cell structures, thus allowing the conduction paths of charge to be partitioned along the lamination direction of the electrode elements. The conduction paths of charge can be limited along the lamination direction of the electrode elements, thus enabling a reduction in scattering loss or recoupling loss of charge. Additionally, the conduction paths of charge are discretized in the edgewise direction orthogonal to the lamination direction of the electrode elements, thus allowing prevention of local concentration of the conduction paths of charge in the plane. The conduction paths are less likely to have extremely low potentials, and potential differences are made unlikely to vary, thus allowing improvement of the efficiency of material transformation by the first electrode 10.

<Fourth Embodiment>

[0110] FIG. 4 is a diagram schematically depicting a photocatalytic apparatus according to a fourth embodiment of the present invention.

[0111] As depicted in FIG. 4, a photocatalytic apparatus 4 according to the fourth embodiment includes the first electrode 10 functioning as an anode, the second electrode 20 functioning as a cathode, the electrolysis cells 100 and 200, and the like as with the photocatalytic apparatus 1 described above.

[0112] The photocatalytic apparatus 4 according to the present embodiment differs from the photocatalytic apparatus 1 described above in that a thin line structure 19 is formed on the front surface of the first electron transport layer 13 on the first light power generation layer 14 side. The other main configuration of the photocatalytic apparatus 4 is similar to that of the photocatalytic apparatus

1 described above.

[0113] The thin line structure 19 forms transport paths through which electrons are selectively transported along the lamination direction of the electrode elements. The thin line structure 19 is embedded in the first light power generation layer 14 in a state of protruding from the front surface of the first electron transport layer 13 toward the first light power generation layer 14 side and extending along the lamination direction of the electrode elements of the first electrode 10. The thin line structure 19 is formed of a crystal shaped like rods, needles, or the like. The thin line structure 19 is formed of a material similar to that of the first electron transport layer 13.

[0114] Examples of a material for the thin line structure 19 include oxide semiconductors such as titanium oxide (TiOz), zinc oxide (ZnO), tin oxide (SnO_2), magnesium oxide (MgO), molybdenum trioxide (MoOs), and niobium oxide (NbO), which are metal excessive.

[0115] The thin line structure 19 can be formed by a method of sintering the oxide semiconductor to the first electron transport layer 13 or a method of crystal-growing the oxide semiconductor on the front surface of the first electron transport layer 13. For example, metallic salt is prepared as a precursor for the oxide semiconductor, and the metallic salt and a stabilizer such as citric acid are mixed in a solvent. Such a material solution is applied onto the substrate, which is then fired to allow growing of a single crystal shaped like rods, needles, or the like on the front surface of the substrate. The first electrode 10 can be formed by deposition on the fired substrate or transfer of the substrate.

[0116] For example, in a case where zinc oxide or molybdenum oxide is synthesized, ammonium orthomolybdate ($(NH_4)_2MoO_4$), ammonium zincate ($(NH_4)_2ZnO_2$), or the like can be used. Firing temperature ranges from approximately 350°C to 450°C. When firing is performed at 400°C for 10 minutes using 0.5 M of metallic salt and 1.5 M of citric acid, a single crystal with a diameter of approximately 15 nm and a length of approximately 200 nm is obtained. The size of the single crystal can be controlled by the ratio between the metallic salt and the stabilizer, the firing temperature, and the firing time.

[0117] The photocatalytic apparatus 4 produces effects similar to those of the photocatalytic apparatus 1 described above. Additionally, the thin line structure 19 is formed on the front surface of the first electron transport layer 13, thus enabling an increase in the area of the interface with the first light power generation layer 14. Additionally, the material with high electron transportability allows formation of conduction paths of charge along the lamination direction of the electrode elements. The conduction paths of charge can be limited in the lamination direction of the electrode elements, thus enabling a reduction in scattering loss and recoupling loss of charge. Additionally, the conduction paths of charge are discretized in the edgewise direction orthogonal to the lamination direction of the electrode elements, thus allowing prevention of local concentration of the conduction paths of charge in the plane. The conduction paths are less likely to have extremely low potentials, and potential differences are made unlikely to vary, thus allowing improvement of the efficiency of material transformation by the first electrode 10.

<Fifth Embodiment>

[0118] FIG. 5 is a diagram schematically depicting a photocatalytic apparatus according to a fifth embodiment of the present invention.

[0119] As depicted in FIG. 5, a photocatalytic apparatus 5 according to the fifth embodiment includes the first electrode 10 functioning as an anode, the second electrode 20 functioning as a cathode, the electrolysis cells 100 and 200, and the like as with the photocatalytic apparatus 1 described above.

[0120] The photocatalytic apparatus 5 according to the present embodiment differs from the photocatalytic apparatus 1 described above in that a conductive adhesion layer 28 is formed between the conductive reflection layer 26 and the catalytic layer 27, with an insulator 29 embedded in the second electrode 20. The other main configuration of the photocatalytic apparatus 5 is similar to that of the photocatalytic apparatus 1 described above.

[0121] The conductive adhesion layer 28 closely contacts the second light power generation layer 24 side with the catalytic layer 27 side and transports electrons from the second light power generation layer 24 side toward the catalytic layer 27 side. Provision of the conductive adhesion layer 28 enables the insulator 29 to be supported in an embedded state, and the surface on which the catalytic layer 27 is formed can be smoothed. The conductive adhesion layer 28 is formed of a material that easily ensures adhesion strength and that has high electron conductivity.

[0122] Examples of a material for the conductive adhesion layer 28 include a composite material of a conducting agent and matrix resin, a conductive oxide, and the like. Examples of the conducting agent include carbon nanotube, carbon fiber, carbon black, and graphene. Examples of the matrix resin include epoxy resin, phenol resin, and the like. Examples of the conductive oxide include zinc oxide (ZnO), tin oxide (SnO_2), and the like.

[0123] The insulator 29 divides the electrode elements of the second electrode 20 into cell structures to electrically insulate the partitioned cell units from one another. The insulator 29 is formed like a lattice as viewed in the lamination direction of the electrode elements of the second electrode 20. The electrode elements of the second electrode 20 are divided into the cell units in the edgewise direction orthogonal to the lamination direction of the electrode elements, the cell units being bounded by the insulator 29. The insulator 29 is formed of an electric insulating material having low electron conductivity similarly to the insulator 18 described above.

[0124] The insulator 29 can be provided in an appropriate shape as viewed in the lamination direction of the electrode elements. Examples of the partitioning shape of the cell units of the insulator 29 include polygons such as a rectangle, a rhombus, and a hexagon. The insulator 29 can be provided as slits, squares, or the like as viewed in the lamination direction of the electrode elements.

[0125] Note that, in FIG. 5, in the lamination direction of the electrode elements, the insulator 29 penetrates the second electron transport layer 25 and the conductive reflection layer 26 and extends up to an intermediate portion of the conductive adhesion layer 28, but can be formed to penetrate any one or more of the second light power generation layer 24, the second electron transport layer 25, and the conductive reflection layer 26. The insulator 29 is preferably formed to penetrate at least the second electron transport layer 25.

[0126] Examples of the deposition method for depositing the conductive adhesion layer 28 and the insulator 29 include PVD such as vacuum deposition or sputtering, CVD such as plasma CVD or organic metal CVD, CSD, and the like. The insulator 29 can be formed by a method of performing patterning using a mask, a method of combining etching and deposition, or the like.

[0127] The photocatalytic apparatus 5 produces effects similar to those of the photocatalytic apparatus 1 described above. Additionally, the insulator 29 is embedded in the second electrode 20, and the electrode elements of the second electrode 20 are divided into cell structures, thus allowing the conduction paths of charge to be partitioned along the lamination direction of the electrode elements. The conduction paths of charge can be limited along the lamination direction of the electrode elements, thus enabling a reduction in scattering loss or recoupling loss of charge. Additionally, the conduction paths of charge are discretized in the edgewise direction orthogonal to the lamination direction of the electrode elements, thus allowing prevention of local concentration of the conduction paths of charge in the plane. The conduction paths are less likely to have extremely low potentials, and potential differences are made unlikely to vary, thus allowing improvement of the efficiency of material transformation by the second electrode 20.

[0128] FIG. 6 is a diagram depicting an example of a relation between an electrode potential and a current density of a known photocatalytic electrode. FIG. 7 is a diagram depicting an example of a relation between an output time and the current density of the known photocatalytic electrode. FIG. 6 and FIG. 7 depict results of analysis of electrode characteristics of a photocatalytic electrode using a photocatalyst, by a photoelectric converting apparatus including the photocatalytic electrode and a reference electrode. FIG. 6 depicts results of linear scanning voltammetry in which a linear electrode potential has been swept. FIG. 7 depicts results of measurement of variation in current density when 1 V of electrode potential is generated.

[0129] The photocatalytic electrode used is an electrode including a photocatalytic layer laminated on a transparent conductive substrate. The photocatalytic layer was formed of bismuth vanadium oxide ($BiVo_4$) and had a film thickness of 200 nm. The reference electrode used is platinum wiring. The photocatalytic electrode and the reference electrode were immersed in a 0.1-mol/L sodium sulfate solution.

[0130] The photocatalytic electrode was irradiated with simulated sunlight. A light source used is a solar simulator HAL-C100 (Asahi Spectra Co., Ltd.). Simulated sunlight adjusted to a standard value of AM1.5G was adjusted to an intensity output (0.6 SUN) corresponding to 60% of the solar light intensity, and the adjusted simulated sunlight was radiated to the surface of the photocatalytic layer of the photocatalytic electrode.

[0131] In FIG. 6, the horizontal axis indicates the electrode potential [V vs. Ag/AgCl] of the photocatalytic electrode, and the vertical axis indicates the current density (mA/cm^2) of the photocatalytic electrode. A solid curve in FIG. 6 indicates results of no light irradiation, and a dashed curve indicates results of light irradiation. In FIG. 7, the horizontal axis indicates the output time (seconds) of the photocatalytic electrode, and the vertical axis indicates the current density (mA/cm^2) of the photocatalytic electrode. The current density of the photocatalytic electrode was determined by dividing the conducting current to the photocatalytic electrode by the electrode area immersed in the electrolytic solution and irradiated with light.

[0132] As depicted in FIG. 6, with no light irradiation, the electrode potential of the photocatalytic electrode did not increase, with no photocurrent flowing. On the other hand, with light irradiation, the electrode potential of the photocatalytic electrode increased due to the photocatalytic action, with a photocurrent corresponding to the electrode potential flowing. In FIG. 6, the photocatalytic action led to an electrode potential of 1.5 V or higher.

[0133] As depicted in FIG. 7, continued use of the photocatalytic electrode causes a gradual decrease in current density as the output time elapses. In FIG. 7, when light irradiation caused the photocatalytic electrode to continuously generate a constant voltage of 1 V, a slight decrease in current density occurred within 180 seconds. The factors for such degradation include peel-off of the photocatalytic layer from another layer, generation of bubbles at the interface of the photocatalytic layer, and the like.

[0134] Such degradation can be mitigated by forming a buffer layer at the interface of the light power generation layer. Provision of the buffer layer enables a reduction in the loss, at the interface, of charge generated by the light power generation layer, and also enables the conduction paths of charge to be discretely dispersed, thus allowing suppression of local alteration of the light power generation layer and local generation of gas.

[0135] FIG. 8 is a diagram depicting an example of a relation between the electrode potential and the current density of the photocatalytic electrode. FIG. 8 depicts a comparison between results of measurement of electrode characteristics of a known photocatalytic electrode using only a photocatalyst and results of prediction of electrode characteristics of a photocatalytic electrode with conjugation of the photocatalytic layer, used as the first electrode of the photocatalytic apparatus, with a light power generation layer. The electrode characteristics of the known photocatalytic electrode were analyzed using cyclic voltammetry and a photoelectric converting apparatus including a photocatalytic electrode similar to that in FIG. 7 and a reference electrode.

[0136] In FIG. 8, the horizontal axis indicates the electrode potential [V vs. Ag/AgCl] of the photocatalytic electrode and a standard electrode potential [V vs. RHE] obtained by converting the electrode potential using a hydrogen electrode potential, and the vertical axis indicates the current density of the photocatalytic electrode. In FIG. 8, a solid curve indicates results of measurement of electrode characteristics of the known photocatalytic electrode using only the photocatalyst, and a dashed curve indicates results of prediction of electrode characteristics of the photocatalytic electrode with conjugation of the photocatalyst with the light power generation layer.

[0137] As depicted in FIG. 8, when the known photocatalytic electrode using only the photocatalyst is irradiated with light having light energy larger than the bandgap of the material forming the light power generation layer, a photocurrent is generated to increase the current density to some degree. On the other hand, for the photocatalytic electrode with conjugation of the photocatalyst with the light power generation layer, the light power generation layer adds photovoltaic power, and thus the electrode characteristic curve is predicted to shift toward a low potential side and a high current density side. Even in a zero bias state with no bias voltage applied, the current density increases, enabling the auxiliary potential to be reduced.

[0138] FIG. 9 is a diagram depicting an example of a relation between the output time and the current density of the photocatalytic electrode per electrode area. FIG. 9 depicts results of analysis of electrode characteristics of the known photocatalytic electrode using only the photocatalyst. The electrode characteristics of the known photocatalytic electrode were analyzed on the basis of irradiation with simulated sunlight, using the photoelectric converting apparatus including the photocatalytic electrode, which is similar to that in FIG. 7, and the reference electrode.

[0139] In FIG. 9, the horizontal axis indicates the output time (seconds) of the photocatalytic electrode, and the vertical axis indicates the amount of photocurrent in the photocatalytic electrode. In FIG. 9, a solid curve indicates results for a case where the photocatalytic electrode has an electrode area of 0.025 mm^2, a dashed curve indicates results for a case where the photocatalytic electrode has an electrode area of 1 mm^2, a curve of an alternate long and short dash line indicates results for a case where the photocatalytic electrode has an electrode area of 25 mm^2, a curve of an alternate long and two short dashes line indicates results for a case where the photocatalytic electrode has an electrode area of 150 mm^2, and a dotted curve indicates results for a case where the photocatalytic electrode has an electrode area of 400 mm^2.

[0140] As depicted in FIG. 9, continued use of the photocatalytic electrode gradually reduces the current density as the output time elapses. The decrease in current density as the output time elapses tends to increase consistently with the electrode area of the photocatalytic electrode. In a case where the photocatalytic electrode has a large electrode area, degradation of electrode output may be affected by peel-off of the photocatalytic layer from another layer, generation of bubbles at the interface of the photocatalytic layer, and the like.

[0141] Such degradation may also be involved in the light power generation layer. However, the degradation can be mitigated by dividing the electrode elements into cell structures and partitioning the conduction paths of charge. When the electrode elements are divided into cell structures and the partitioned cell units are electrically insulated from one another, the conduction paths of charge are discretized to make the potential difference less likely to vary in the edgewise direction orthogonal to the lamination direction of the electrode elements. This enables a reduction in shunt loss due to occurrence of tributaries. This also allows suppression of scattered charge and inappropriate transport, thus enabling a reduction in scattering loss and recoupling loss of charge.

[0142] The embodiments of the present invention have been described. However, the present invention is not limited to the above-described embodiments and can be varied without departing from the scope of the present invention. For example, the present invention is not necessarily limited to the configuration including all the components provided in the embodiments described above. A part of the configuration of an embodiment can be replaced with another configuration, a part of the configuration of an embodiment can be added to another form, or a part of the configuration of an embodiment can be omitted.

[0143] For example, in the photocatalytic apparatuses 1, 2, 3, 4, and 5, the first electrolysis cell 100 and the second electrolysis cell 200 accommodate the electrolytic solutions 110 and 210, which are liquid. However, as an electrolytic medium, conductive steam that can transport charge may be sealed in the first electrolysis cell 100 and the second electrolysis cell 200. In a case where steam is used as an electrolytic medium, feeding of a reductant and an oxidant and recovery of a product can be performed by the first gas feeding apparatus 101, the first gas discharge apparatus 102, the second gas feeding apparatus 201, and the second gas discharge apparatus 202.

[0144] Additionally, each of the photocatalytic apparatuses 1, 2, 3, 4, and 5 described above is partitioned into two chambers, i.e., into the first electrolysis cell 100 and the second electrolysis cell 200. However, in a case where concentration polarization of the electrolytic medium is achieved between the anode side and the cathode side, installation of the diaphragm 30 may be omitted. In a case where separation of gas is achieved between the anode side and the cathode side, one-chamber structure can be provided.

[0145] Additionally, in each of the photocatalytic apparatuses 1, 2, 3, 4, and 5, the external power supply 50 is electrically connected between the first electrode 10 and the second electrode 20. However, in a case where reaction potential required for material transformation can be obtained simply by light irradiation, the installation of the external power supply 50 can be omitted. In FIG. 1, the voltmeter 60 and the reference electrode 61 are installed on the anode side. However, the voltmeter 60 and the reference electrode 61 may be installed on the cathode side. Additionally, the voltmeter 60 and the reference electrode 61 may be omitted.

[0146] Additionally, in each of the photocatalytic apparatuses 1, 3, 4, and 5 described above, the first electrode 10 includes the promotor 16. However, in a case where the photocatalytic layer 15 exhibits sufficient material transformation efficiency, the support of the promotor 16 may be omitted.

[0147] Additionally, in each of the photocatalytic apparatuses 1, 2, 3, 4, and 5 described above, the second electrode 20 includes the second electron transport layer 25 and the conductive reflection layer 26. However, in a case where the second electrode 20 can achieve material transformation efficiency, or in a case where adhesion between the second light power generation layer 24 side and the catalytic layer 27 side can be achieved, the installation of the second electron transport layer 25 or the conductive reflection layer 26 may be omitted. The charge transport layer 23 and the second electron transport layer 25 are disposed at the interface of the second light power generation layer 24. However, exclusively one of the charge transport layer 23 and the second electron transport layer 25 may be disposed.

Claims

1. A photocatalytic apparatus comprising:

a first electrode (10) disposed in an electrolytic solution or in steam and functioning as an anode; and

a second electrode (20) electrically connected to the first electrode (10) and disposed in an electrolytic solution or in steam, the second electrode (20) functioning as a cathode, wherein

the first electrode (10) includes a first transparent conductive substrate (11) having light transmittivity and electrical conductivity, a first light power generation layer (14) that is disposed on the first transparent conductive substrate (11) and absorbs light to generate electrons and holes, and a photocatalytic layer (15) that is disposed on the first light power generation layer (14) and catalyzes an oxidation reaction when being irradiated with light, and

the second electrode (20) includes a second transparent conductive substrate (21) having light transmittivity and electrical conductivity, a second light power generation layer (24) that is disposed on the second transparent conductive substrate (21) and absorbs light to generate electrons and holes, and a catalytic layer (27) that is disposed on the second light power generation layer (24) and catalyzes a reduction reaction.

2. The photocatalytic apparatus according to claim 1, wherein
the first electrode (10) includes a first electron transport layer (13) between the first transparent conductive substrate (11) and the first light power generation layer (14), the first electron transport layer (13) selectively transporting electrons.

3. The photocatalytic apparatus according to claim 1 or 2, wherein
the second electrode (20) includes a charge transport layer (23) between the second transparent conductive substrate (21) and the second light power generation layer (24), the charge transport layer (23) transporting charge.

4. The photocatalytic apparatus according to one of claims 1 - 3, wherein
the second electrode (20) includes a second electron transport layer (25) between the second light power generation layer (24) and the catalytic layer (27), the second electron transport (25) layer selectively transporting electrons.

5. The photocatalytic apparatus according to claim 4, wherein
the second electrode (20) includes a conductive reflection layer (26) between the second electron transport layer (25) and the photocatalytic layer (15), the conductive reflection layer (26) having electrical conductivity and reflecting irradiation light.

6. The photocatalytic apparatus according to one of the preceding claims, wherein
a promotor (16) is supported or a promotor layer is laminated on the photocatalytic layer (15).

7. The photocatalytic apparatus according to one of the preceding claims, wherein
electrode elements of the first electrode (10) are divided into cell structures by an insulator (18).

8. The photocatalytic apparatus according to one of the preceding claims, wherein
electrode elements of the second electrode (20) are

divided into cell structures by an insulator (18).

9. The photocatalytic apparatus according to one of the preceding claims, further comprising:

a recovery mechanism (104, 204) that recovers a product generated by the first electrode (10); and
a recovery mechanism (104, 204) that recovers a product generated by the second electrode (20).

10. The photocatalytic apparatus according to one of the preceding claims, further comprising:

a feeding mechanism (103, 203) that feeds a reactant of the oxidation reaction to the first electrode (10); and
a feeding mechanism (103, 203) that feeds a reactant of the reduction reaction to the second electrode (20).

11. The photocatalytic apparatus according to one of the preceding claims, wherein the first electrode (10) oxidizes water to generate oxygen, and the second electrode (20) reduces carbon dioxide.

FIG. 1

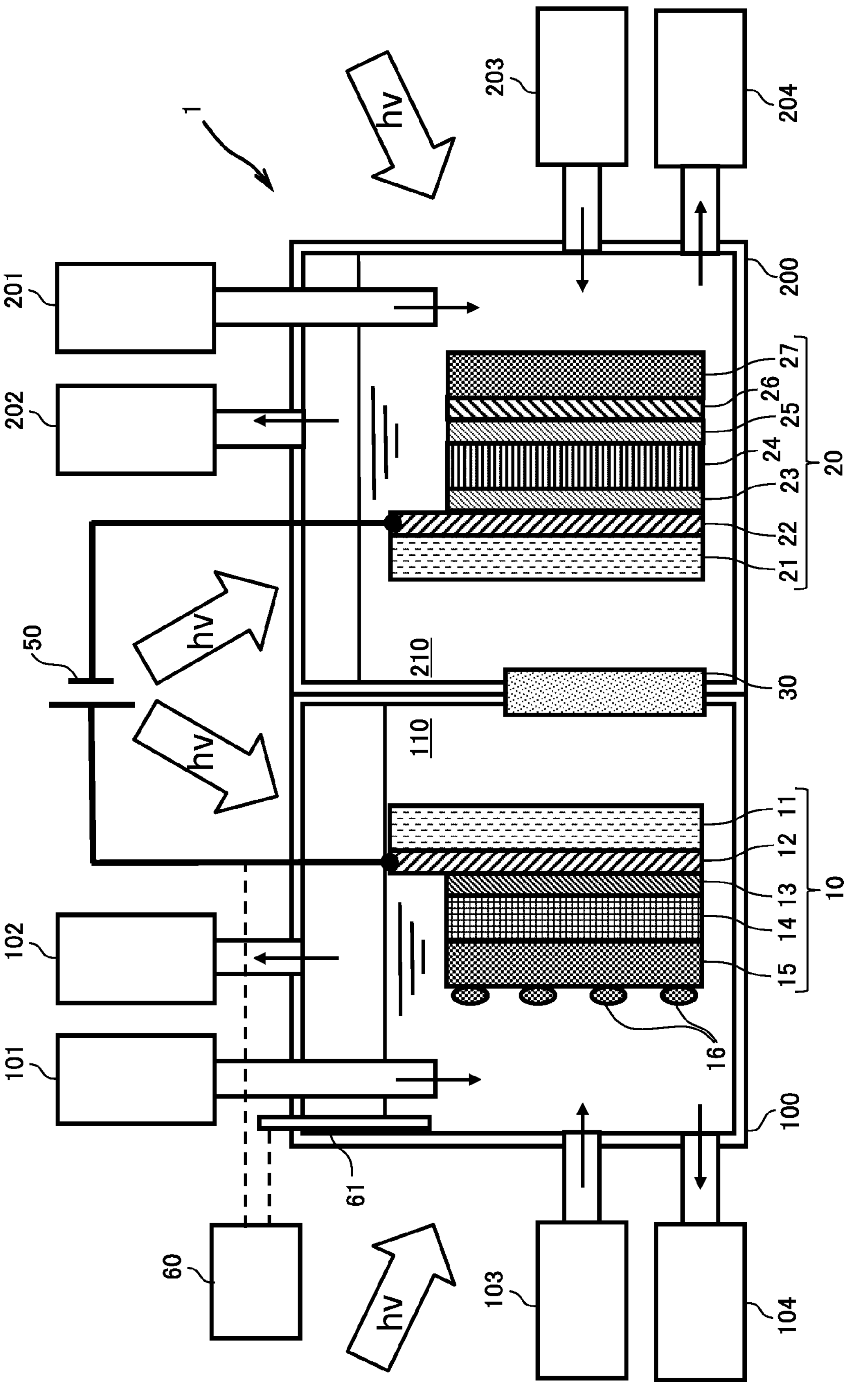

1
hν
203
204
201
202
200
27
26
25
24
23
22
21
20
50
hν
hν
210
30
110
11
12
13
14
15
10
16
102
101
100
61
60
hν
103
104

FIG. 2

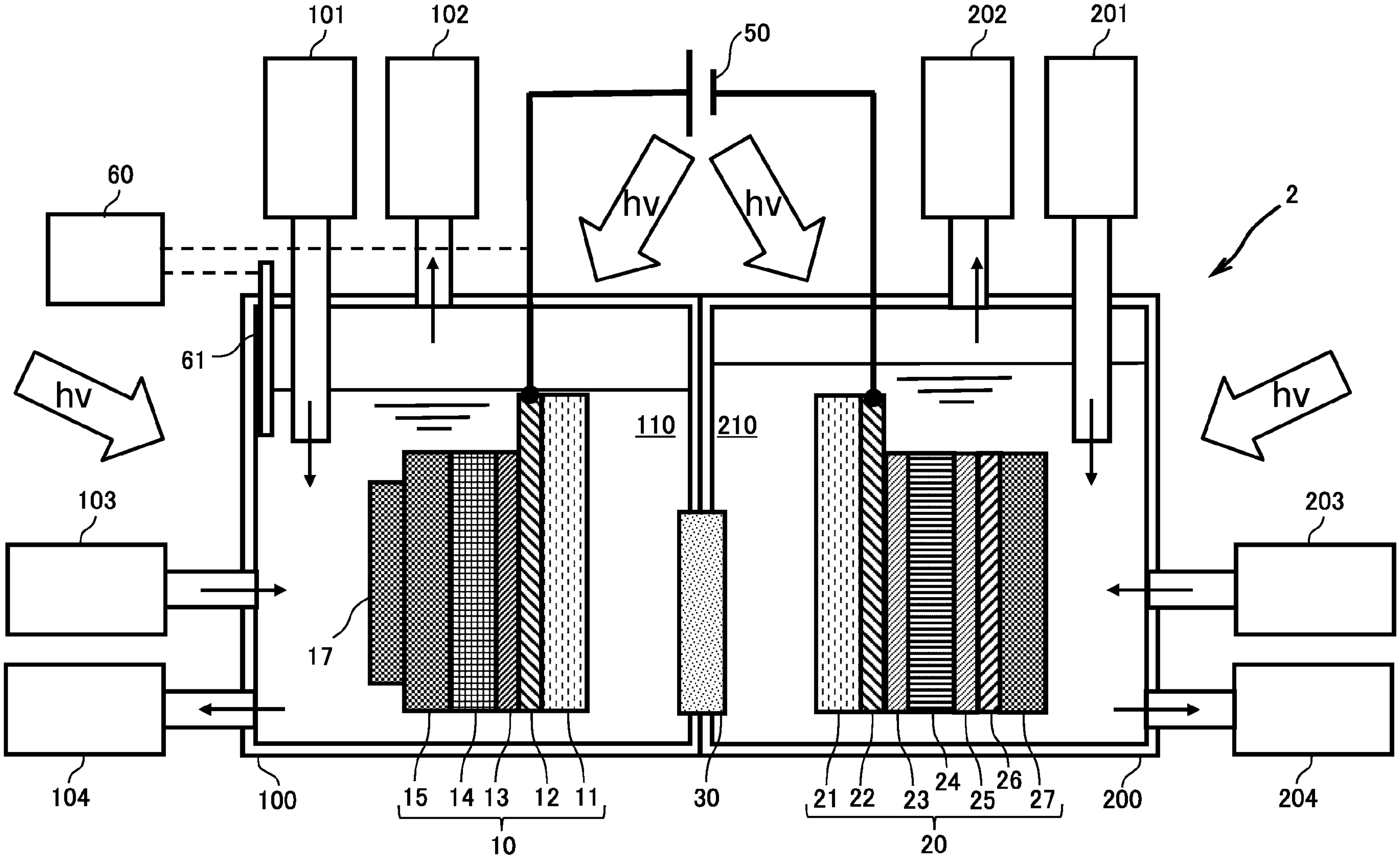

101
102
50
202
201
60
hv
hv
2
61
hv
hv
110
210
103
203
17
104
100
15
14
13
12
11
30
21
22
23
24
25
26
27
200
204
10
20

FIG. 3

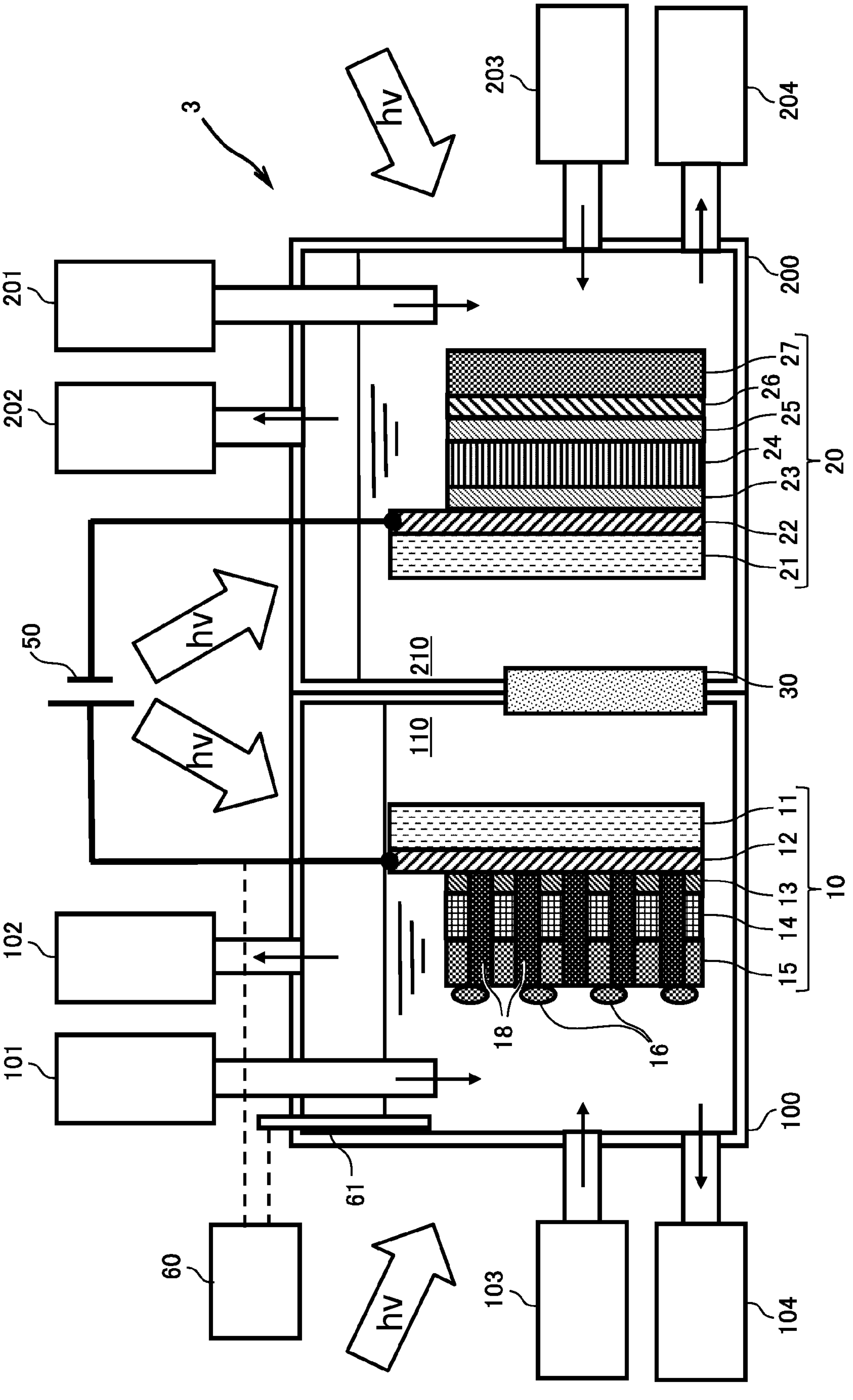

3
hv
hv
hv
hv
201
202
203
204
200
210
27
26
25
24
23
22
21
20
50
30
110
11
12
13
14
15
10
18
16
102
101
100
61
60
103
104

FIG. 4

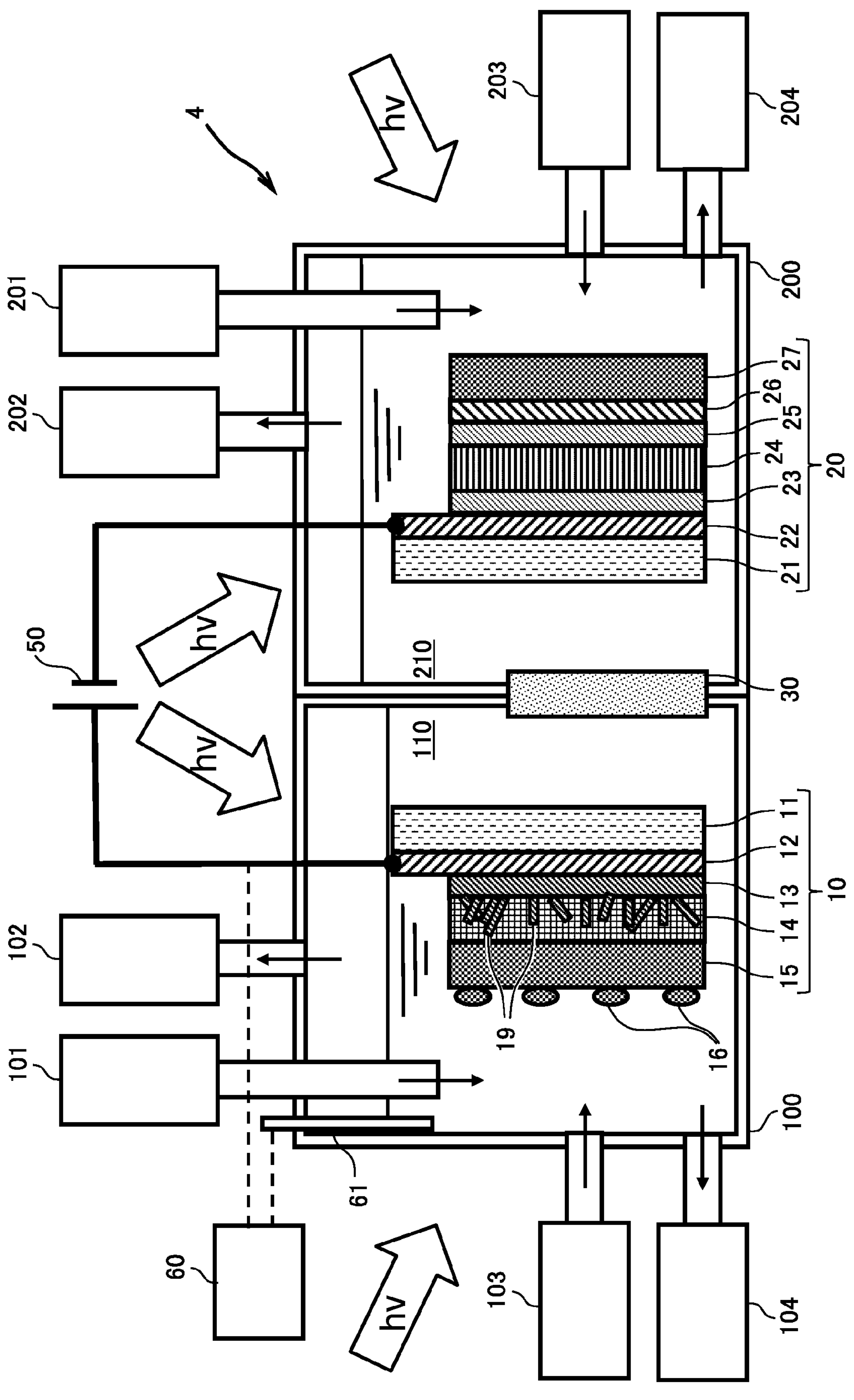

4
hv
hv
hv
hv
201
202
203
204
200
210
27
26
25
24
23
22
21
20
50
30
110
11
12
13
14
15
10
19
16
101
102
100
61
60
103
104

FIG. 5

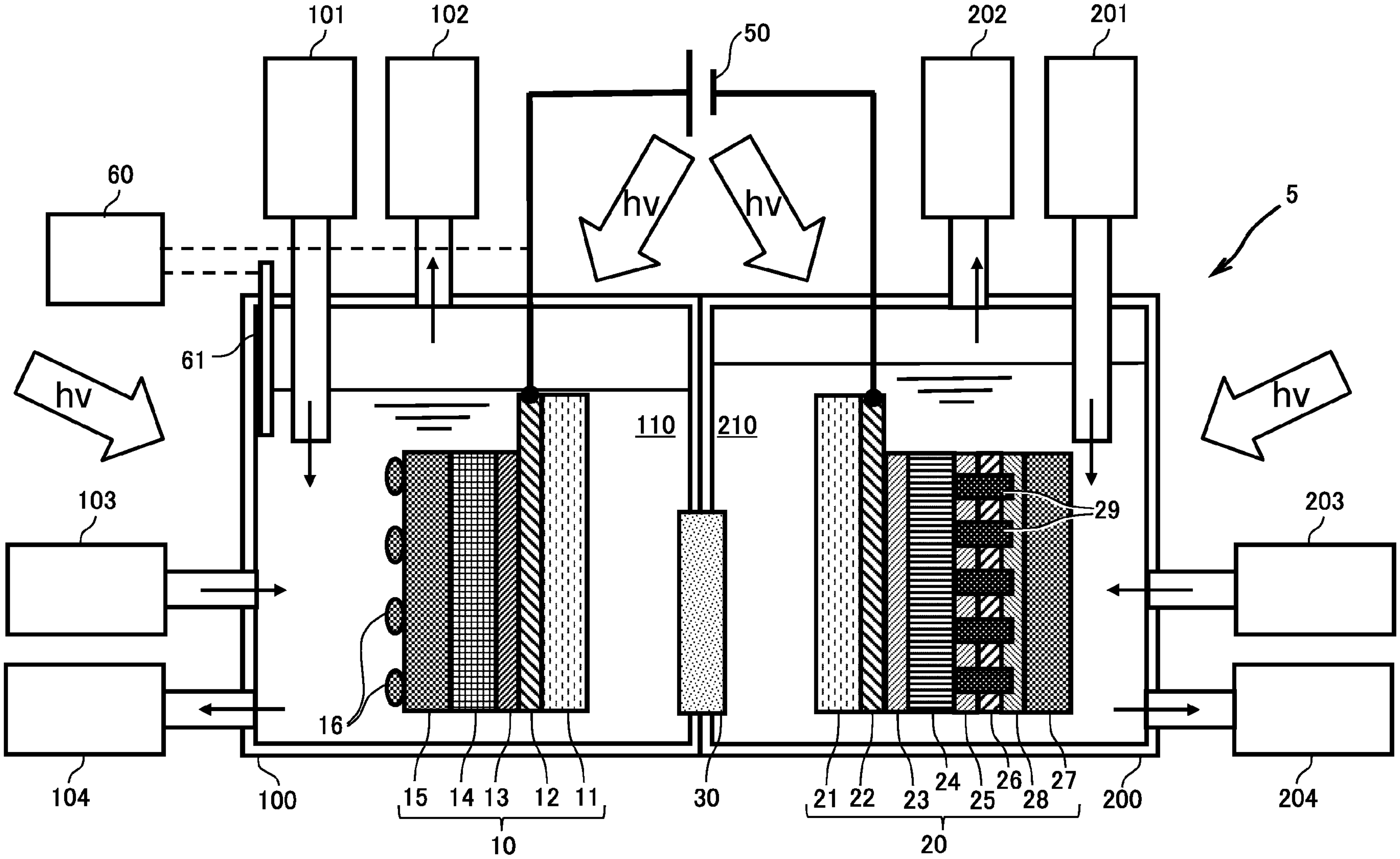

5
50
60
61
101
102
103
104
100
hv
hv
hv
hv
110
210
201
202
203
204
200
16
15
14
13
12
11
10
30
29
21
22
23
24
25
26
28
27
20

FIG. 6

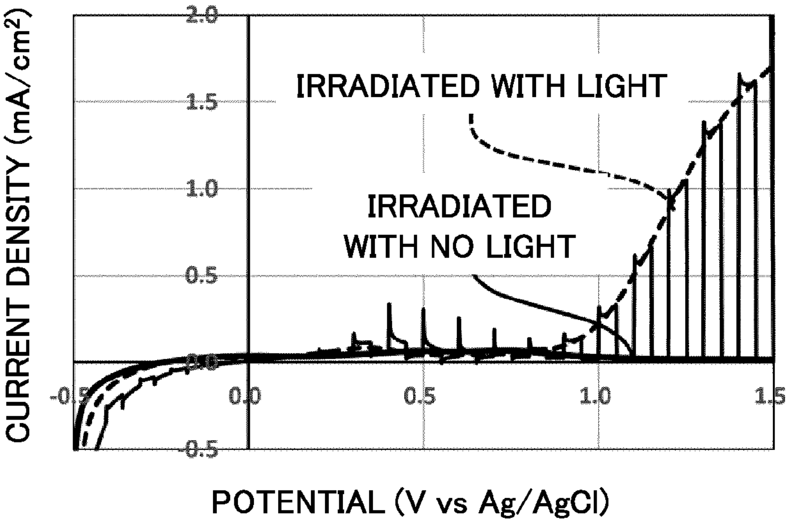

CURRENT DENSITY (mA/cm²)
2.0
1.5
1.0
0.5
0.0
-0.5
-0.5
0.0
0.5
1.0
1.5
IRRADIATED WITH LIGHT
IRRADIATED WITH NO LIGHT
POTENTIAL (V vs Ag/AgCl)

FIG. 7

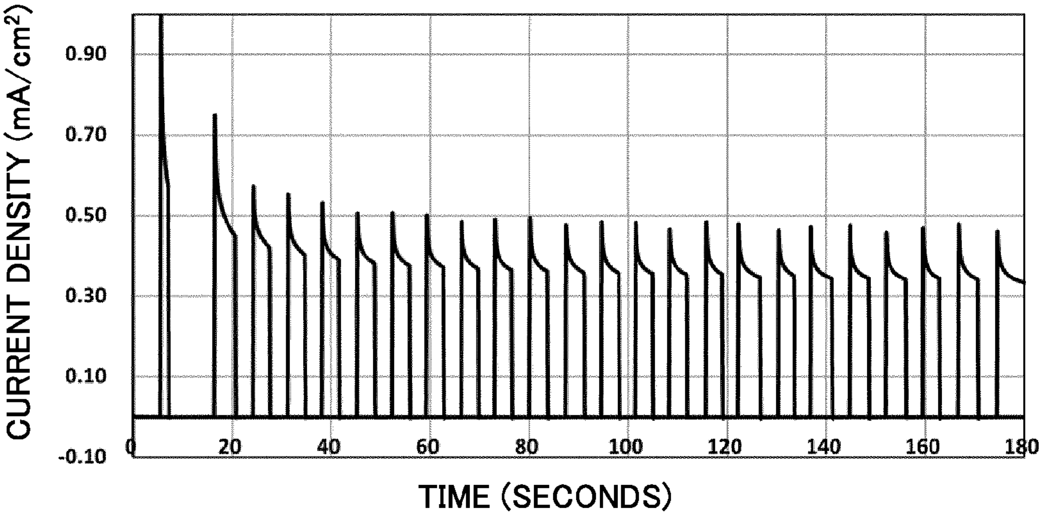

CURRENT DENSITY (mA/cm²)
0.90
0.70
0.50
0.30
0.10
-0.10
0
20
40
60
80
100
120
140
160
180
TIME (SECONDS)

FIG. 8

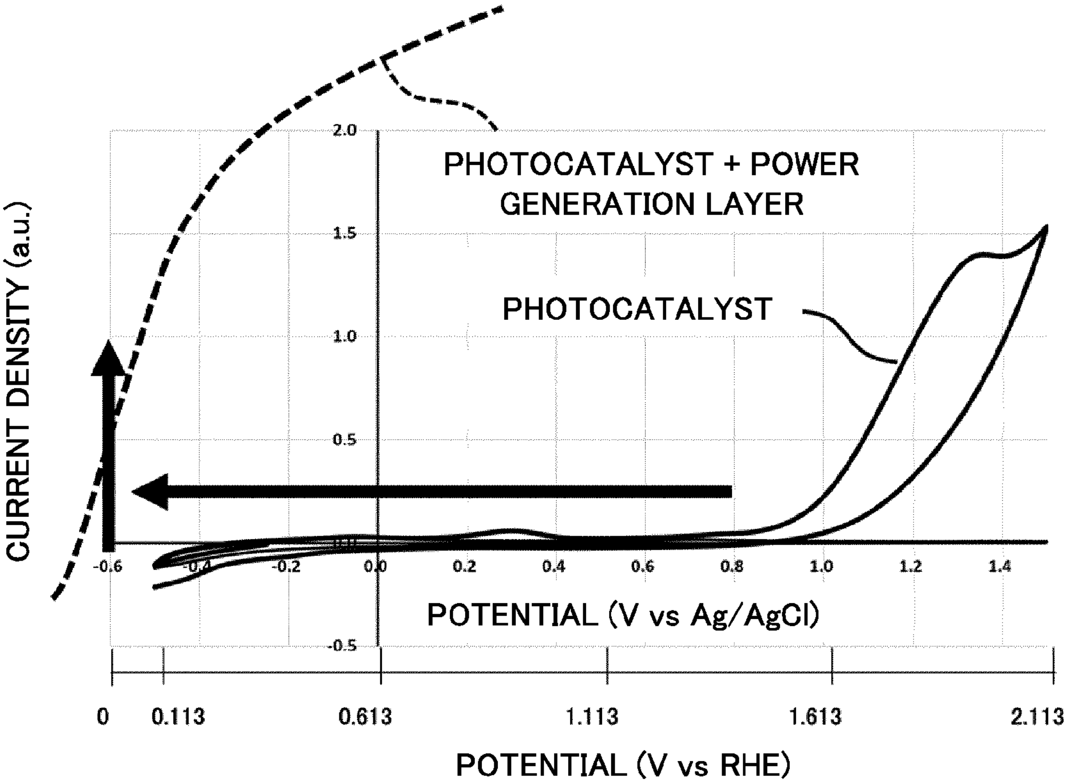
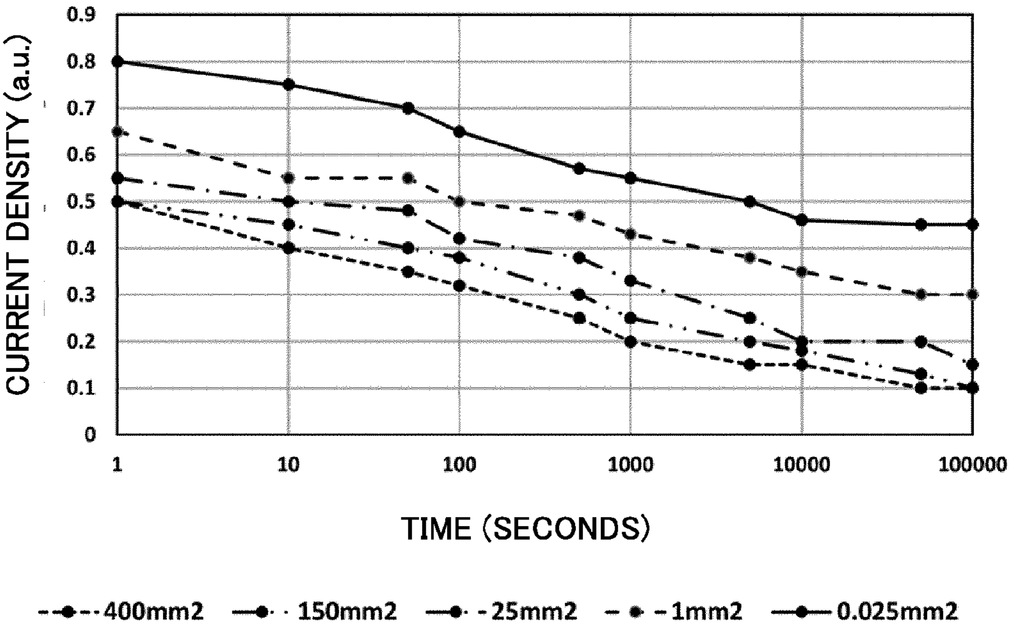

PHOTOCATALYST + POWER GENERATION LAYER
PHOTOCATALYST
CURRENT DENSITY (a.u.)
2.0
1.5
1.0
0.5
-0.5
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
POTENTIAL (V vs Ag/AgCl)
0
0.113
0.613
1.113
1.613
2.113
POTENTIAL (V vs RHE)

FIG. 9


CURRENT DENSITY (a.u.)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
10
100
1000
10000
100000
TIME (SECONDS)
400mm2
150mm2
25mm2
1mm2
0.025mm2

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 6774165 B **[0005] [0011]**
- JP 6316436 B **[0006] [0011]**