

NEW TECHNOLOGIES FOR WATER CLEAVAGE INTO HYDROGEN AND OXYGEN BY SOLAR RADIATION

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INTRODUCTION

Light energy converts to chemical energy through photosynthesis process was undertaken by organic solar cells. The majority of these cells have similar structures with anorganics, based on semiconductors (*p-n* junction or Schottky barrier). The conduction mechanism is incomplete elucidated yet, because of the energetic bands formation (valence and conduction) from anorganic semiconductors is not registered practically and in case of cells with organic substances films.

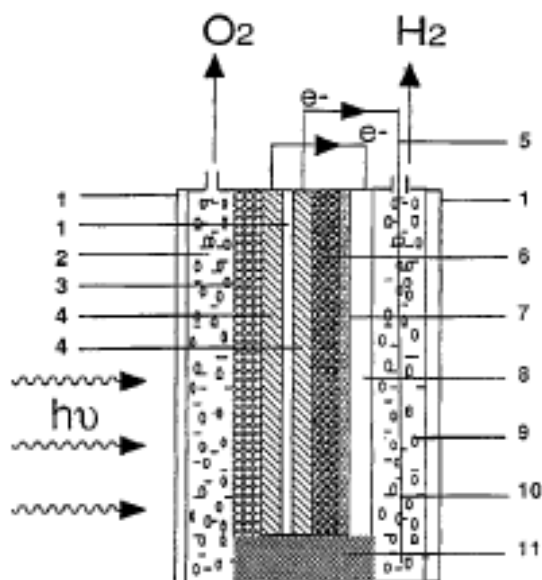


Figure 1. Schematic drawing of Graetzel photoelectrochemical tandem cell [3].

The actual tendency analyze in hydrogen energetic relieves the photo-electrochemical conversion of solar energy method by water cleavage into hydrogen and oxygen with tandem cells proposed by Michael Graetzel [1-3]. The tandem cells, without the advantages and perspectives offered, present also the disadvantage of a not too long life time, that why exist great reserves about the amelioration of the conversion yield.

1. GRAETZEL TANDEM CELL FOR WATER CLEAVAGE BY VISIBLE LIGHT

The solar radiation converters to electric energy are based on the photovoltaic effect, discovered by

Becquerel in 1839. The very first photovoltaic cells with *p-n* junction between two different doped silicon layers it was made in 1950 in Bell's laboratories. In present, the efficiency of the commercial photovoltaic cells vary between 18...20% for monocrystalline silicon cells and 10...12% for amorphous silicon cells, in conditions in which the polycrystalline silicon cells (the most effused cells from the market) has a intermediary efficiency.

Beginning with 1970, it was registered a new revolving interest for photovoltaic cells sensibilized with pigments (coloring agents). A new idea in this way dates from 1991 and belongs to Graetzel [2, 3]. Graetzel's cells are based on TiO₂ porous nanocrystalyn electrodes, which have a very big specific intern surface. Electrodes consist by TiO₂ particles with colloidal dimensions (5-50 nm), that are connected in a sintering face, at low temperatures. A pigment monolayer deposited on a suchlike electrode it is enough to absorb the mass of the radiation from solar light spectrum. These cells are mass-produced by two firms and have 12% conversion efficiency.

The installation for water cleavage into hydrogen and oxygen by action of visible light (fig.1), patented by Graetzel in 1999 [4], is constituted by two photo-electrochemical cells, tandem inseriated and sensible to visible light. First cell has a box for oxidation of the aqueous electrolyte 2 with window 1 for solar light input and with the anode 4, transparent in yellow and red interval of solar light spectrum, covered on contact part with aqueous electrolyte 2 with a semiconductor oxide mesoporous layer 3, absorbent in blue and green interval of solar light spectrum. The second photo-electrochemical cell contain an solid organic electrolyte layer 7, placed between transparent electrode 4, covered on the contact side with organic electrolyte, with photovoltaic layer 6 by susceptible colorant, absorbent in yellow, red and part infrared interval of the sun light spectrum, and between the contraelectrode 8, galvanic bounded with the anode 4 from the first photo-electrochemical cell, as well as a reduction enclosure with aqueous electrolyte 9, in which is immersed the cathode 10 for the reduction of the protons formed in the oxidation enclosure of the aqueous electrolyte 2, cathode which is galvanic

bounded by conductor 5 with the transparent electrode 4 from the second photo-electrochemical cell. On the aqueous electrolyte side 2, the oxidation enclosure is separated from the reduction enclosure by the ions exchange membrane 11, which can be a frit glass wall.

The known installation present the advantage of a simple, cheap construction, because are utilized nanotechnological simple processed materials at cut rate.

The disadvantages of the installation are:

- the presence of liquid electrolyte which conduct to diminution of life time (by evaporation in time);
- the necessity to charge the reduction enclosure with aqueous electrolyte that has the same composition like aqueous electrolyte from oxidation enclosure, concerning to the corrosion surface extension of metallic elements in contact with water and make necessary the control of the maintenance at same level, the aqueous electrolytes composition from both enclosures and the utilization of a hydrogen separator from steam;
- the presence in electrochemical circuit of three auxiliary electric resistances (contact resistances for interfaces: ions exchanger membrane – aqueous electrolyte; aqueous electrolyte – cathode and contraelectrode – aqueous electrolyte) conduct to additional losses of electric energy converted from

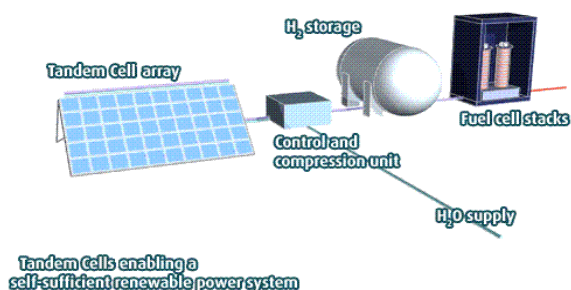


Figure 3. Renewable energy delivery system based on Graetzel photo-electrochemical cells [5]

solar energy and so, limit the yield of solar energy conversion in chemical energy of the water decomposition components at 5%, in standard test conditions of photovoltaic cells AM1,5 (temperature 25°C, the density of radiation flux 1000 W/m², at earth surface), what with a great part of this energy is not converted also, videlicet the energy from infrared interval that represent 55% of the solar radiation spectrum;

- the modality of ion exchange membrane layout, which reduce the active surface of photo-electrochemical cells illumination and the contact surfaces of the membrane with aqueous electrolytes from oxidation and reduction boxes.

The operating principle of the installation is (fig.2) [5]: after the absorption of a photon, the pigment molecules pass into an excited state and from this condition it is injected one electron in the conduction band of semiconductor. At the other end

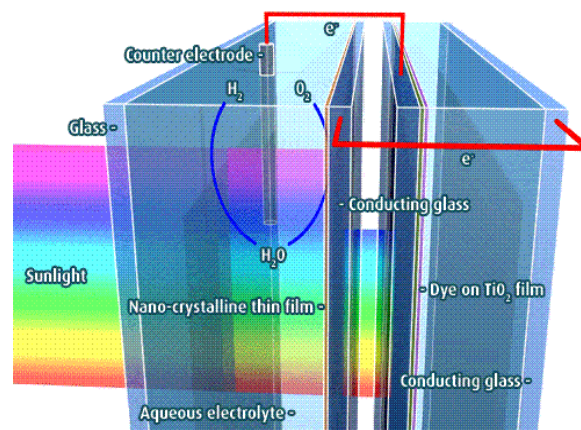


Figure 2. The operating principle of solar installation with Graetzel photo-electrochemical tandem cells [5]

of the *n*-type semiconductor, the electron is taking-up and can be inserted into an extern circuit (of the consumer) before returning into the system, by contraelectrode where reduce the oxidizing species. Concomitant, the oxidized pigment is regenerated by the acceptance of one electron from the reducing species of electrolyte. Along with the described electrochemical reactions come a suite of transformations which decrease the efficiency of the global process, determining great internal resistances, a great number of pigment molecules and a small active area. It was observed that a pigment monolayer absorbs only a few percents of incident radiation and the multilayer's structures determine the systematic diminution of the efficiency of electron injection in semiconductor.

Great reserves of the amelioration of these modern installations exist, which will be integrated more and more in the conversion systems of renewable energies in close future (fig.3) [5].

2. SOLAR INSTALATION FOR WATER CLEAVAGE INTO OXYGEN AND HYDROGEN WITH A TRANSPARENT PROTONS EXCHANGE MEMBRANE

The proposed installation (fig.4) [6], same with Graetzel installation, is constituted by two photo-electrochemical tandem inserted cells.

The first photo-electrochemical cell has the transparent glass window 1, which permit the solar

visible light input into aqueous electrolyte oxidation enclosure 2 and their propagation through the electrolyte layer to transparent anode, in yellow and red interval of solar light spectrum, covered with mesoporous semiconductive oxide layer 3 on aqueous electrolyte contact side, absorbent in blue and green interval of solar light spectrum, and the electroconductive glass 4. The layer 3, for example, tungsten trioxide WO_3 or iron trioxide Fe_2O_3 , it is formed by a sol-gel type process. For this, it is prepared a WO_3 or Fe_2O_3 colloidal precursor solution, doped with selected elements from Si, Ge, Sn, Pb, Ti, Zr, Hf, Sb, Bi, V, Nb, Ta, Mo, Te and Re

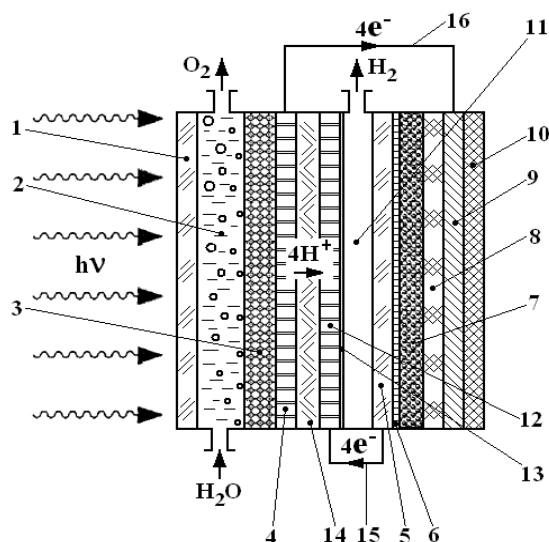


Figure 4. Schematic drawing of solar installation for water cleavage in oxygen and hydrogen with a transparent protons exchange membrane

series or F, Cl, Br and I series, which, after mixing with polyvinyl alcohol, it will be deposited in fine film from 50 nm to 5 μm on the relative electroconductive surface of the plane perforated

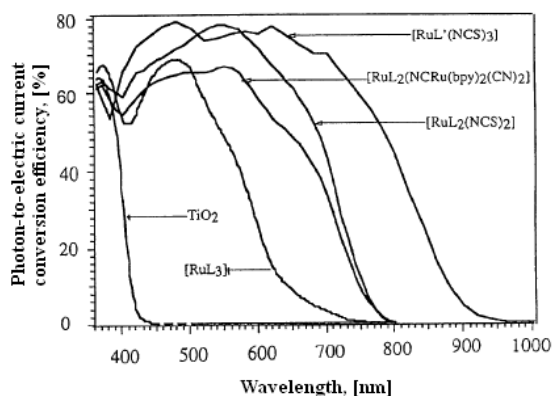


Figure 5. The spectral dependency of the photon-to-electric current conversion achieved with the sensitized TiO_2 films for several ruthenium complexes [3]

glass 4 (Nippon Sheet Glass, formed by a SnO_2 film, doped with fluorine ($\text{SnO}_2:\text{F}$), 10 Ohm/o), which served like electrons collector. The tungsten trioxide and iron trioxide are the single metallic oxides which can oxidize water in visible light and are resistant to photo-electrochemical corrosion, same to those in dark phase.

The second photo-electrochemical cell contains the transparent electrode 5, with the surface from right side covered with $\text{SnO}_2:\text{F}$ film, whereon is deposited a monomolecular sensitized layer 6 based on a ruthenium polypyridyl complex from $\text{RuL}_2(\text{NCS})_2$ and $\text{RuL}'(\text{NCS})_3$ series, where $L = 4,4'$ - dicarboxyl-2,2',6',2''-bipyridine and $L' = 4,4'4''$ - tricarboxyl-2,2'-tripyrindine. The best sensibility for yellow, red and partial infrared interval of sun light spectrum has the sensitized $\text{RuL}'(\text{NCS})_3$ (fig.5). The titanium dioxide, TiO_2 mesoporous film 7 is deposited on sensitized layer 6. Its function is to polarize away the light from yellow, red and partial infrared interval of the spectrum that will amplify the electrochemical potential of electrons generated on the interface of semiconductor layer 3 with conductive layer $\text{SnO}_2:\text{F}$ of perforated glass 4. Then, the TiO_2 film 7 is put on contact with the solid organic electrolyte layer 8 and this, with the metallic contraelectrode 9, isolated on external surface by isolating layer 10.

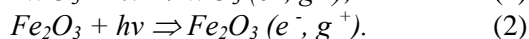
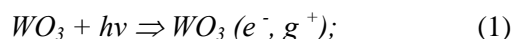
Between the two photo-electrochemical cells is a hydrogen enclosure 11 with the reduction cathode 12, executed in perforated plate Nippon glass form with conductive layers $\text{SnO}_2:\text{F}$ covered surfaces and with surface next to enclosure 11, supplementary covered with mesoporous fine layer 13 from reduction catalyst, chosen from Ni, Pt, Pd, Ru, Rh and Ir series or tungsten, vanadium or molybdenum polyacid and heteropolyacid. Cathode 12 with anode 3,4 formed together a parallel electrodes system, between which is placed the proton exchange membrane 14, manufactured by nanocomposite material transparent polymer-oxide based on organic/anorganic hybrid macromolecular polymers, for example, a tetramethylene (poly)oxide, ethylene (poly)oxide or a diagonal polyether's, with homogeneous incorporations of polyoxometalate from $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ or $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ series.

The transparent electrode 5 and cathode 12 are inserted by external circuit 15 and the anode collector 3, 4 and contraelectrode 9 by external circuit 16.

The solar installation for water cleavage into hydrogen and oxygen functions in that mode.

The oxidation enclosure 2 is filled in with transparent aqueous electrolyte (in deionized water are dissolved NaOH, KOH, for electric conductivity improvement, or it is utilized the sea water).

The sun light come in by window 1, travels across the aqueous electrolyte layer from enclosure 2 and caves on semiconductor oxide mesoporous layer surface 3. The tungsten trioxide WO_3 or iron trioxide Fe_2O_3 thin film absorbs the blue and green part of sun light spectrum, than generate electron-hole pairs, in conformity with electrochemical reactions:



The holes (g^+) from valence band (fig.6), created

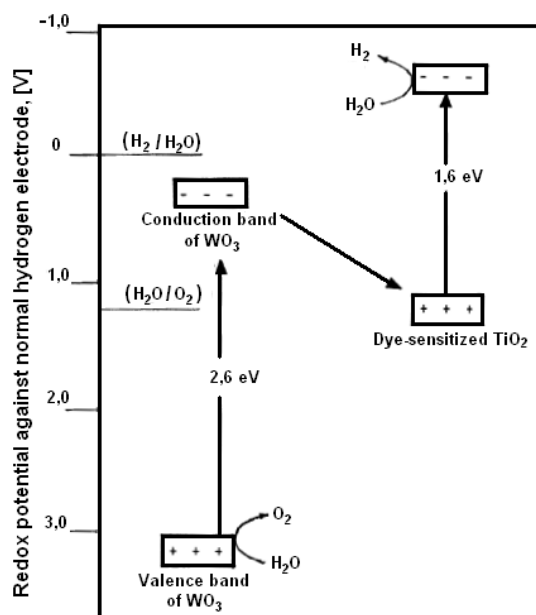
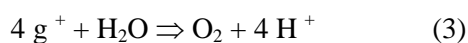


Figure 6. The Z scheme of biphotonic water photolysis.

in excitation band of the tungsten or iron trioxide on the action of photons with short waves (380-565 nm), oxidize the water from aqueous electrolyte, forming oxygen and protons:

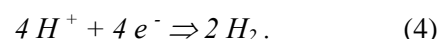


Electrons from the conduction band will be collected on conductive surface of the perforated glass 4. By extern circuit 16, these electrons are transmitted to contraelectrode 9 of the second photo-electrochemical cell.

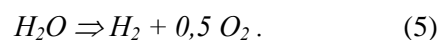
The yellow, red and partial infrared part of the solar light spectrum (photons with long wavelength, 565-900 nm) traverses the transparent optic medium, formed by anode 3, 4, protons exchange membrane 14, cathode 12, 13, enclosure with gaseous hydrogen 11 and transparent electrode 5 and is absorbed by the sensibilized layer 6 and TiO_2 film 7. Hereupon, the solid organic electrolyte 8 it polarized, which amplify the electrochemical potential of the photons emitted by water oxidation in the first photo-electrochemical cell. So, the electrons collected on the conductive surface of

transparent electrode 5 will had an adequate potential for protons reduction.

By extern circuit 15, electrons from transparent electrode 5 will be conducted on conductive surface of cathode 12, which is in contact with the catalyst layer 13, between the anode 3, 4 and cathode 12, 13 will be appear a potential difference which will conduct to the transfer of protons formed on the interface aqueous electrolyte – trioxide layer 3 by perforations of transparent conductor 4, protons exchange membrane 14, the cathode perforations 12. In catalyst layer 13 will have place the reduction of the protons transported with electrons displaced from electrode 5 with hydrogen formation:



The summary reaction corresponds to the water cleavage process into hydrogen and oxygen under visible light action. So, the solar water cleavage installation into hydrogen and oxygen assures:



- the average of global energetic yield increase was 1,6-2,0 fold, yield of the conversion of solar energy to chemical energy of the elements in which is decomposed the water;
- pure hydrogen production (without steams);
- contact surface reduction of aqueous electrolyte with installation metallic elements and its corrosion probability, consequently;
- the simplification of the installation construction and it exploitation fiability improvement.

The proposed invention can be easily implemented, great capital investments are not necessary, and permit to get global energetic yields of the solar light conversion to chemical energy of water decomposition components about 8-10%. The installation function even in case of diffuse solar light and it is not dependent by atmosphere nebulosity.

3. SOLAR INSTALATION FOR WATER CLEAVAGE INTO HYDROGEN AND OXYGEN WITH SEMICONDUCTIVE MATRIX ABSORBENT IN INFRARED SOLAR RADIATION

Another Graetzel installation improvement it's referring to conversion of infrared interval energy, which represent 55% of solar radiation spectrum.

The installation [7] is constituted by two photo-electrochemical tandem cells (fig.7). The first photo-electrochemical cell has the transparent glass window 1, which permits the solar radiation input in oxidation enclosure 2 of aqueous electrolyte and it

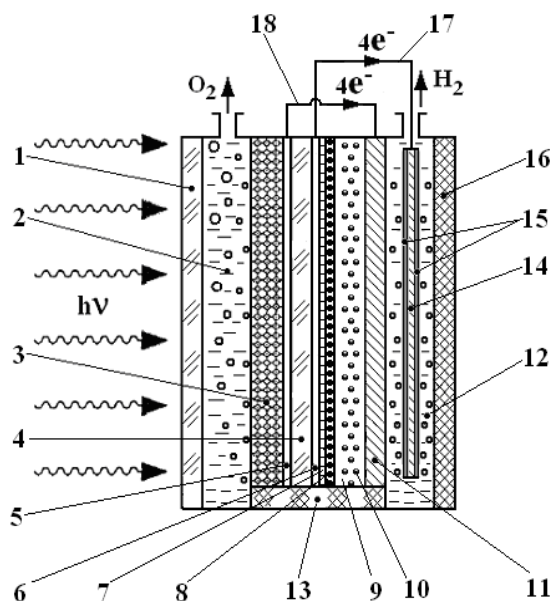


Figure 7. Solar instalation for water decomposition in hydrogen and oxygen with semiconductive matrix absorbent in infrared solar radiation spectrum

propagation across the electrolyte layer to transparent anode in yellow and red interval of solar radiation spectrum, covered on the aqueous electrolyte contact part with the semiconductor oxide mesoporous layer 3, absorbent in ultraviolet, violet, blue and green interval of solar light spectrum, and the electroconductive glass 4. The layer 3, for example, by tungsten trioxide WO_3 or iron trioxide Fe_2O_3 it is formed by a sol-gel type process, described in p.2.

The second photo-electrochemical cell contained a transparent electrode, which function it is realized by electroconductive layer 6 ($\text{SnO}_2:\text{F}$) of the electroconductive glass 4, on which is deposited the monomolecular sensitizer layer 7, based on a ruthenium polypyridil complex from the series presented in fig.5. On the sensitizer layer 7 is deposited the titanium dioxide, TiO_2 mesoporous film 8. It function is to polarize on action of solar radiation from yellow, red and partial infrared interval of the spectrum, which amplify electrochemical potential of the electrons generated at the interface of semiconductor layer 3 and conductive layer $\text{SnO}_2:\text{F}$ of the electroconductive glass 4.

Than, the TiO_2 film 8 is put on contact with the semiconductor composit layer formed by a half transparent matrix 9 by polymeric material, inorganic or glass mated, for example, based on a polar polymers structures poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1, 4-phenylen vinylen)], in which are dispersed nanoparticles 10 of photosensible to infrared radiation semiconductor, for example, PbS,

PbSe or InAs nanocrystals (fig.8) [8].

The colloidal PbS, PbSe or InAs crystals can be produced utilizing an organometallic procedure based on solution and precursor, respectively. For example, to prepare PbS crystals, it must be dissolved PbO in oleic acid and it warming to 150°C to obtain the lead oleate precursor. Like sulphur source it is utilize bis (trimethylsilyl) sulphite (TMS) in oktadecane, which it is add to lead oleate solution, and the liquid phase is removed by warming. The temperature increase is admitted below the nucleation temperature line and it keep up to maximum admissible value. Oleic acid adheres to nanocrystals surface formed, head off their agglomeration and surface passivation by oxidation, which reduces non-radiative recombination, also. The nanocrystals dimension is controlled by the

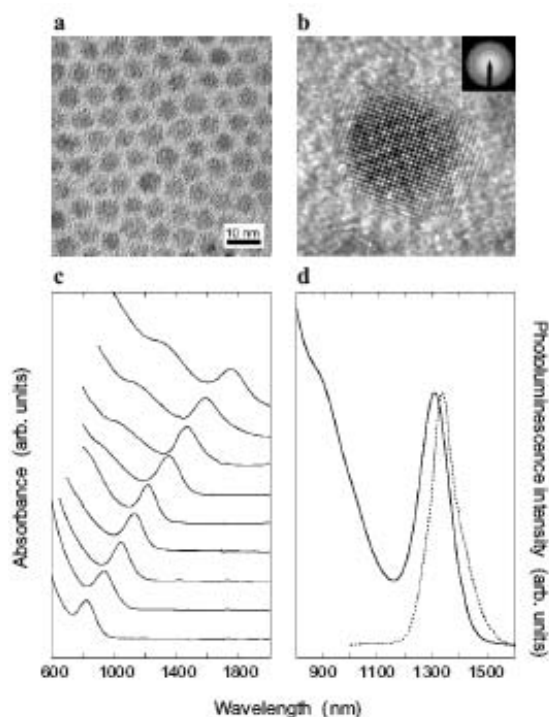


Figure 8. Physical properties of PbS quantum dots synthesized by an organometallic route [8]:

a, b – high resolution TEM images of quantum dots with peak luminescence at 1440 nm; *c*) absorption spectra of PbS dots with exciton peaks size-effect tuned from 800-1800 nm; *d*) absorption and photoluminescence features of 6.5 nm diameter dots.

variation of protective binder concentration, temperature and injection time, of the maximum temperature and maximum processing time, of oleic acid participation in PbO and TMS solution. After the nanocrystals growth to necessary dimensions (1-8 nm), these sediments by adding polar solvent, like methanol, and redispersed in a non-polar solvent, like toluene. This is added in liquid phase of the matrix before it solidification. The Bohr

excitation ray for PbS crystals is 20 nm, for InAs, 34 nm, for PbSe, 46 nm, and ray allow determining the volumetric concentration of photosensible nanocrystals from half transparent matrix (fig.9). Absorbance and the photoluminescence intensity of these advanced materials are presented in fig.8, c [8].

The role of the half transparent matrix 9 with nanoparticles 10 is to absorb the infrared solar radiation and, so, to amplify supplementary the electrochemical potential of the electrons generated on interface of semiconductor layer 3 and conductor layer SnO₂:F of electroconductive glass 4. The composite semiconductor layer, formed by half transparent matrix 9 with nanoparticles 10, contact by metallic contraelectrode 11, which is one of enclosure walls 12 of aqueous electrolyte reduction, separated from oxidation enclosure 2 on aqueous electrolyte side by ions exchange membrane 13. In aqueous electrolyte from enclosure 12, which have the same composition with aqueous electrolyte from enclosure 2, is immersed the cathode 14, with surfaces covered by fine mesoporous layers 15 from reduction catalyst, chose from Ni, Pt, Pd, Ru, Rh and Ir series or tungsten, vanadium or molybdenum polyacid and heteropolyacid. The reduction enclosure 12 is limited by isolating wall 16 from exterior.

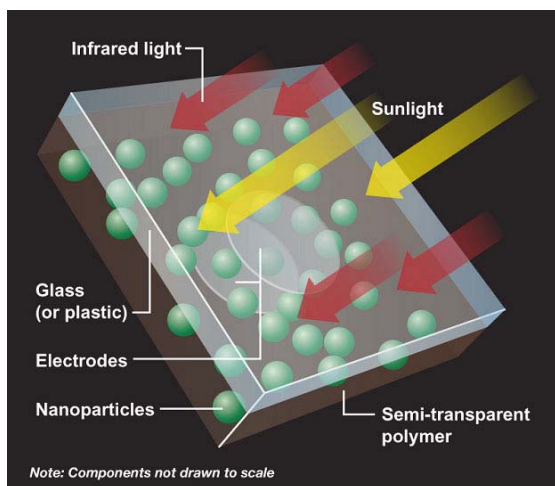


Figure 9. The schematic presentation of a semi-conductive absorbent matrix with nanoparticles sensible in infrared solar radiation spectrum

The transparent electrode 6 and cathode 14 are galvanic bounded by exterior circuit 17, and collector 5 of anode 3, 5 and contraelectrode 11 by exterior circuit 18. The solar water decomposition installation to hydrogen and oxygen functions in that mode. The oxidation enclosure 2 it is maintained full with transparent aqueous electrolyte (in deionized water it is dissolved NaOH, KOH, to improve electric conductivity or it is utilized sea water).

The solar radiation get through window 1, it propagates through aqueous electrolyte layer from enclosure 2 and drops to surface of mesoporous oxide semiconductor layer 3. The tungsten trioxide WO₃ or iron trioxide Fe₂O₃ thin film absorbs the blue and green part of solar radiation spectrum, generating electrons-holes pairs, according to electrochemical reactions (1)-(2).

The holes (g^+) from valence band, created in excitation band of the tungsten or iron trioxide, under short wavelength photons (190-565 nm) action, oxidizes the water from aqueous electrolyte, producing oxygen and protons according to electrochemical reaction (3). The electrons from the conduction band will be collected on conductive surface 5 of the electroconductive glass 4. By exterior circuit 18, these electrons are transmitted to the contraelectrode 11 from the component of the second photo-electrochemical cell.

The yellow, red and infrared part of the solar radiation spectrum (photons with long wavelengths, 565-3000 nm) cross transparent optic medium, formed by anode 3, 5, electroconductive glass 4, transparent electrode 6 and is absorbed (the yellow and red radiation total and infrared radiation partial) by sensibilized layer 7 and by TiO₂ film 8. The part of infrared radiation with long wavelengths crosses the layers 7 and 8 and is absorbed by semiconductor composite, composed by half transparent matrix 9 with nanoparticles 10. Hereupon, the medium between transparent electrode 6 and contraelectrode 11 it is polarized, which amplify powerfully the electrochemical potential of photoelectrons emission of water oxidation from the first photo-electrochemical cell. So, the electrons collected on the transparent electrode 6 will had an adequate potential to reduce the protons of the aqueous electrolyte from enclosure 12, which swap with aqueous electrolyte from enclosure 2 through ions exchange membrane 13.

By extern circuit 17 the electrons from transparent electrode 6 will be conducted to the cathode 14 covered by catalyst layer 15. At interface aqueous electrolyte from enclosure 12-catalyst 15 from cathode surface 14 occur the protons reduction with the transferred electrons from transparent electrode 6 with hydrogen production (reaction (4)).

The summary reaction corresponds to the process of water decomposition in hydrogen and oxygen under visible light action, resulted by reaction (5). So, the solar installation for water cleavage into hydrogen and oxygen can be utilized in pure ecological chemical and energetic technologies for hydrogen and oxygen production and for the renewable energy conversion, because from hydrogen burning it is obtain again water, which is

not a pollutant like in fossil combustible burning case. The proposed invention can be easily implemented, great capital investments are not necessary, and permit to obtain global energetic yields of solar light conversion in chemical energy of the components that is decomposed water round to 30%. The installation function also in diffuse solar light case, in case of partial or total atmosphere nebulosity and also, at night time, in presence of natural and artificial sources of ultraviolet, visible and infrared radiations.

4. CONCLUSIONS

1. The development of photovoltaic technologies begins with the study and fabrication of organic cells. The producers of silicon cells were collided with a serious technical problem about its purity. The advance purity silicon it can be obtain only through powerful separation/purification processes, so that energy consumption for a photovoltaic cell fabrication, and in adequate mode, the conversion costs are very big, which challenge their sustainability like renewable energy system.

2. More recent research was oriented to obtain a reduced cost cells, by other materials utilization like CdS, CuInSe₂ or CdTe. Although these can be produced at reasonable costs, ecologically still represent a less attractive choice, because of the toxic substances from its composition.

3. Light energy transformation to chemical energy through photosynthesis process was undertaken by organic solar cells. The majority of these cells have similar structures with anorganics, based on semiconductors (p-n junction or Schottky barrier). The conduction mechanism is incomplete elucidated yet, because of the energetic bands formation (valence and conduction) from anorganic semiconductors is not registered practically and in case of cells with organic substances films, where the specters indicates dimly superposed molecular orbital's (peaks present in specters are clear and a little different from their of dissolved molecules). The conductivity of these films can be improved by adding of doping agents like oxygen or iodine for p type films.

4. The actual tendency analyze in hydrogen energetic field relieves the photo-electrochemical conversion of solar energy method by water cleavage into hydrogen and oxygen with help of tandem cells proposed by Michael Graetzel. The tandem cells, without the advantages and perspectives offered, present also the disadvantage of a not too long life time, that why exist great reserves about the amelioration of the conversion yield.

5. Its were proposed two improvements of the photo-electrochemical solar energy conversion principled scheme:

a) the substitution of cathode-aqueous electrolyte system for proton reduction with a protons exchange membrane, produced by nanocomposite material - transparent polymer-oxide based on organic/inorganic macromolecular hybrid polymers, for example, a poly(tetramethylene oxide), poly(ethylene oxide) or diagonal polyethers, with polyoxometalate homogeneous incorporations from H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀ or H₆P₂W₁₈O₆₂ series; this solution presents the advantage of increasing sun visible light conversion yield in chemical energy of water decomposition products, by simplicity and high exploitation fiability of installation;

b) the replacement of solid organic electrolyte with a semiconductor composite formed by a half transparent matrix of polymeric material, inorganic or glass maded, for example, based on conjugated polymers structures like poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylen vinylen)], in which are dispersed nanoparticles from infrared radiation photosensible semiconductor, for example, PbS, PbSe or InAs nanocrystals; this solution present the advantage that converses the energy from infrared interval which constitute 55% of solar radiation spectrum.

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