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(71) Applicant (for all designated States except US): **Eni S.p.A.** [IT/IT]; Piazzale E. Mattei, 1, I-00144 Rome (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MEDA, Laura** [IT/IT]; Via Adamello 20, I-28066 Galliate (IT). **BIGNOZZI, Carlo Alberto** [IT/IT]; Via Valle Rillo 7, I-44124 Ferrara (IT). **CARAMORI, Stefano** [IT/IT]; V. Bertolda 46, I-44020 Viconovo/Ferrara (IT). **CRISTINO, Vito** [IT/IT]; Via Borgoleoni 88, I-44121 Ferrara (IT). **PEREGO, Carlo** [IT/IT]; Via Ss. Cornelio e Cipriano, 15/E, I-20040 Carnate (IT).

(74) Agent: **MAIWALD PATENTANWALTS GMBH**; Elisenstr. 3, Elisenhof, 80335 Munich (DE).

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(57) Abstract: The invention relates to a system of photoanodes in tandem, in a photoelectrolytic cell, for the production of solar hydrogen, i.e. hydrogen generated using solar radiation alone. In particular the photo-production of solar hydrogen which uses this system of photoanodes is obtained by photo-oxidation of aqueous solutions containing sulfides deriving from the neutralization of H₂S.



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TANDEM PHOTOELECTROLYTIC CELL FOR THE PHOTO-OXIDATION
OF SULFIDES WITH THE PRODUCTION OF HYDROGEN

The present invention relates to a system of photoanodes in tandem, in a photoelectrolytic cell, for the production of solar hydrogen, i.e. of hydrogen generated using only solar radiation. In particular, the photo-production of solar hydrogen according to the present invention is obtained by means of photo-oxidation of aqueous solutions containing sulfides deriving from the neutralization of H_2S .

Hydrogen sulfide (H_2S) is a toxic gaseous substance which can be found in sulfide water, it is acidic, corrosive, creates explosion risks when in critical concentrations. This product is formed, for example, in the technological transformation cycle of the hide into leather, in wastewater of the paper industry, in volcanic gases, in the anaerobic decomposition of animal proteins on the part of sulfate-reducing bacteria (in biogas), as a by-product of high-temperature industrial processes (for example, distillation of sulfur), in natural products such as oil and gas (up to 100 mbar in Sauer), in refinery wastewater, in the desulfurization of oil for the production, for example, of fuels.

H_2S has a chemical structure similar to that of water, but it has very different physical properties due to the non-availability of forming hydrogen bonds. It has a moderate solubility in water (about 3 g/l at room temperature).

As H₂S is obtained as a wasteproduct, its recovery is only justified by the necessity of purifying the product rather than the intrinsic value of its recovery.

5 There are industrial consolidated processes for the removal of H₂S from industrial gases, and these processes are based on the following techniques:

- chemical absorption, for example, in alkaline liquids, aliphatic amines, ammonia solutions,
10 solutions of alkaline salts, such as described in US 3,962,410 and US 4,163,044;
- physical absorption, for example in water or organic solvents:
- dry oxidation, i.e. not in solution but in the
15 solid state, for example effected on active carbon, to form S or oxides;
- liquid oxidation, for example, using dissolved catalysts which lead to the formation of S.

Various technologies are therefore known for the
20 removal of H₂S, and the choice is essentially based on the concentration and on the flow-rate of the gaseous stream to be treated. Starting from pure acid or in concentrations of up to about 10% by weight, the most widely spread industrial processes are based on washing
25 with amines followed by the Claus process which converts the acid into water and high-quality sulfur. This technology however has high investment and maintenance costs. For the recovery of 99.9% of sulfur, a treatment section of the tail gas must be included in

order to comply with current regulations of atmospheric emissions. The SCOT process is an example of this technology.

When the amount of H_2S is lower than 10%, it is
5 advantageous to effect a recovery treatment based on oxidation in liquid phase. The reference process is the LO-CAT process, wherein H_2S is absorbed in an alkaline solution containing a trivalent iron complex and subsequently transformed into sulfur and water. The
10 iron solution is subsequently re-oxidized to trivalent iron in air. The system however has the drawback that the sulfur produced contains impurities of iron sulfide and the complex containing iron is slowly degraded due to the highly alkaline environment. These facts lead to
15 an increase in the costs for the purification and running of the overall process.

In the case of small amounts (below 1,000 ppm) the hydrogen sulfide is preferably removed by means of suitable absorbing materials. There are, for example,
20 adsorption technologies of H_2S on iron oxide with the formation of the relative sulfide. To regenerate the adsorbing material, a thermal oxidation in air is effected to form sulfur in addition to the starting ferric oxide. These technologies are only economically
25 advantageous in the case of gaseous streams with a low sulfur concentration, but with relatively significant flow-rates: the necessity of having to remove H_2S in low concentrations and from gaseous streams with a low flow-rate volume, such as, for example, those coming

from tanning processings or from the production of paper and cardboard, consequently remains unsolved.

Activities have emerged in recent years, which are also suitable for obtaining value added from H_2S , such as, for example, thermal decomposition ($T > 1,300^\circ\text{C}$) for the production of H_2 : this process however gives low yields and is not commercially.

In general, an industrial system for the removal of H_2S involving high temperatures therefore implies a high energy consumption with the consequent production of CO_2 . For the treatment of small amounts, oxidation and/or adsorption processes, used more frequently, also imply high-temperature treatment and costs for the purification and regeneration of the absorbing materials.

The necessity is therefore felt for finding methods for the neutralization and dissociation of this toxic molecule, downstream of processes which produce it. For this purpose, electrolysis was considered for producing H_2 and S . H_2S splitting processes are described, for example, in D. Robert et al., *J.Photochem. Photobiol. A* 163, 2004, 569-580 (homogeneous photocatalysis), WO 2006/096692, WO 2003/051512 and WO 2006/106784.

A method has now been found for the removal of H_2S with the contemporaneous formation of hydrogen, based on the combination of suitable photoactive materials having the capacity of activating redox reactions, also

at room temperature, by illumination with solar light. Said method consequently does not imply significant thermal increases or high energy consumptions or CO₂ emissions or regeneration phases of the adsorbing
5 materials.

The process is based on the splitting (homolytic dissociation), in an aqueous solution, of a sulfide, preferably a sulfide having the formula M₂S, wherein M is selected from Na, K and R₄N wherein the substituents
10 R, equal to or different from each other, are selected from H and an alkyl containing from 1 to 4 carbon atoms. The sulfide is obtained by reaction of H₂S with any base, inorganic or organic, preferably a hydroxide. Bases which can be conveniently used are, for example,
15 NaOH, KOH or R₄NOH, wherein the substituents R, equal to or different from each other, are selected from H and an alkyl containing from 1 to 4 carbon atoms.

In particular, the new method is based on the photo-electrochemical treatment of said aqueous solutions
20 containing S²⁻ ions in order to obtain decomposition into elemental S, H₂ and a hydroxide, exploiting solar energy and the photoelectric properties of a new system of photoanodes in tandem in a photoelectrochemical cell.

25 The use of a hydroxide as base, preferably NaOH, KOH or R₄NOH is particularly advantageous, also considering that the process of the present invention, as it leads to the formation of a hydroxide,

regenerates the hydroxides used in the preparation of the aqueous solution of the sulfide. In the process of the present invention, the production of photocurrent, resulting in the photo-generation of charge carriers
5 (electrons (e) - holes (h)), occurs without the contribution of an external bias and solely with illumination in the region of visible solar light. With this new method, it is therefore possible to contemporaneously obtain both the purification of
10 streams containing H_2S , by transformation into the corresponding sulfides and subsequent photo-oxidation to S, and also the formation of H_2 , with a high yield, by means of solar energy.

With respect to the state of the art, this process
15 therefore has the following characteristics:

- it allows the handling, with a low environmental impact, of gaseous streams having a low content of H_2S of a wide range of productive origins;
- it allows a production of high-purity H_2 ;
- 20 - it allows the production of S which can be used in the production of chemicals, which can be recovered according to various methods, among which, for example, that described in US 5,861,099;
- 25 - it does not require costly investments;
- it does not require high temperatures, it is possible to operate at room temperature;

- it does not produce CO₂;
- it does not require separation or purification steps;
- it does not use adsorbing materials with
5 regeneration passages;
- it can use direct solar light, it does not require UV irradiation sources, as described in other methods of the prior art, such as, for example, US 7,220,391 and US 6,964,755 B, but
- 10 - it does not produce waste-products to be managed;
- it does not require the use of additional oxidizing gases, as described for example in US 7,378,068;
- by operating with sulfides, it is not only possible to avoid the use of toxic gas H₂S, but also to
15 treat higher concentrations in solution, rather than operating directly with H₂S, as described, for example, in US 2006/0196776.

The process of the present invention uses a new system of photoanodes in tandem which is capable of
20 absorbing, in different regions of the solar spectrum and summing the single effects of the photocurrent produced: said system of photoanodes uses two photoanodes in parallel based on TiO₂, one sensitized with CdS, or CdSe, and the other one with Bi₂S₃.

25 An object of the present invention therefore relates to a system of photoanodes in tandem comprising:

- a photoanode based on titanium dioxide (TiO_2) and a cadmium compound selected from cadmium sulfide (CdS) and cadmium selenide (CdSe),
- a photoanode based on titanium dioxide (TiO_2) and bismuth sulfide (Bi_2S_3).

The cadmium sulfide, or selenide and bismuth sulfide are present in the relative photoanode as a thin layer, possibly discontinuous. The photoanodes based on titanium dioxide and a compound of cadmium selected from sulfide and selenide ($\text{TiO}_2\text{-CdS}$ or $\text{TiO}_2\text{-CdSe}$) absorb the visible radiation, up to 550 nm the CdS and up to 700 nm the CdSe , in both cases with a high quantic efficiency (IPCE 40-60%): the use of the anode of the tandem consisting of $\text{TiO}_2\text{-CdS}$ or $\text{TiO}_2\text{-CdSe}$, and the photoanode based on titanium oxide and bismuth sulfide ($\text{TiO}_2\text{-Bi}_2\text{S}_3$) extends the possibility of absorption of solar radiation up to 800 nm. In particular, the photoanode based on $\text{TiO}_2\text{-CdS}$ or the photoanode based on $\text{TiO}_2\text{-CdSe}$ are used for capturing the high frequency part of the visible spectrum, with a high efficiency, whereas the photoanode based on $\text{TiO}_2\text{-Bi}_2\text{S}_3$ absorbs low-frequency photons, up to the near infrared (NIR), thanks to a photo-action threshold situated at 830 nm. The two electrodes are connected in parallel so as to be able to sum the respective photocurrents produced: this is enabled by the fact that the two photo-electrodes substantially have the same impedance and therefore generate the same photo-potential: the resulting photocurrent curves (J-V) are

therefore substantially determined by the sum of the photocurrents due to the single electrodes. In this way, what is defined hereunder as a "tandem" photoanode is obtained.

5 The photoanode based on titanium oxide (TiO_2) and bismuth sulfide (Bi_2S_3), which, coupled with the known TiO_2 -CdS or TiO_2 -CdSe photoanodes, allows said unexpected results to be reached, is in turn new and a further and particular object of the present invention.

10 All the methods described in literature can be used for the preparation of the TiO_2 -CdS photoanode.

Methods which can be conveniently used are those described, for example, in *J. Phys. Chem. B*, 2003, 107, 14154 and in *J.A.C.S.* 2008, 130, 1124, based on the
15 reaction in situ of S^{2-} and Cd^{2+} , which can be obtained by repeated immersions of a photo-electrode of titanium oxide alternately in separate solutions containing sulfide ions, such as for example Na_2S , in a concentration ranging for example from 10^{-3} to 1 M, and
20 containing $\text{Cd}(\text{NO}_3)_2$, or CdCl_2 , in a concentration within the range of 10^{-3} to 0.1 M.

Macro-accumulations of CdS and particles weakly interacting with the TiO_2 surface are removed by washings with deionized water, thus leaving a
25 homogeneous and transparent deposit of cadmium sulfide. The photo-electrodes thus obtained are slowly dried by means of moderate heating, for example from 30 to 60°C , before being sintered at a temperature ranging from 400 to 500°C for a time ranging from 30 minutes to 1 hour.

In the case of CdSe preparation, Na_2SeSO_3 can be conveniently used, in turn obtained by the reaction of elemental selenium with an excess of Na_2SO_3 , as described for example in *J. Electrochem Soc.*, 1984, 131, 2514 and in *Journal of Colloid and interface Science*, 2006, 302, 133. The photoanodes thus obtained are then subjected to thermal treatment in air, preferably at a temperature ranging from 200 to 450°C.

The $\text{TiO}_2\text{-CdS}$ or $\text{TiO}_2\text{-CdSe}$ photoanodes can also be prepared by means of electrochemical methods. The $\text{TiO}_2\text{-CdS}$ photoanode, for example, can be prepared by the cathodic electrodeposition of CdS from a solution, in DMSO, of elemental sulfur, in a concentration preferably from 10^{-3} to saturation, and Cd^{2+} ions, in a concentration preferably ranging from 10^{-3} to 0.1 M ; the $\text{TiO}_2\text{-CdSe}$ photoanode can be prepared by cathodic electrodeposition using Cd^{2+} ions and a solution of selenium oxide in sulfuric acid. The deposition is effected by the potentiostatic or potentiodynamic procedure, i.e. with potential linear scan cycles, or it can be effected by the galvanostatic procedure.

When operating in potentiodynamic mode, for example, the maximum range for the deposition is situated between 0 and -1.4 V vs. SCE (calomel reference electrode) at a rate ranging from 10 to 100 mV/s, adopting a variable number of cycles, from 3 to 100, depending on the quantity of material to be deposited. Alternatively, it is possible to choose a constant potential technique, operating at a potential

ranging from -0.5 V to -1.4 V vs SCE, which is maintained for a few tens of seconds. These electrodeposition methods are described for example in *J. Electrochemical Science and Technology*, 1981, 128, 963, with respect to the deposition of CdS, and in *J. Phys. Chem.* 1993, 97, 10769, with respect to the deposition of CdSe.

According to another preparation method, the photo-electrodes of TiO₂-CdSe can be prepared by means of a procedure which consists of mixing a CdS powder with an aqueous gel preferably with 7-15% by weight of nanocrystalline TiO₂, in the presence of an organic binder, in a quantity preferably ranging from 20 to 40% by weight with respect to the weight of the TiO₂. Said aqueous gel containing TiO₂ is prepared by the hydrothermal growth, preferably at a temperature ranging from 200 to 220°C, of a TiO₂ sol obtained by the acid hydrolysis, using, for example, HNO₃ or acetic acid, of titanium (IV) alkoxides, preferably titanium tetra-isopropylate. Convenient organic sintering agents are, for example, Carbowax or other polymers based on polyethyleneglycol. After accurate mixing by mechanical stirring and ultrasonic dispersion, the resulting suspension can be distributed directly on the conductor substrate, for example fluorinated tin oxide (FTO), indium-tin-oxide (ITO), or metallic titanium, by means of the blade casting method, i.e. by means of a distributor blade. The film is dried at room temperature or through moderate heating, for example

50-60°C, and subsequently sintered at a temperature preferably ranging from 400 to 550°C for 30-60 minutes. This preparation procedure is new and is a particular object of the present invention.

5 For the preparation of the photoanode based on Bi_2S_3 on TiO_2 , this can be effected by the repeated immersions of a photo-electrode of titanium oxide alternately in chemical baths composed of separate aqueous solutions containing sulfide ions, such as for
10 example, Na_2S and Bi^{3+} ions, such as for example, $\text{Bi}(\text{NO}_3)_3$, or $\text{Bi}(\text{Ac})_3$. The solutions preferably have a concentration ranging from 10^{-3} to 1 M with respect to S^{2-} and are preferably saturated solutions with respect to the compound containing Bi^{3+} ion. From 5 to 50
15 immersions can be adopted, each for a time ranging from 5 to 30 seconds. The photoanodes thus obtained are then subjected to thermal treatment in air, preferably at a temperature ranging from 150 to 250°C, even more preferably from 210 to 230°C. The thermal treatment can
20 also be effected in nitrogen at a temperature ranging from 200 to 400°C.

The photoanode based on Bi_2S_3 on TiO_2 can also be conveniently prepared by means of electrochemical methods, using, for example, a TiO_2 electrode, a
25 saturated solution of sulfur in DMSO and a compound containing Bi^{3+} ions, preferably $\text{Bi}(\text{NO}_3)_3$. Electrodeposition methods are preferred as they provide more homogeneous surfaces, leading to the nucleation and growth of the photoactive material starting from

the surface of TiO_2 oxide. The method is based on the electrochemical generation of the anion (S^{2-}) directly on the surface of TiO_2 , and subsequent reaction with the excess of metallic ions (Bi^{3+}) present at the electrode-
5 solution interface which leads to the direct deposition of the photoactive material Bi_2S_3 . The electrolyte precursor Bi_2S_3 , essentially consisting of a saturated solution of S in dimethylsulfoxide, is obtained by dissolving an excess of elemental sulfur at reflux
10 temperature. After cooling to room temperature, part of the elemental sulfur re-precipitates and is removed by filtration. $\text{Bi}(\text{NO}_3)_3$ is added to the remaining solution, at a concentration ranging from 10^{-3} to 0.1 M. The range for the deposition of Bi_2S_3 varies from -0.3 to -1.1 V
15 vs SCE, at rates ranging from 20 to 10 mV/s, adopting a variable number of cycles (from 5 to 100) depending on the quantity of material to be deposited. Alternatively, a constant potential technique can be used, operating at values ranging from -0.7 V to -1.1 V
20 vs SCE. In both cases, the electrodes thus obtained are subjected to thermal treatment at temperatures ranging from 220 to 260°C in air for a time ranging from 15 to 30 minutes.

The new photoanode based on titanium oxide and
25 bismuth sulfide ($\text{TiO}_2\text{-Bi}_2\text{S}_3$) absorbs solar radiation at a low frequency, up to NIR.

The absorption spectrum of the striking radiation, on the part, for example, of photoanodes based on titanium oxide and bismuth sulfide prepared by chemical

bath deposition, shows a continuous spectrum in the whole visible region, without resolved bands. The repetition of the immersion in the chemical baths used leads to electrodes marked by optical densities higher than 1 in the whole visible region and NIR. The absorption of photons in these spectral regions is almost complete. From the onset of the absorption spectrum, an optical band gap of 1.46 eV is estimated, in reasonable accordance with the value indicated in literature (1.3 eV) relating to Bi_2S_3 alone (*J.Electrochem.Soc.*, 1983, 130 (12), 2423). The photoelectrochemical response at 0 V vs SCE of electrodes based on titanium oxide and bismuth sulfide generates a photocurrent ranging from 7 to 4 mA/cm², in the presence of a striking irradiance equal to about 0.2 W/cm².

The advantage deriving from the use of a panchromatic absorber is evident from the curves J-V relating to electrodes based on Bi_2S_3 on colloidal TiO_2 : the removal of the UV portion and part of the visible by means of a cut-off filter at 420 nm does not lead to a substantial lowering of the performances of the photoanode $\text{TiO}_2\text{-Bi}_2\text{S}_3$, thus demonstrating the photoactivity in the visible of said photoanode.

In the system of photoanodes of the present invention, the photoanode $\text{TiO}_2\text{-CdS}$ or $\text{TiO}_2\text{-CdSe}$ and the photoanode $\text{TiO}_2\text{-Bi}_2\text{S}_3$ are connected in parallel.

A further object of the present invention relates to a photoelectrolytic cell comprising a system of photoanodes in tandem which comprises:

- a photoanode based on titanium dioxide (TiO_2) and a cadmium compound selected from cadmium sulfide (CdS) and cadmium selenide (CdSe),
 - a photoanode based on titanium dioxide (TiO_2) and
- 5 bismuth sulfide (Bi_2S_3).

The system of electrodes, object of the invention, and the photoelectrolytic cell containing said system of electrodes is suitable for applications based on photoanodic reactions, and is particularly suitable for

10 the production of hydrogen from aqueous solutions containing sulfides, wherein said sulfide is obtained by neutralization of H_2S with any base, organic or inorganic, preferably a hydroxide.

In particular, it is useful in the production of

15 hydrogen from aqueous solutions containing sulfides having the formula M_2S , obtained from H_2S by neutralization with a hydroxide having the formula MOH , wherein M is selected from Na, K and R_4N , wherein the substituents R, equal to or different from each other,

20 are selected from H and alkyl containing from 1 to 4 carbon atoms.

A further object of the present invention therefore relates to a process for the photo-production of H_2 from aqueous solutions containing sulfides, effected using a

25 system of photoanodes in tandem comprising:

- a photoanode based on titanium dioxide (TiO_2) and a cadmium compound selected from cadmium sulfide (CdS) and cadmium selenide (CdSe),

- a photoanode based on titanium dioxide (TiO_2) and bismuth sulfide (Bi_2S_3).

The sulfide preferably has the formula M_2S , wherein M is selected from Na, K and R_4N , wherein the
5 substituents R, equal to or different from each other, are selected from H and alkyl containing from 1 to 4 carbon atoms.

In the process for the production of hydrogen of the present invention, there is the contemporaneous
10 formation of S from the sulfides present and a hydroxide, preferably having the formula MOH , wherein M is selected from Na, K and R_4N , wherein the substituents R, equal to or different from each other, are selected from H and alkyl containing from 1 to 4 carbon atoms.

15 Without being bound to any theory, it is believed that the formation of sulfur passes through the initial formation of polysulfides S_x^{2-} , which subsequently oxidize to elemental sulfur. The process of the present invention therefore contemporaneously provides a double
20 result:

- producing hydrogen using solar radiation,
- purifying mixtures containing H_2S by the photo-treatment of aqueous solutions of sulfides, obtained from said mixtures containing H_2S by
25 neutralization with a base, providing, in addition to hydrogen, also elemental sulfur and hydroxide.

The aqueous solution containing the sulfide used in the process of the present invention is obtained by treating the mixture containing H_2S to be purified with

any base capable of neutralizing the H_2S , preferably with a hydroxide, even more preferably with a hydroxide having the formula MOH , wherein M is selected from Na , K and R_4N , wherein the substituents R , equal to or
5 different from each other, are selected from H and alkyl containing from 1 to 4 carbon atoms.

The mixture containing H_2S can be either liquid or gaseous. Said mixture is put in contact with the base, wherein said base is preferably a saturated hydroxide
10 solution: in the case of gaseous mixtures, a separator can be used, for example, in the case of liquid mixtures, a solution is used. At the end, the base solution containing the sulfide deriving from the neutralization of the H_2S can be used directly as
15 electrolyte in the photoelectric cell.

The cathode used in the photoproduction process of hydrogen of the present invention can consist for example of a high-surface network of a good metal conductor, for example Pt . Any material known to
20 experts in the field as catalytic material with respect to the development of H_2 can be conveniently used as cathode.

In the photoelectric cell, the system of photoanodes of the present invention and the cathode
25 are immersed in the basic aqueous solution containing the sulfide. The solution preferably contains a hydroxide and even more preferably the solution contains a sulfide having the formula M_2S and a hydroxide having the formula MOH , wherein M is selected

from Na, K, NH₄ and R₄N, wherein the substituents R, equal to or different from each other, are selected from H and alkyl containing 1 to 4 carbon atoms, prepared as described above. The hydroxide present is
5 in a concentration which preferably ranges from 0.9 to 1.1 M. The pH of the solution is equal to 14.

By illuminating the tandem system of photoanodes TiO₂-CdS or TiO₂-CdSe, and the photoanode TiO₂-Bi₂S₃, in the photoelectric cell, with a solar radiation source,
10 the oxidation of sulfide ions is promoted, in particular sulfide ions deriving from the complete dissociation of M₂S in water (solubility = 154 g/l at room temperature) with the production of elemental sulfur and a hydroxide, in particular MOH, wherein M is
15 selected from Na, K, NH₄ and R₄N, wherein the substituents R, equal to or different from each other, are selected from H and alkyl containing 1 to 4 carbon atoms. At the cathode, on the contrary, the reduction reaction of water to H₂ takes place.

20 The energy position of the bands of CdS or CdSe ensures that both redox reactions are effected.

The S²⁻ ion is not inert from an acid-base point of view, and in fact it hydrolyzes according to the following reaction:

25 $S^{2-} + H_2O \rightarrow HS^- + OH^-$, and this in turn contributes to the strongly basic pH of the solution. Even if the oxidation of HS⁻ at the photoanode, on the basis of the reaction $HS^- \rightarrow 2e^- + S + H^+$, involves the formation of H⁺ ions which neutralize the OH⁻ ions produced by the

hydrolysis of S^{2-} , no variation in the decrease in the pH is observed, said decrease is in fact neutralized by the reaction which takes place at the cathode: $2 H_2O + 2e^- \rightarrow H_2 + 2 OH^-$

5 A further significant advantage of the process of the present invention relates to the fact that the sulfide, in particular the sulfide having the formula M_2S , can also act as sacrificial element, i.e. providing the photo-electrodes with sulfur which goes into
10 solution, thus preventing the corrosion of the photo-electrode based on CdS or CdSe.

 In the process of the present invention, the layer of CdS, CdSe and Bi_2S_3 , remains stable with time, whereas the sulfide is consumed with the production of
15 S, H_2 and hydroxide. At the end of the photo-electrolysis, when substantially all the sulfur in solution has been converted, the hydroxide is recovered in a quantity corresponding to that possibly used initially for the transformation of H_2S into the
20 corresponding sulfide. The sulfur formed is recovered by precipitation and the aqueous solution of hydroxide can be re-used in the neutralization step of H_2S .

 The tandem system of electrodes of the present invention allows significant performances to be
25 reached, varying from 4 to 7 mA/cm^2 , at 0 V vs SCE; the illumination conditions which can be used can range from 1 to 2 suns, corresponding to an irradiance which varies from 0.1-0.2 W/cm^2 .

The following embodiment examples are provided for purely illustrative purposes of the present invention and should not be considered as limiting the protection scope defined by the enclosed claims.

5 Example 1 - Preparation of the photoanode TiO₂-CdS

The substrate of colloidal TiO₂ is obtained by laying a gel of nanocrystalline TiO₂ on a conductor of the FTO type, followed by sintering at 450°C for 45'. The TiO₂ gel is obtained following the method described
10 in Inorg. Chem., 2003, 42, 6655. The electrode is impregnated with CdS by alternating depositions from two different chemical baths containing Cd(NO₃)₂ and Na₂S both in a concentration of 0.1 M. The photo-electrodes thus obtained are slowly dried by means of
15 moderate heating to 60°C, before being sintered at a temperature of 500°C for 1 hour.

Example 2 - Preparation of the photoanode TiO₂-Bi₂S₃

The electrode is prepared by deposition from a chemical bath on colloidal TiO₂, using Bi(Ac)₃ and Na₂S,
20 in a concentration of 1 M, operating by the alternating repeated immersion of a photo-electrode of titanium oxide. The absorption spectrum of the photoanode thus prepared relating to a UV-Vis striking radiation is indicated in figure 1: the spectrum is continuous in
25 the whole visible region and has no unresolved bands.

Figure 2 shows the curve J-V relating to the electrode thus prepared, with an irradiance of 0.12 W/cm², AM 1.5 G, red cut-off 420 nm. The removal of the UV portion and part of the visible by means of a cut-

off filter at 420 nm (continuous curve) does not involve a substantial lowering of the performances of the photoanode $\text{TiO}_2\text{-Bi}_2\text{S}_3$ with respect to when non-filtered radiation is used (dashed curve): from 5 mA/cm^2 to 4 mA/cm^2 at 0.0 V.

Example 3 - Photo-oxidation test

The photoanodes of Examples 1 and 2 are connected in parallel and placed in a photoelectric cell, using a platinum cathode and an electrolytic solution containing Na_2S and NaOH in a concentration of 1 M. The results obtained, relating to the photocurrent generated, are indicated in Figure 3, which shows the curve J-V in the presence of a striking radiation equal to 0.14 W/cm^2 (AM 1.5 G). The achievement of a photocurrent equal to 15 mA/cm^2 at 0 V vs SCE is observed: the photocurrent values thus obtained (15 mA/cm^2) are capable of producing about 6.3 [litres $\text{H}_2/\text{hour m}^2$]. The sulfur produced is equal to the hydrogen produced. The equation used is: $J / 2 F =$ [moles $\text{H}_2 / \text{s cm}^2$], with F= Faraday coeff.

CLAIMS

1. A system of photoanodes in tandem comprising:
 - a photoanode based on titanium dioxide (TiO_2)
and a cadmium compound selected from cadmium
5 sulfide (CdS) and cadmium selenide (CdSe)
 - a photoanode based on titanium dioxide (TiO_2)
and bismuth sulfide (Bi_2S_3).
2. The photoanode system according to claim 1, wherein
the cadmium compound and/or bismuth sulfide are present
10 in the relative photoanode as a thin layer, possibly
discontinuous.
3. A photoelectrolytic cell comprising a system of
photoanodes in tandem according to claim 1 or 2.
4. A process for the photoproduction of H_2 from
15 aqueous solutions containing sulfides, effected using a
system of photoanodes in tandem according to claim 1 or
2.
5. The process according to claim 4, wherein the
sulfides have the formula M_2S , wherein M is selected
20 from Na, K and R_4N , wherein the substituents R, equal to
or different from each other, are selected from H and
alkyl containing from 1 to 4 carbon atoms.
6. The process for the photoproduction of hydrogen
according to claim 4, wherein the contemporaneous
25 formation of S and hydroxide is obtained.
7. The process according to claim 4 effected in a
photoelectrolytic cell.
8. The process according to claim 4 or 7, wherein the
aqueous solution containing the sulfide is prepared by

reaction of a mixture containing H_2S with an organic or inorganic base.

9. The process according to claim 7, wherein the base is a hydroxide.

5 10. The process according to claim 8, wherein the mixture containing H_2S is liquid or gaseous.

11. The process according to claim 4 or 7, wherein a cathode consisting of a metal conductor is used.

12. The process according to claim 4, wherein the
10 aqueous solution containing the sulfide also contains a hydroxide.

13. A photoanode based on titanium dioxide (TiO_2) and bismuth sulfide (Bi_2S_3), said bismuth sulfide possibly being in a continuous or discontinuous thin layer.

15 14. A process for preparing photoanodes based on titanium dioxide (TiO_2) and a cadmium compound selected from cadmium sulfide (CdS) and cadmium selenide ($CdSe$), comprising the following steps:

a) mixing a CdS powder with an aqueous gel of
20 nanocrystalline TiO_2 in the presence of an organic binder, obtaining a suspension;

b) distribution of the suspension obtained in step (a) on a conductor substrate by means of the blade casting technique;

25 c) drying and sintering at a temperature ranging from 400 to 550°C for 30-60 minutes.

15. A process for the preparation of the photoanode based on titanium dioxide and bismuth sulfide of claim 13, which comprises the repeated immersion of a photo-

electrode of titanium oxide alternately in separate aqueous solutions containing sulfide ions and Bi^{3+} ions, and the thermal treatment of the resulting photoanode, at a temperature ranging from 150 to 250°C, in air.

5 16. A process for the preparation of the photoanode based on titanium dioxide and bismuth sulfide of claim 13 by means of an electrochemical method, using a saturated solution of sulfur in DMSO and Bi^{3+} , at -0.3 and -1.1 V vs SCE, at rates ranging from 20 to 10 mV/s,
10 using a number of cycles ranging from 5 to 100.

17. A process for the preparation of the photoanode based on titanium dioxide and bismuth sulfide of claim 13 by means of an electrochemical method, using a saturated solution of sulfur in DMSO and Bi^{3+} , using a
15 constant potential, at values ranging from -0.7 V to -1.1 V vs SCE.

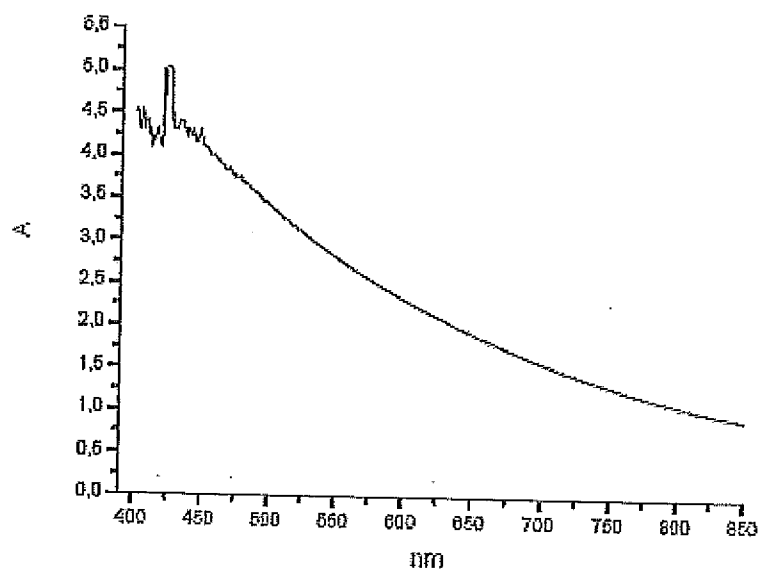


Fig. 1

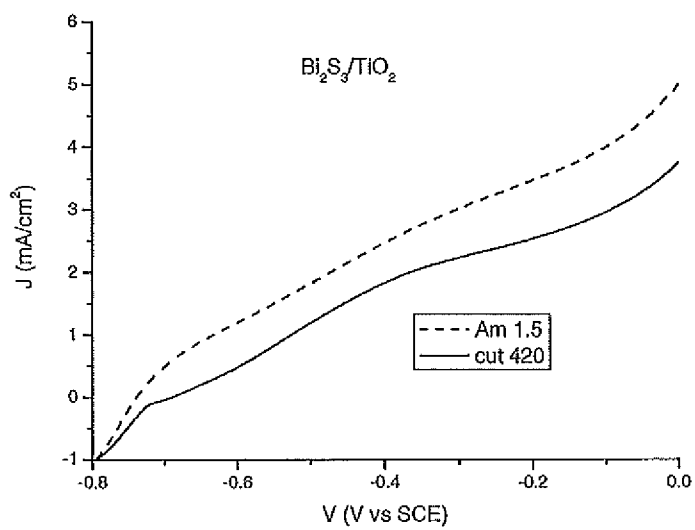


Fig. 2

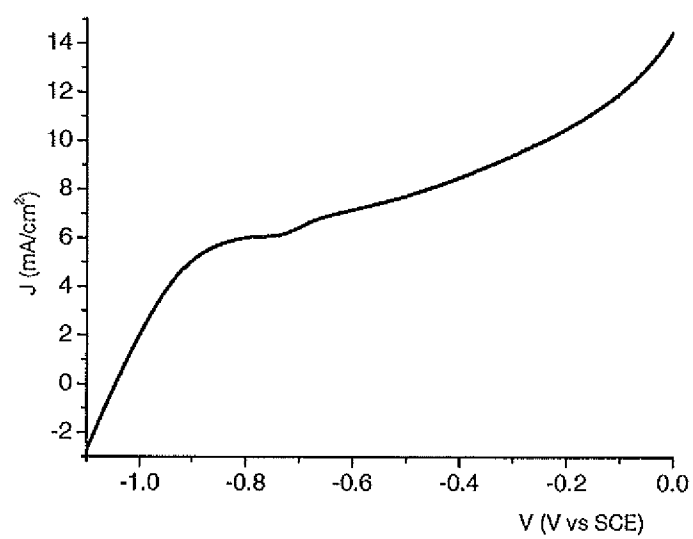


Fig.3