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Near Ultraviolet and Visible light photoelectrochemical degradation of organic substances producing electricity and hydrogen

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ABSTRACT

A two-compartment, chemically biased photoelectrochemical cell was used to photodegrade several organic substances and produce electricity and hydrogen. The photoanode of the cell was based on commercial nanocrystalline titania, which may be functionalized with CdS to absorb Visible light. The dark cathode was made also of commercial nanocrystalline titania with cast Pt nanoparticles. The cell was run under Near Ultraviolet or Visible radiation and the efficiencies in the two cases have been compared. Short chain-length alcohols and glycerol produced the highest energy yield but water-soluble waste materials are also interesting for the same purpose. The overall efficiency of cells made by CdS-functionalized titania was higher than those made of pure titania. However, larger currents were obtained with pure TiO_2 under Near Ultraviolet excitation. Under anaerobic conditions, molecular hydrogen can be produced at the dark cathode by the reduction of hydrogen ions generated at the photoanode.

1. Introduction

There is a recent revived interest in the production of hydrogen by the photocatalytic decomposition of organic substances [1–5]. The process is as follows: a nanocrystalline semiconductor photocatalyst (typically, nanocrystalline titania) is excited by the absorption of photons that create electron–hole pairs. Holes oxidize the target substance giving oxidation products and liberating hydrogen ions. In turn, hydrogen ions are reduced by excited electrons leading to molecular hydrogen evolution. This simplified process may proceed by intermediate steps, for example, hydroxyl radical formation [6] but the net effect, i.e. production of hydrogen, is the same [7]. However, the process has to compete with electron–hole recombination. Recombination is the favored event unless something is done to avoid it. There are two major routes to avoid electron–hole recombination. In the so-called photocatalytic (PC) process, noble metal nanoparticles are deposited on the semiconductor nanoparticles, acting as electron relay, which retains electrons and facilitates hydrogen ion reduction. Pt or Pd nanoparticles are recognized as best choice for this purpose [1]. Also, in the so-called photoelectrochemical (PEC) process, the semiconductor nanoparticles are deposited on an electrode, the (photo)anode, externally connected with the (dark)cathode, typically made of Pt. Holes, being created at the photoanode, as a result of photon absorption, oxidize the target substance leading to the formation of hydrogen ions. Hydrogen ions diffuse through the electrolyte and can reach cathode. Meanwhile, excited electrons are externally channeled from the anode to the cathode, owing to potential difference or to applied bias, where they reduce hydrogen ions and produce molecular hydrogen.

The oxidation process leads to the formation of hydrogen ions and oxidation products. These products are further oxidized until complete mineralization is achieved. For example, in a generally acknowledged scheme of step-by-step methanol oxidation and mineralization the following reactions might take place [4,8]:

$$CH_3OH + 2h^+ \rightarrow HCHO + 2H^+ \tag{1}$$

$$HCHO + H_2O + 2h^+ \rightarrow HCOOH + 2H^+ \tag{2}$$

$$HCOOH + 2h^+ \rightarrow CO_2 + 2H^+ \tag{3}$$

Hydrogen ions in turn are reduced by excited electrons producing molecular hydrogen:

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

The overall chemical reaction is then represented by

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{5}$$

Reaction (5) is equivalent to methanol reforming. Reforming is always obtained in the presence of water and it is mostly known as a high temperature process. However, the above Reactions (1)–(4) show that reforming can be also obtained photocatalytically at room temperature. Photocatalytic reforming (i.e. Reaction (5)) not only involves alcohol decomposition and mineralization but it also

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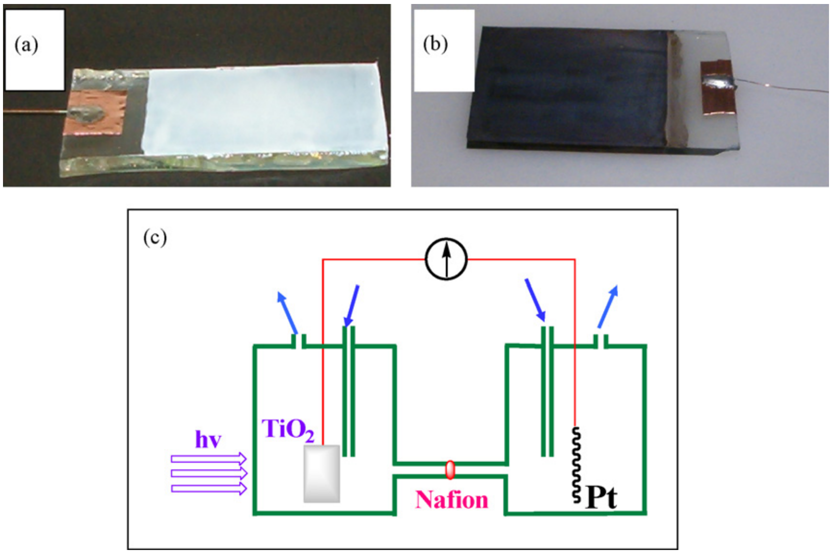

Fig. 1. (a) Photograph of the anode assembly depicting transparent conductive electrode, titania film and wire connection; (b) photograph of the cathode assembly depicting transparent conductive electrode, titania film, adsorbed Pt and wire connection; (c) schematic representation of the H-shaped PEC reactor.

involves water decomposition and hydrogen production. Therefore, photocatalytic reforming leads to both water splitting and water cleaning. Reactions similar to Reaction (5) can be obtained for essentially any organic substance under the following general scheme [2]:

$$C_xH_yO_z + (2x - z)H_2O \rightarrow xCO_2 + (2x - z + y/2)H_2 \quad (6)$$

In the present work, hydrogen production has been studied by the PEC oxidation of several different organic substances.

Typical photocatalyst is nanocrystalline titania, the most popular of all studied photocatalysts. Its popularity stems from the fact that it is a very stable and efficient photocatalyst, which can be easily produced in nanocrystalline form by simple “soft” chemistry procedures such as the sol–gel process. However, one of the major issues that preoccupy researchers dealing with photocatalytic oxidation is that titania does not absorb Visible light but absorbs in the UVA (315–400 nm) part of the spectrum, where only a small percentage of the Solar radiation reaches the surface of the Earth. Since photocatalytic applications are directly related with Renewable Energy Resources and thus with Solar radiation, an intensive effort is being made to utilize photocatalysts absorbing Visible light. As part of this effort, the present work studies PEC processes based either on pure nanocrystalline titania or combination of nanocrystalline titania with deposited cadmium sulfide. CdS, as it is well known, absorbs Visible light up to about 520 nm. Comparison of efficiencies has been made for oxidation of several organic substances. As already said, the evolution of hydrogen in a PEC system is accompanied by electron flow [9], hence current flow, in the external circuit. Therefore, the process has been studied by monitoring both hydrogen evolution and current flow. The PEC cell used in the present work was a two-compartment, chemically biased cell, as it will be described below.

Works being recently carried out on such processes are not new. As a matter of fact, PEC sells have been broadly studied in the 1970s and in the 1980s [10–14]. The recent revived interest exploits the present advanced knowledge on nanomaterials and the experience gained through the study of fuel cells. In addition, the target of the earlier works was photoelectrochemical water splitting. Nowadays, as it will be also shown in the present work, it is understood that photoelectrochemical oxidation of organic substances is a much easier and more efficient process than water oxidation [2,3]. Oxidation of sacrificial agents originating from industrial wastes to produce hydrogen has also been previously studied [15–19]. However, most of these works are on photocatalytic operation [15–18] aiming only at hydrogen production and they were limited to sulfide or sulfate-based compounds [15–19]. The recent works have a broader choice of target agents [9,20] and they focus, among others, on surplus materials derived from biomass, like glycerol [21]. For these reasons there exists a renewed interest with broad environmental implications.

2. Experimental

2.1. Materials

The nanocrystalline titania used in the present work was commercial Degussa P25, which consists of 25–30 nm nanoparticles. All the other reagents were from Aldrich and Merck, while Millipore water was used in all experiments. SnO_2:F transparent electrodes (Resistance 8 Ω/□) were purchased from Hartford, USA.

2.2. Preparation of nanocrystalline titania films and anode electrodes

Nanocrystalline Degussa P25 was dispersed in aqueous Carbowax solution [22], as previously described [23]. Carbowax solution was prepared according to the following recipe: 8.5 ml of water were mixed with 10.5 ml of EtOH. To this mixture we added 0.8 ml of a concentrated polyethylene glycol-2000 (PEG 2000) aqueous solution made of 30 g PEG 2000 and 30 g water. Degussa P25 was dispersed in this aqueous Carbowax solution by mixing 0.3 g Degussa with 3 ml of the solution. The resulting material was a white paste, which can be easily cast on any solid substrate. Films were thus made by casting the paste on SnO_2:F transparent electrodes. After casting, the films were calcined at 550 °C. This relatively high temperature was necessary to assure that all organic templates were destroyed. High calcination temperature adversely affects the conductivity of the transparent conductive electrode. This problem is less pronounced when SnO_2:F is used, as in the present case (compared, for example, to Indium-Tin-Oxide, ITO, electrodes). The procedure was repeated once more. The final quantity of titania on the support was 25 mg, while the dimensions of the film was $4 \times 2.5 = 10\ cm^2$. Thanks to the high calcination temperature, the film adhered well on the support and withstood the hard alkaline conditions during PEC operation. A photograph of such a film is shown in Fig. 1a, depicting also the wire connection, which was made with the help of copper ribbon attached on the uncovered part of the SnO_2:F electrode.

2.3. Deposition of CdS on nanocrystalline titania

Cadmium sulfide was deposited on nanocrystalline titania films by the adsorption of the reagents from aqueous solutions. We first prepared an aqueous solution of 0.1 mol/L $Cd(NO_3)_2$ and an aqueous solution of 0.1 mol/L Na_2S. The as-prepared TiO_2/SnO_2:F electrode was dipped for 5 min in the $Cd(NO_3)_2$ solution. Cd^{2+} ions were then adsorbed on the titania nanocrystalline film. Then the electrode was taken out of the solution, thoroughly washed with water and dipped in the Na_2S solution for 5 min. During the contact with the sulfur-ion-containing solution, CdS was formed on the titania film. The procedure was repeated 10 times, by taking care to wash with water all excess ions possibly adsorbed. The deposition of CdS was monitored by absorption spectrophotometry. Ten dipping procedures were judged enough to saturate the titania film with CdS.

2.4. Construction of the cathode

The cathode was made by using an identical electrode like that of the anode, i.e. a titania film on SnO_2:F (of course, without CdS), and cast an aqueous solution of sodium tetrachloroplatinate on it. Then it was heated up to 500 °C, to assure reduction of $PtCl_4{}^{2-}$ to metallic Pt and permanent adhesion on the film. The quantity of cast Pt on the above TiO_2/SnO_2:F electrode was approximately 1 mg. This is a substantial quantity of Pt that gave the electrode a deep dark color. A photograph of such a film is shown in Fig. 1b, depicting also the wire connection, which was also made with the help of copper ribbon attached on the uncovered part of the SnO_2:F electrode.

2.5. Description of the reactor

The PEC cell was a two-compartment (H-shaped) reactor made of Pyrex glass, schematically shown in Fig. 1c. The anode was made of one single SnO_2:F electrode with deposited nanocrystalline titania (and CdS, when necessary), while the cathode was similar to the anode with the addition of Pt nanoparticles, as already described. The electrolyte of the anode compartment contained 1.0 mol/L NaOH and that of the cathode contained 1.0 mol/L H_2SO_4. These different electrolytes were used to apply a chemical forward bias between anode and cathode. The cathode compartment was either continuously supplied with air by means of a small pump to run under aerobic conditions or with Ar gas to produce hydrogen under anaerobic conditions and carry it to a gas chromatograph for detection. In the case of TiO_2/SnO_2:F photoanode, exciting radiation was generated by a homemade source employing Black Light tubes with spectral maximum around 360 nm [5]. Four tubes of 4 W nominal power each were symmetrically placed inside a cylindrical cavity with reflective wall. The intensity of radiation at the position of the film and by facing a Black Light tube was 0.80 mW/cm^2. Radiation intensity was measured by using a radiant power meter with the probe placed at the position of the electrode, facing a lamp. Since the photoanode can absorb light from all four tubes, we roughly estimated that the total light intensity incident on the photoanode was $4 \times 0.80 = 3.2$ mW/cm^2. In some cases, excitation was obtained with a 400-W Xenon lamp equipped with a water filter to absorb IR radiation. In the case when $CdS/TiO_2/SnO_2$:F was used as photoanode, excitation was made with the Xe lamp.

2.6. Measurements

UV–vis absorption measurements were made with a Cary 1E spectrophotometer. The intensity of radiation at the position of the catalyst was measured with a Radiant Power/Energy Meter (Oriel-70260). Electrical measurements were made with a Keithley 196 while IV scans were recorded with a computerized Keithley 2601 source meter. Detection of hydrogen was made online by using an SRI 8610C gas-chromatograph and Ar as carrier gas. Samples were periodically collected via an automatic gas sampling valve and the concentration of H_2 present in the reactor effluent was determined as a function of time of irradiation. Calibration of the gas-chromatograph signal was accomplished with the use of a standard mixture of 0.25% H_2 in Ar. Comparison between the signal of the sample with that of the standard was made by calculating the areas of the corresponding gas chromatograph peaks.

3. Results and discussion

The PEC cell used in the present work was a chemically biased two-compartment cell. For this purpose, the anode compartment always contained a basic electrolyte, i.e. 1.0 mol/L NaOH, while the cathode compartment contained an acidic electrolyte, i.e. 1.0 mol/L H_2SO_4. The chemical bias expected for such electrolytes can be calculated from the equation $\Delta V = 0.059\,\Delta pH$ [24]. The measured pH value was 1.1 for the cathode and 13.0 for the anode compartment. This corresponds to 700 mV. Bias is always necessary, when the photoanode is made of nanocrystalline titania and the dark cathode of platinum. Indeed, negligible current flowed through the external circuit when no bias was applied, that is, when the electrolyte was the same in the two compartments. In the present work, the cathode was, as already discussed in Section 2.4, a $Pt/TiO_2/SnO_2$:F electrode. We have chosen such electrode for the following reason. It is known that the efficiency of the cell increases when the electrodes have high specific area. For this reason it is advantageous to use nanostructured electrodes [25]. The idea of depositing Pt on titania is very attractive since such an electrode is easy to make. Provided, of course, that the cathode is kept in the dark, as it was indeed the present case.

3.1. Oxidation of organic substances using a TiO_2/SnO_2:F photoanode

Several different organic reagents were introduced in the anode compartment and the photocurrent was measured. The cathode compartment was run under aerobic conditions; therefore, the cell produced an electric current but did not produce hydrogen. The cell *I*–*V* values as well as the cell photovoltaic efficiencies are listed in Table 1. Dark open-circuit voltage V_{oc} ranged between 720 and 840 mV. The biggest part of these values comes from the already mentioned chemical bias of 700 mV. Dark currents were negligible. It is obvious that the measured current was in all cases a photocurrent. Current, however, depended on the type of the sacrificial reagent present in the anode compartment. In the absence of any such reagent, current was very low and the corresponding efficiency was also very low.

Currents are listed in Table 1 as short-circuit current density J_{sc}, expressed in mA/cm^2. Since the surface area of the photoanode was 10 cm^2, the J values were found by simply dividing the actual measured currents by 10. This is not the best way to calculate current density. The proper way is to construct a photoanode of as small as possible surface area because losses are in that case minimized. This presents some practical difficulties. Therefore, we have opted for relatively large electrodes and we consider the ensuing error not important for the present application. Table 1 also

Table 1
Cell current–voltage characteristics under UVA (Black Light) illumination for various reactants in the anode compartment.

Reactant and its concentration	V_{oc} (mV)	J_{sc} (mA/cm^2)	η (%)
No additive	1400	0.11	0.9
MeOH (20%v.)	1650	1.12	10.9
EtOH (20% v.)	1670	1.03	9.2
PrOH (20% v.)	1650	1.00	8.0
Glycerol (20% v.)	1790	1.12	10.5
Ammonia (1% v.)[a]	1580	0.44	5.9
Urea (0.83 mol/L)	1570	0.20	3.8
Triton X-100 (2% v.)[b]	1710	0.19	5.9
SDS (0.033 mol/L)[c]	1210	0.49	5.8
CTAB (0.033 mol/L)[d]	1500	0.24	2.9
Dish-wash detergent (1% v.)[e]	1610	0.35	4.2

The anode compartment also contained 1.0 mol/L aqueous NaOH and the cathode compartment contained 1.0 mol/L aqueous H_2SO_4.

[a] Obtained by the dilution of a 25% ammonia solution.

[b] A nonionic surfactant: Polyoxyethylene-(10) isooctylphenyl ether.

[c] An ionic surfactant: Sodium Dodecylsulfate.

[d] A cationic surfactant: Cetyltrimethylammonium Bromide.

[e] Commercial dish-wash detergent under the brand name AVA.

lists the open-circuit voltage values, which were, thanks to the applied chemical bias, relatively large. The efficiency η of Table 1 is a pseudo-photovoltaic efficiency, which was calculated by plotting JV curves under reverse bias, as in Fig. 2. By definition [26], the photovoltaic efficiency is the ratio of the actual maximum (electric) power produced by the cell over the incident light power,

$$\eta = \frac{(JV)_{max}}{P} \tag{7}$$

where $(JV)_{max}$ is the maximum value of the JV product, as extracted from the JV plot, and P is the power density of the incident radiation, i.e. 3.2 W/cm^2, in the present case. The $(JV)_{max}$ value of Fig. 2 (corresponds to the crossing point of the perpendicular lines) was 0.29 mW/cm^2, therefore, the corresponding η value was 9.2% (case of 20% v. EtOH).

The use of Eq. (7) to calculate efficiency does not take into account the chemical energy liberated by the oxidation of the organic substance. During the first step, for example, of EtOH oxidation, the following reaction, analogous to Eq. (1) will take place [8]:

$$C_2H_5OH + 2h^+ \rightarrow CH_3CHO + 2H^+ \quad (\Delta G = 47.2\,\text{kJ mol}^{-1}) \tag{8}$$

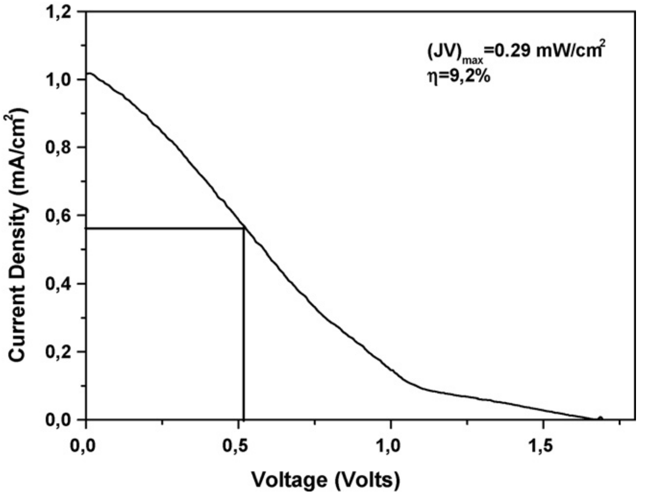

Fig. 2. JV plot under UVA (Black Light) illumination of the cell containing the following electrolytes: 1.0 mol/L NaOH + 20% vs. EtOH vs. 1.0 mol/L H_2SO_4.

The Gibbs free energy change for this reaction is about +47.2 kJ mol^{-1}. It is an endergonic reaction, that is, energy must be given to ethanol in order to oxidize it. Of course, this energy comes from the excited semiconductor that is from the absorbed light. Since two holes are involved in this reaction, according to the relation $\Delta G = EqN$, where q is the charge ($q = 2$ units of charge, in the present case) and N the Avogadro's number, it is derived that the corresponding potential is $E = 0.24$ V. For some authors [27,28], the net energy yield should be calculated by taking into account this potential. Thus for the first stage of EtOH oxidation and for an open-circuit current density J_{oc} equal to 1.03 mA/cm^2 (see Table 1), the net power density yield is equal to $EJ_{oc} = 0.25$ mW/cm^2. This is not very different from the value of 0.29 mW/cm^2 calculated from Fig. 2, as given above. However, this is not the only oxidation reaction that can take place. In a second stage, acetaldehyde can be oxidized as well as its products that will make a different net energy yield. Water splitting, corresponds to a potential $E = 1.23$ V. The corresponding open-circuit current density J_{oc} in the absence of any organic additive was equal to 0.11 mA/cm^2, as seen in Table 1. This makes a net power density yield equal to $EJ_{oc} = 0.14$ mW/cm^2. However, the corresponding $(JV)_{max}$ was only 0.029 mW/cm^2, i.e. it was very different from the product EJ_{oc}, in that case. It is obvious that it is hard to calculate efficiency by taking into account the chemical potential E, since the percentage of contribution of each oxidation reaction is not known. We then believe that the efficiency calculation according to Eq. (7) is useful for practical applications but it must be only used to compare the behavior of similar systems.

The above value of 9.2% calculated for ethanol is a relatively large efficiency and it is so because the incident radiation was only UVA radiation fitting titania band gap and thus all absorbed by titania. The efficiency was much smaller when the exciting radiation was produced by a Xe lamp. In that case, the incident power density at the position of the photoanode was 50 mW/cm^2 but only a small percentage of it is in the UV range where TiO_2 absorbs. Thus the overall efficiency dropped to 0.16%. Natural (Solar) light gave a little better performance of 0.20%. All these considerations must be carefully taken into account [7,29] to properly estimate cell efficiency. Practically speaking, the efficiency of the cell used in this work was low. The employed cell was, however, not optimized, since optimization of the cell was not the purpose of the present work. As can be seen in Table 1, the highest values of both short-circuit current density and overall efficiency η was obtained in the presence of alcohols or glycerol. Other substances induced much lower currents, thus showing that photocatalytic reforming is most efficient in the case of alcohols and polyols. Among the rest of the studied reagents, ammonia gave substantial currents as well as ionic surfactants. The latter may be a result of the increased conductivity due to the presence of additional ionic species. The substances listed in Table 1 were chosen to represent some categories of either surplus material derived from biomass, like alcohols and polyols, or some model substances of human waste or substances of urban pollution, like surfactants. Kaneko and coworkers have previously studied the oxidation of various organic substances by using a single compartment cell and they have established a rich protocol of the cell performance [9,20]. They found that best performance, in terms of current flow, was obtained in the case of pure methanol [20]. The present data are in accordance with those results.

Under anaerobic conditions, i.e. by passing Ar through the cathode compartment, hydrogen was produced and could be registered by means of a gas chromatograph, as explained in Section 2. Fig. 3 shows hydrogen evolution in the case of glycerol together with the value of the short-circuit current flowing through the external circuit. The two values evolved in a parallel manner. This was expected and it verifies the fact that hydrogen molecules are produced by the reduction of hydrogen ions by electrons arriving at the cathode through the external circuit. Therefore, they are

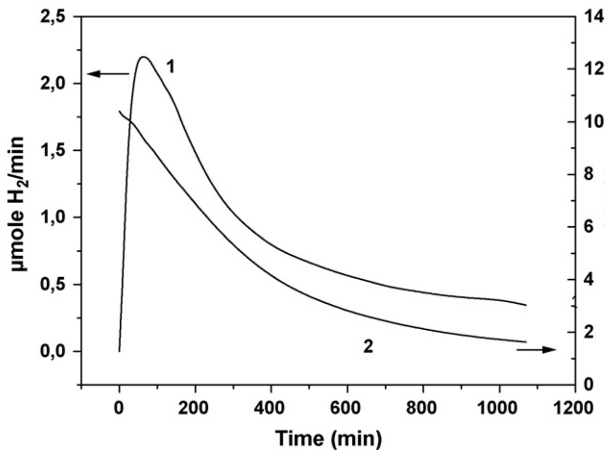

Fig. 3. Hydrogen evolution rate (1) and short-circuit current (2) as a function of time for a cell bearing a TiO_2/SnO_2:F photoanode, run under UVA (Black Light) illumination and containing the following electrolytes: 1.0 mol/L NaOH + 20% vs. Glycerol vs. 1.0 mol/L H_2SO_4.

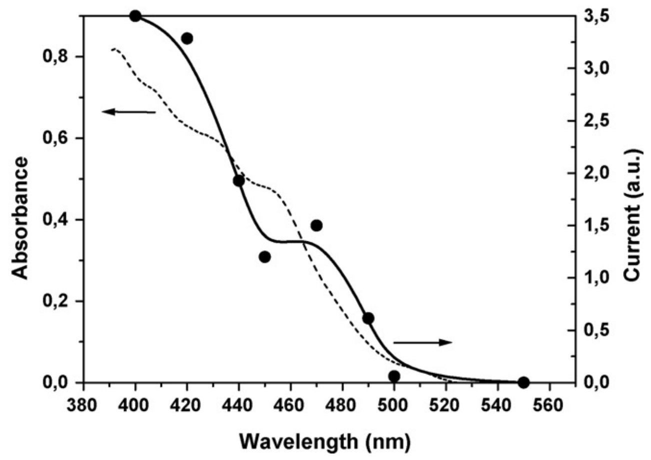

Fig. 4. Visible-light absorbance (dashed curve) and short-circuit current (solid curve) as a function of the wavelength for a cell based on a $CdS/TiO_2/SnO_2$:F photoanode and containing the following electrolytes: 1.0 mol/L NaOH + 20% vs. EtOH vs. 1.0 mol/L H_2SO_4.

proportional. Both the current and the hydrogen production rate decreased in the course of time. We have no clear picture of what causes this decrease. Most probably there are more than one single reason. An obvious one is the consumption of the pure reagent initially introduced in the reactor. However, the system was still far from complete mineralization after several hours of illumination, as preliminary data have indicated. Another possible reason is the exchange of cations through the nafion membrane that could decrease the chemical bias. Such an exchange would affect the pH value in each compartment. pH was measured at the beginning and at the end of each experiment. A small increase of the pH was indeed detected in the cathode compartment. It was 1.1 at the beginning and became 1.3 at the end. The pH in the anode compartment was practically stable. The overall pH modification justifies a voltage drop of only 12 mV. Therefore, the variation of the chemical bias was very small and it cannot justify the large drop in current and hydrogen production. A further reason of drop of efficiency could be the deterioration of the electrodes. No signs of anode deterioration have been observed. However, a fresh cathode improves efficiency by about 10%. This could come from loss, migration and agglomeration of platinum nanoparticles, as it is known for cathode electrodes in fuel cells. However, it can still not justify the current loss seen in Fig. 3. We believe, that the main reason for the decrease of cell performance is the chemical modifications taking place within the anode compartment, since a fresh electrolyte in the anode compartment recovers efficiency to a large extent. This matter is beyond the scope of the present work but it is further studied in our laboratory. Some preliminary data indicated that the formation of organic species of higher molecular weight, contrary to the scheme of Reactions (1)–(3), might complicate the oxidation process and the continuous hydrogen ion generation.

3.2. Oxidation of organic substances using a Visible-light responsive CdS/TiO2/SnO2:F photoanode

When the photoanode was derivatized by the deposition of the Visible-light responsive CdS [28], the cell could work with Visible light produced by a Xe source. The incident radiation in this case had a density of 50 mW/cm^2 at the position of the photoanode. We have first verified that the modified photoanode indeed responded to Visible radiation. For this purpose, we have registered the short-circuit current produced by the cell at various wavelengths, modified by using narrow band-pass interference filters. Then the currents were normalized to the radiation density incident on the photoanode, which varied from one filter to the other. The obtained spectral response is given by the solid curve of Fig. 4. The onset was around 520 nm and had a typical semiconductor behavior expected for CdS. The dashed line of Fig. 4 shows the corresponding absorption spectrum of deposited CdS, also characteristic of this semiconductor. The curves are not coincident, but this is reasonable, since error affects the recording of both curves, especially, the corrected current curve. The Visible-light photoresponse of the cell is obviously due to the excitation of CdS. The above results are not conclusive as to whether CdS acts as photosensitizer of titania substrate or whether it directly transfers the excited electron to the underlying SnO_2:F electrode. Most probably the first case is in effect. The conduction band of CdS is more electronegative than that of Titania (cf. energy diagram in Refs. [7,30]), therefore, the transfer of the excited electron from CdS to titania is encouraged. However, it is not excluded that part of the adsorbed CdS nanoparticles may be in direct conduct with the SnO_2:F electrode.

Once the Visible-light response was verified, the cell was used to oxidize some characteristic substances chosen among those of Table 1. The results are listed in Table 2. Both open-circuit voltage and short-circuit current densities were all smaller than in the case of the TiO_2/SnO_2:F photoanode and UVA excitation. They were again much higher in the case of ethanol and glycerol, and they were the lowest in the absence of any additive. However, the photovoltaic efficiencies η were larger in the present case. Indeed, as already said, in the absence of CdS and for 20% EtOH, the efficiency was only 0.16% but became 0.58% in its presence. Therefore, the Visible-responsive photoanode does make a better performance than the UVA-limited photoanode. However, this performance must be properly judged

Table 2
Cell current–voltage characteristics under Visible-light illumination for various reactants in the anode compartment.

Reactant and its concentration	V_{oc} (mV)	J_{sc} (mA/cm^2)	η (%)
No additive	1020	0.06	0.05
EtOH (20% v.)	1420	0.71	0.58
Glycerol (20% v.)	1570	0.95	0.47
Ammonia (1% v.)[a]	1440	0.25	0.27
SDS (0.033 mol/L)[b]	1120	0.08	0.06

The anode was made of a $CdS/TiO_2/SnO_2$:F electrode. The anode compartment contained 1.0 mol/L aqueous NaOH and the cathode compartment contained 1.0 mol/L aqueous H_2SO_4.

[a] Obtained by the dilution of a 25% ammonia solution.

[b] An ionic surfactant: Sodium Dodecylsulfate.

in view of the toxicity of CdS and its possible photodegradation. In the present work, we did not observe any CdS photodegradation, apparently because the oxidizing holes are consumed by the target organic substance.

4. Conclusions

The above-described PEC cell can be used to photocatalytically oxidize a large variety of organic substances and produce electricity and hydrogen. The efficiency of the cell was very limited when only water and electrolytes were present. On the contrary, the efficiency increased 10-fold in the presence of short chain-length alcohols and glycerol and it also obtained substantial values in the presence of a variety of other substances. Many of these substances are urban or industrial pollutants while glycerol and similar substances may nowadays be considered as surplus waste materials [21]. Therefore, the above cell could potentially be employed for combined water cleaning applications with energy yield. The use of Visible-light responsive photoanode increases efficiency, therefore, it can be promising for Solar applications.

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