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Photocatalytic and photoelectrochemical hydrogen production by photodegradation of organic substances*

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Abstract: Commercial nanocrystalline titania (titanium dioxide, TiO_2) has been used to make TiO_2 films, which were employed to photodegrade several organic substances under photocatalytic (PC) or photoelectrochemical (PEC) operation. Hydrogen was produced during both operations while electricity was additionally produced during the PEC operation. Both processes were studied as typical examples of the current trend in the effort to produce useful forms of energy by photodegradation of organic waste materials.

Keywords: photocatalytic; photoelectrochemical; nanocrystalline titania films; photodegradation; wastes.

INTRODUCTION

Nanocrystalline titania (titanium dioxide, TiO_2) is one of the most popular photocatalysts, and it is studied by a large number of research groups worldwide. 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. The number of works dealing with TiO_2 these days surpasses those of any other material, as one can verify by a simple Internet search. Highlights of TiO_2 photocatalysts are its employment for pollutant photodegradation and water treatment [1–3] and its employment in the construction of dye-sensitized solar cells [4]. As a matter of fact, TiO_2 first attracted attention through some early efforts to photoelectrochemically split water and produce hydrogen [5]. This matter is continuously attracting attention, even though photocatalytic (PC) water splitting is not an efficient process. Recently, a strong revival of interest on this matter is being observed, since hydrogen economy becomes an increasingly important issue. PC water splitting may not be particularly promising, however, production of hydrogen by PC decomposition of organic wastes appears to be an exciting idea. In the present work, we present a short account of what is being done in this domain and give some related recent results obtained by our own research group.

Hydrogen production by decomposition of organic substances can be classified into two major processes, known as the photocatalytic (PC) [6,7] and the photoelectrochemical (PEC) [8] processes. In the PC process, a semiconductor nanocrystal is excited by absorption of a photon, which creates an electron-hole pair. Holes oxidize the target substance. The oxidation process leads to the production 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 take place [6,9]:

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$$CH_3OH + 2h^+ \rightarrow HCHO + 2H^+ \quad (1)$$

$$HCHO + H_2O + 2h^+ \rightarrow HCOOH + 2H^+ \quad (2)$$

$$HCOOH + 2h^+ \rightarrow CO_2 + 2H^+ \quad (3)$$

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

$$2H^+ + 2e^- \rightarrow H_2 \quad (4)$$

The overall chemical reaction is then represented by

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad (5)$$

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 [10]. However, reactions 1–4 show that reforming can be also obtained photocatalytically at room temperature [11]. PC reforming (i.e., reaction 5) involves alcohol decomposition and mineralization, but it also involves water decomposition and hydrogen production. Therefore, PC 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 [10,11]:

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

PC reforming competes with electron-hole recombination. In fact, if no appropriate measures are taken, recombination prevails and reforming may become negligible. There are several ways to prevent or diminish recombination [7]. A very successful one is to deposit a noble metal nanoparticle on the semiconductor nanoparticle [12,13]. The metal acts as electron scavenger, thus preventing recombination and facilitating transfer and reduction of H^+. An alternative possibility has been proposed in ref. [9] where the reducible MV^{2+} ion is used as electron relay, by simply dissolving this substance in the photodegradable solution. Still another possibility is to combine two semiconductors, e.g., TiO_2 and RuO_2 [9,14], of different bandgaps, where the one becomes an electron sink for the other. Among all these possibilities, Pt/TiO_2 photocatalyst seems to offer the best combination [13].

The second process of hydrogen production by employment of photocatalysts is the so-called photoelectrochemical (PEC) process [8]. PEC process is the oldest known process [5]. The semiconductor photocatalyst is deposited on an electrode, making the anode, while the cathode is made of a high-work-function metal, usually Pt. The two electrodes are immersed in the photodegradable solution, and they are externally electrically connected. In order to increase conductivity, it is necessary to add an electrolyte. When the photoanode is excited, electrons and holes are created. Holes oxidize the target substance, as in reactions 1–3, and hydrogen ions are reduced at the cathode by the electrons, which move there through the external circuit. The overall result is production of molecular hydrogen and electricity by consuming light energy and by decomposing the target substance. A PEC cell can be constructed in one single compartment [8,15] or two compartments [16,17], one containing the anode and the other the cathode, communicating through a proton-transfer membrane, for example, Nafion. Two-compartment cells provide the advantage of allowing the use of two different electrolytes in the two compartments: an alkaline electrolyte in the anode compartment facilitating oxidation and an acidic electrolyte in the cathode compartment facilitating hydrogen reduction. PEC cells do not work without an electric bias [8,18] in the case of anodes made of certain semiconductors, including TiO_2. The reason is that the reduction level H_2/H_2O (level zero) is higher than the Fermi level of a Pt cathode [8]. A forward bias is then necessary, otherwise no water and no organic decomposition can be obtained in a cyclic manner. In a single-compartment cell, bias can be only applied through the external load [19]. In a two-compartment cell, bias can be obtained by simply using two different electrolytes [16,17,20]. In the present work, some results will be included, obtained by using a chemically biased two compartment cell. Under aerobic conditions, hydrogen ions in the cathode compartment of a two-compartment cell can interact with O_2 and electrons and produce water, according to the following equation:

$$2H^+ + 1/2O_2 + 2e^- \rightarrow H_2O \tag{7}$$

In that case, the net energy conversion is production of electricity by fuel consumption in the presence of light. Such a cell acts as a "photo-fuel-cell" (PFC) [21], providing an additional interesting possibility. As it will be shown later, PC operation yields higher quantities of hydrogen, however, PEC operation offers the advantage of electricity generation.

EXPERIMENTAL

Materials

The TiO_2 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/square) were purchased from Hartford, CT, USA.

Preparation of TiO_2 films

Nanocrystalline Degussa P25 was dispersed in aqueous Carbowax solution [22], as previously described [20]. Carbowax solution was prepared according to the following recipe: 8.5 ml of water was mixed with 10.5 ml of EtOH. To this mixture, we added 0.8 ml of a concentrated 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 either on microscope glass slides or on SnO_2:F transparent electrodes. Microscope glass slides were used for PC and SnO_2:F transparent electrodes for PEC applications, respectively. 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, e.g., to indium tin oxide, ITO, electrodes). The procedure was repeated once more. The final quantity of TiO_2 on the support was 25 mg, while the dimensions of the film were $4 \times 2.5 = 10$ cm^2. Thanks to the high calcination temperature, the film adhered well on the support and withstood the hard alkaline conditions in the case of PEC operation. As can be seen in the atomic force microscopy (AFM) image of Fig. 1, the surface of such films was very rough. The size of the nanoparticles measured by AFM appeared much larger, i.e., about 70–100 nm, than the 25–30 nm of the original Degussa P25. Agglomeration and sintering during calcination, apparently, lead to larger nanoparticles.

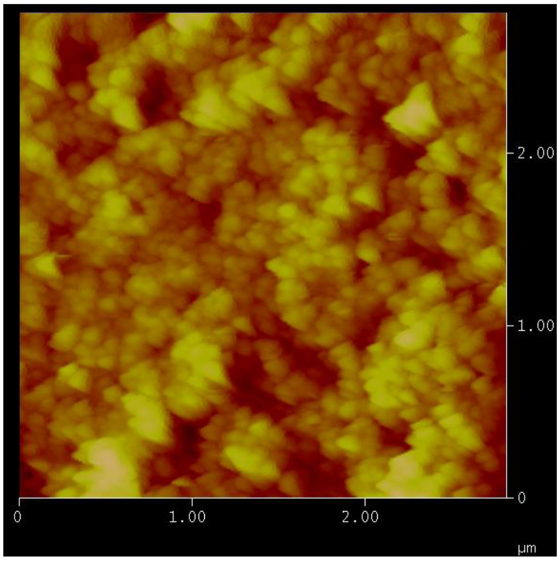

Fig. 1 AFM image of the surface of a typical TiO_2 film used in the present work.

Preparation of metal/TiO_2 catalyst for PC operation

Metals were deposited on the surface of TiO_2 films, as previously [13,23], by adsorption from aqueous solutions containing about 5×10^{-4} M of one of the following metal salts: $Na_2PtCl_4 \cdot xH_2O$; $Na_2AuCl_4 \cdot 2H_2O$; $RuCl_3 \cdot xH_2O$; $RhCl_3 \cdot xH_2O$; $AgNO_3$; $Na_2PdCl_4 \cdot xH_2O$; and $NiC_2H_4O_2 \cdot 4H_2O$. After the second layer of TiO_2 was deposited and immediately after the film was taken out from the oven, the slide was submerged in the solution and was left there for half an hour in the dark. Then it was washed, dried, and subjected to UV radiation for 15 min for each side of the slide. UV treatment is made in order to assure reduction of cationic species to neutral metallic nanocrystals.

Description of the reactor for PC operation

The reactor used for PC operation was a Pyrex cylinder of 4.4 cm diameter and 10 cm length, with provisions for gas inlet and outlet [23]. Inside the cylinder were placed four microscope slides covered on both sides with the TiO_2/metal catalyst. Around the glass cylinder were fitted four commercial black light tubes of 10 cm active length, each of 4 W electric power. The light intensity reaching directly to a slide facing one light source was measured to be 0.40 mW/cm^2. The reactor was filled with a water–ethanol mixture. The total volume of the solution was 85–90 ml. We used a 50 vol % water–ethanol mixture, which is approximately 3:1 molar ratio, as in reaction 8, which is reaction 6 applied to ethanol ($m = 2$):

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{8}$$

Experiments were conducted under Ar flow of 20 cc/min, which served as a means of collection and transfer of product H_2 to the analysis system. The pH of the solution was the natural pH of the water–alcohol mixtures without acid, base, or salt addition.

Description of the reactor for PEC operation

The PEC cell used in the present work was a two-compartment (H-shaped) reactor made of Pyrex glass. The two compartments were separated by a Nafion membrane. The anode was made of one single SnO_2:F electrode with deposited TiO_2, while the cathode was similar to the anode with addition of Pt nanoparticles. This was done by casting an aqueous solution of sodium tetrachloroplatinate on the TiO_2/SnO_2:F electrode. Then it was heated to 500 °C, to assure reduction of $PtCl_4^{2-}$ to metallic Pt and permanent adhesion on the film. The substantial quantity of Pt cast on this TiO_2/SnO_2:F electrode gave it a deep dark color. Such a cathode was more efficient than using a pure Pt metal cathode. Use of a $Pt/TiO_2/SnO_2$:F electrode as cathode has the advantage that it needs less Pt, thus it is less costly, and by adhering on a nanostructured film it achieves a large interface with the electrolyte. A similar approach was also made in previous works [24,25]. In this respect, care was taken to keep the cathode in the dark. The electrolyte of the anode compartment contained 1.0 mol l^{-1} NaOH and that of the cathode compartment contained 1.0 mol l^{-1} H_2SO_4. These different electrolytes were used to apply a chemical forward bias between anode and cathode. The cathode compartment was in some cases continuously supplied with air by means of a small pump, therefore, the cell was run under aerobic conditions. However, in other cases, Ar gas was supplied through the cathode compartment, in order to produce hydrogen under anaerobic conditions and carry it to a gas chromatograph (GC) for detection. Exciting radiation was generated by a homemade source employing black light tubes, as in the case of the PC operation.

Measurements

The intensity of radiation at the position of the catalyst was measured with an Oriel Radiant Power Meter. Electrical measurements were made with a Keithley 196 multimeter. Detection of hydrogen was made online by using an SRI 8610C GC 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 GC 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 GC peaks. AFM images were obtained with a Digital Instruments microscope in the tapping mode.

RESULTS AND DISCUSSION

Waste materials, which could be photodegraded with the intention to produce chemical energy (e.g., hydrogen) or electricity, are of a large variety of origin and chemical composition [21,26,27]. It is obvious that most hydrogen could be generated by decomposition of alcohols, polyols, and sugars. Most of the works done so far have shown that small chain-length alcohols yield high quantity of hydrogen by PC treatment [7,13,14,23,28]. Thus, it is common practice to employ methanol or ethanol as target substance to study such a PC operation. In the following subsection, we present some results obtained with a 50–50 vol % ethanol–water mixture, which, as already said, approximately corresponds to a 1:3 molar ratio, as in reaction 8.

Hydrogen production by decomposition of ethanol during a PC operation

A reactor, like the one described in the Experimental section, filled with a water–ethanol mixture and containing a metal/TiO_2 photocatalyst deposited on glass substrates can produce hydrogen under UVA radiation. Black light tubes were used for this purpose. Figure 2 shows hydrogen evolution under optimized conditions [23] obtained by various metal/TiO_2 photocatalysts. A large variety of metals have been employed but Pt/TiO_2 photocatalyst once more [13] gave the highest hydrogen yield followed by Pd/TiO_2. It should be emphasized at this point that in the absence of any deposited metal, hydrogen pro-

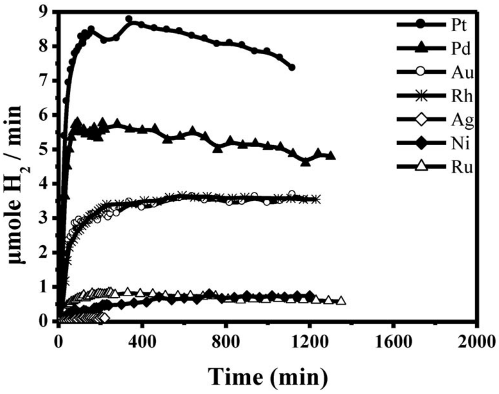

Fig. 2 Hydrogen evolution rate from a water–ethanol mixture as a function of time under PC operation in the presence of various metal/TiO_2 photocatalysts.

duction was negligible. Experiments were also run using a Pt/TiO_2 photocatalyst with the reactor filled exclusively with water, in the absence of any additive. No hydrogen was detected in that case, indicating that PC water splitting was negligible.

Hydrogen and electricity generation during a PEC operation

Alcohols and polyols as well as other potential waste materials have been treated in a PEC operation using the cell described in the Experimental section. As already discussed, hydrogen production is obtained in the cathode compartment [20] under unaerobic conditions (i.e., in the absence of oxygen) if electrons flow in the external circuit from the anode to the cathode. Current flow and hydrogen evolution should then go in parallel. This was indeed observed, as can be seen in Fig. 3. Hydrogen production was smaller in the case of PEC operation, compared to PC operation, but as it is understood, the cell geometric characteristics influence the internal resistance, hence the current intensity and the quantity of hydrogen produced. The data of Fig. 3 were obtained with a 20 vol % water–ethanol mixture introduced in the anode compartment. Table 1 lists currents obtained during PEC treatment of a few organic substances. Even though ethanol and glycerol gave the highest currents and the highest hydrogen production rates, other substances, some of them potential pollutants, gave substantial currents as well.

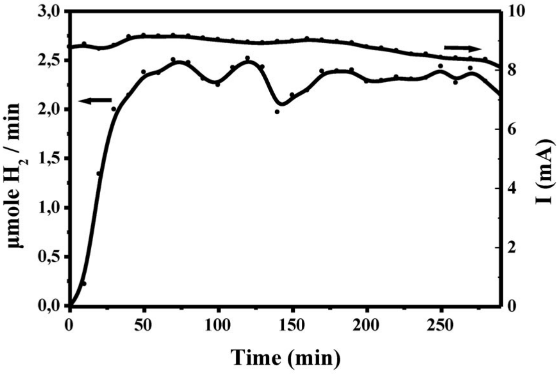

Fig. 3 Current intensity (upper curve) and hydrogen production rate (lower curve) in a two-compartment PEC cell containing 1.0 mol l^{-1} NaOH + 20 vol %. EtOH in the anode compartment and 1.0 mol l^{-1} H_2SO_4 in the cathode compartment.

Table 1 shows that in the absence of any additive, i.e., when only water and electrolyte are present, the current was the smallest of all. This clearly shows the importance of the presence of a sacrificial agent (i.e., a photodegradable substance) to carry out the process. Therefore, the proposed procedure is very promising for actual applications.

Table 1 Maximum short-circuit current values under PEC operation and UVA (black light) illumination for various reactants in the anode compartment. The anode compartment also contained 1.0 mol l^{-1} aqueous NaOH and the cathode compartment contained 1.0 mol l^{-1} aqueous H_2SO_4.

Reactant and its concentration	I_{sc} (mA)
No additive	1.1
EtOH (20 vol %)	10.3
Glycerol (20 vol %)	11.2
Ammonia (1 vol %)[a]	4.4
Triton X-100 (2 vol %)[b]	1.9
SDS[c] (0.033 mol l^{-1})	4.9

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

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

[c] An ionic surfactant: sodium dodecylsulfate.

CONCLUSIONS

Hydrogen can be produced by PC processes involving metal/TiO_2 photocatalysts. Among several metals tried, Pt/TiO_2 and Pd/TiO_2 photocatalysts gave the highest hydrogen production rates. TiO_2 films have been deposited on glass slides or transparent conductive SnO_2:F electrodes by using commercial Degussa P25 mixed with organic dispersion agents. Both hydrogen and electricity can be produced by PEC processes where a variety of chemical species can be photodegraded. The exciting radiation used in the present work was black light UVA radiation. However, the radiance levels were very low, comparably smaller than the UVA portion of solar radiation. Therefore, solar light could be employed to carry out the above processes.

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