

Photoelectrochemistry on TiO₂/Ti anodes as a tool to increase the knowledge about some photo-oxidation mechanisms in CH₃CN

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Through current efficiency measurements, obtained from the photoelectrochemical oxidation at TiO₂ (rutile)/Ti anodes, further mechanistic information has been obtained regarding the TiO₂ photosensitized oxidation of benzylic alcohols, ethers and 1,2-diols in CH₃CN. In deaerated medium, two electrons are captured by the semiconductor from all the considered substrates (one from the substrate, the second from the intermediate benzylic radical). In contrast, in aerated CH₃CN, the number of TiO₂-captured electrons can be reduced to one because, depending on its oxidizability, the benzylic radical can be competitively captured by oxygen. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: TiO₂; photoelectrochemistry; current efficiency; oxidation; radical cation

INTRODUCTION

Semiconductors, such as TiO₂, can sensitize the photo-oxidative degradation of organic pollutants in waste water. Generally, TiO₂ is used as a dispersed powder.^[1] Alternatively, in the photoelectrochemical technology, a film of semiconductor supported on Ti, such as the anode of an electrolytic cell, can be used.^[2] This technology is more complex but has the following advantages: (i) the semiconductor is immobilized at the electrode surface, (ii) the process efficiency can be improved because the anode, when polarized, reduces the rate of the (unproductive) recombination of the hole, (TiO₂)_{h+}, with the photogenerated electron and (iii) the anodic and cathodic reactions occur in physically separated compartments (therefore, the corresponding intermediates do not interact).

On principle, the photoelectrochemical technology should allow an experimentally observed electrical parameter, as the current efficiency (c.e.), to be used to acquire mechanistic information relative to previously investigated oxidative processes; in particular, the kinetically significant steps of the primary oxidation products and of the reaction stoichiometry (the number of electrons exchanged per molecule of formed product) can be confirmed. The c.e. can be defined as the amount of current passed (f) in relation to the number of electrons exchanged per molecule of the formed product (n) and to the product amount (m moles), provided the quantitative material balance is observed. From Eqn (1), the corrected n value is that giving a quantitative c.e. (100 ± 20%).

$$\text{c.e.} = \left(\frac{n \times m}{f} \right) \times 100 \quad (1)$$

Generally, when m_i moles of different i products are formed with different involved electrons (n_i), Eqn (2) can be considered

$$\text{c.e.} = \left[\sum_i \frac{n_i \times m_i}{f} \right] \times 100 \quad (2)$$

In this way, after all the m_i and f values are determined, a suitable combination of all the n_i values that corresponds to a quantitative c.e. can be obtained.

The organic solvent considered in this paper, CH₃CN, does not significantly compete, in contrast to water, with the substrate oxidation; therefore, whereas c.e. is always << 100% in water, a quantitative c.e. can be observed in CH₃CN, making the process more useful for mechanistic purposes.

In this context, recently, we have obtained mechanistic information on the TiO₂ sensitized photo-oxidation of some benzylic derivatives by the photoelectrochemical technique with TiO₂/Ti anodes in CH₃CN.^[3] This information could be useful for

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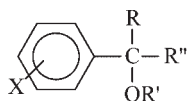
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applicative purposes because we have observed that, at least with respect to the primary oxidation steps of these substrates, the mechanism should be the same as in the aqueous medium.^[4]

In this paper, we report the data of c.e. obtained in the photoelectrochemical oxidation of other benzylic substrates (alcohol **1**, ethers **2a–2b** and 1,2-diols **3a–3f**).



	X	R	R'	R''
1	4-CH ₃ O	CH ₃	H	H
2a	4-CH ₃ O	H	CH ₃	H
2b	4-CH ₃ O	CH ₃	CH ₃	H
3a	H	H	H	CH ₂ OH
3b	H	CH ₃	H	CH ₂ OH
3c	H	H	H	PhCHOH
3d	4-CH ₃ O	H	H	4-CH ₃ OPhCHOH
3e	3-CH ₃ O	H	H	3-CH ₃ OPhCHOH
3f	4-CF ₃	H	H	4-CF ₃ PhCHOH

These results verify and complete the previously suggested mechanisms of the TiO₂ sensitized photo-oxidation of the above substrates,^[5] that is determining: (i) the involvement of an electron transfer to the benzylic radical intermediate within the initial steps, (ii) if, in deaerated medium (under N₂ bubbling, indicated as 'X₂'), a second electron transfer is operative in the steps from the benzylic radical intermediate to the final product and (iii) if, in aerated medium (atmospheric O₂, indicated as 'O₂'), the radical intermediate is trapped by oxygen and/or is oxidized to the corresponding cation.

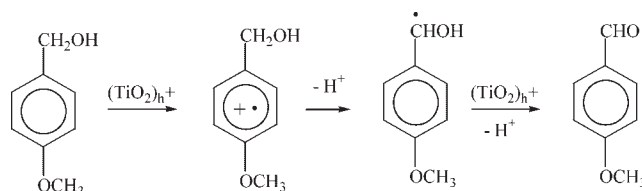
It must be observed that the confirmed ET mechanisms for **1**, **2a** and **2b** in this heterogeneous medium^[5b,e,f] are very similar to those reported in ET homogeneous oxidations.^[6] On the contrary we showed that, owing to adsorption phenomena, the electron is extracted from oxygen of one OH group of diols **3a–3f**^[5a] and not from the aromatic ring, as happens in homogeneous oxidations;^[7] consequently, this phenomenon involves a different C—C fragmentation path of the cation radical.^[5a]

Finally, it should be noted that the photoelectrochemical technology previously reported by us^[3a] has been improved in this paper by preparing a more efficient TiO₂ (rutile) film at the Ti surface. In this way, it has been possible to extend the study to the photoelectrochemical oxidation of substrates (**1**, **2a** and **2b**) that did not significantly react under the previous experimental conditions.

RESULTS AND DISCUSSION

Improvement of the photoelectrochemical technology

As previously reported,^[3a] the photoelectrochemical oxidation of 4-methoxybenzyl alcohol in CH₃CN is considered as the reference reaction to evaluate, through current density measurements, the photocatalytic efficiency of TiO₂/Ti anodes, in which the TiO₂ (rutile) film is prepared by thermal treatment of a Ti plate under different experimental conditions.



Scheme 1.

Regarding the known mechanistic aspects of the above reaction,^[3,5g] (TiO₂)_h⁺ captures an electron from the alcohol to give the corresponding cation radical; this intermediate, after C—H deprotonation,^[5c,5f,6] gives an α -hydroxy-4-methoxybenzyl radical that, after oxidation, finally leads to 4-methoxybenzaldehyde (Scheme 1).

At the same time, the electron in the conduction band, which is transferred through the external circuit, is captured by Li⁺ (furnished by LiClO₄ as the support electrolyte) to give Li (as a metallic layer deposited on the Pt cathode).

Previously, we observed that, after the same time of thermal treatment (2 h), 700 °C is the temperature at which the highest current density is measured.^[3a]

In this paper, we report that the current density increases (at this temperature) on going from 2 h (0.15 mA/cm²) to 4 h (0.23 mA/cm²) of thermal treatment. This behaviour can be justified on the basis of the increased film thickness from 1.8 μ m to 2.3 μ m (Fig. 1); this phenomenon can be attributed to a better (TiO₂)_h⁺/(TiO₂)_e[−] separation (larger space charge layer) as the TiO₂ film becomes thicker.

Photoelectrochemical oxidation of 1-(4-methoxyphenyl) ethanol (**1**)

With the more efficient photoanode (700 °C of thermal treatment for 4 h) it has been possible to perform the photo-oxidation of alcohol **1** on TiO₂/Ti. As previously observed in the photo-oxidation sensitized by TiO₂ as powder^[5d] and as colloid,^[5f] the reaction product is the corresponding acetophenone, in both

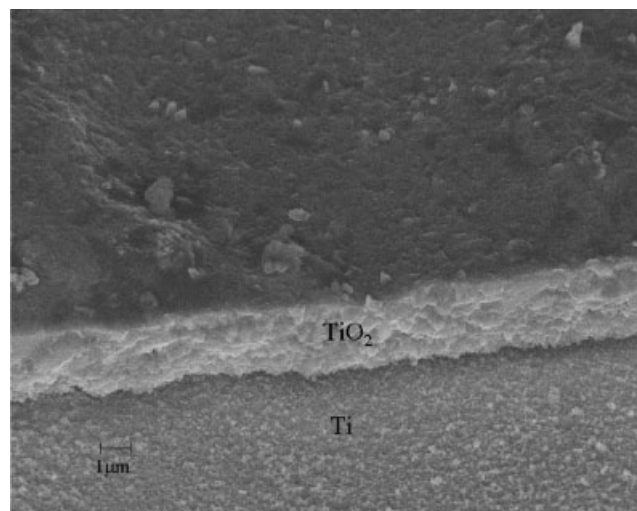


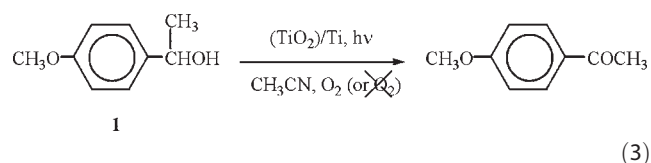
Figure 1. Field emission scanning electron microscopy (FESEM) of cross section of the TiO₂ film after 4 h of thermal treatment at 700 °C

Table 1. Current efficiency and conversion in 4-methoxyacetophenone for the photoelectrochemical oxidation of 1-(4-methoxyphenyl) ethanol (**1**) on TiO₂ (rutile)/Ti in CH₃CN

Substrate	Unreacted substrate (%)	4-Methoxy acetophenone (%)	Current efficiency (%) ^a	<i>n</i> ^b
1 ($\times$)	60	30	110	2
1 (O ₂)	58	30	85	2

^a Error = ± 20 .
^b Electrons exchanged per molecule of formed acetophenone.

aerated and deaerated medium (Eqn (3)).



As reported in Table 1, material recovery is *ca.* 90%.

On the basis of the previous results obtained from competitive and quantum yield measurements^[5f] and from the c.e. determinations with TiO₂ photoanode in an electrolytic cell (this work), our definitive hypothesis about the mechanism, valid for both the deaerated and aerated medium, is reported in Scheme 2.

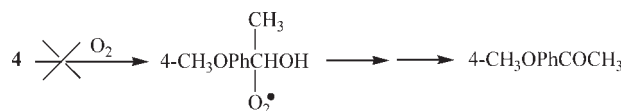
In deaerated CH₃CN, the c.e. is nearly quantitative considering two electrons involved per molecule of formed product (4-methoxyacetophenone) (Table 1), one electron is captured by (TiO₂)_h⁺ from the substrate and the second is captured from the benzylic radical by a second hole (or by the conduction band of TiO₂, if the phenomenon of 'current doubling'^[8] is involved).

In aerated medium, the results obtained in the photoelectrochemical experiments, that is a quantitative c.e. for two electrons exchanged (Table 1), exclude a competitive path (Scheme 3) that involves the capture of the benzylic radical intermediate by oxygen where a second hole does not participate. This exclusion can be explained on the basis of the low oxidation potential of the benzylic radical, due to the presence of an α -OH group (the oxidation to cation is favoured).^[9]

As a confirmation, the c.e. measurements performed in the photoelectrochemical reaction of 4-methoxybenzyltrimethylsilane to 4-methoxybenzaldehyde^[3b] showed that the corresponding benzylic radical intermediate (less oxidizable due to the α -OH group absence) is captured by oxygen instead of being oxidized to cation.

Photoelectrochemical oxidation of benzylic ethers (2)

As previously reported in the photo-oxidation sensitized by TiO₂ as powder,^[5b,d] the photoelectrochemical oxidation of 4-methoxybenzyl

**Scheme 3.**

methyl ethers **2a** and **2b** gives (Scheme 4) the corresponding carbonyl compound (**C**) in deaerated CH₃CN accompanied, in aerated medium, by methyl 4-methoxybenzoate (**E**). As reported in Table 2, the material recovery is quantitative ($\geq 90\%$).

On the basis of the previous results obtained with TiO₂ powder^[5b,d] and from c.e. determinations, our complete mechanistic suggestion is reported in Scheme 5, both in deaerated and in aerated medium.

In the first medium (aldehyde formation from **2a**) the c.e. (Table 2) is nearly quantitative considering that two electrons are involved per molecule of formed product that is, the first electron is captured from the substrate by (TiO₂)_h⁺ and a second electron is captured from the benzylic radical **5** (via **a** in Scheme 5).

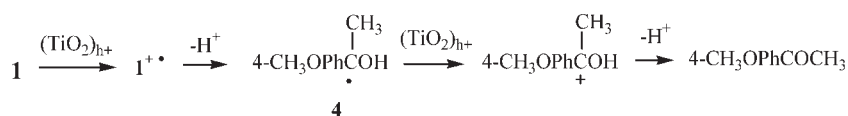
In aerated medium, the current efficiency is nearly quantitative considering that two electrons per molecule of carbonyl compound (as observed above in deaerated CH₃CN) and one electron for the methyl benzoate formation are necessary (Table 2). According to Scheme 5, the benzylic radical can give the carbonylic compound through the oxidation of the free radical (via **a**) and the ester through the competitive capture by oxygen (via **b**).

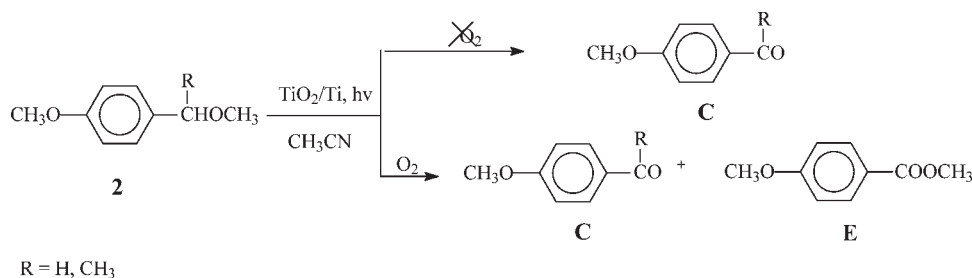
It must be observed that, in aerated CH₃CN, the radical **5** competitively undergoes both oxidation to cation and capture by oxygen, whereas the radical **4** (from alcohol **1**) is only oxidized. Therefore, under the experimental conditions of this work, the oxidizability order should be 4-CH₃OPhC'(R)OCH₃ < 4-CH₃OPhC'(R)OH. Accordingly to this behaviour, the reported half-wave oxidation potentials of two structurally related radicals as PhC'(CH₃)OCH₃ and PhC'(CH₃)OH are -0.11 and -0.24 V (vs. SCE), respectively.^[9]

Photoelectrochemical oxidation of 1,2-diols (3)

In a previous work,^[5a] we have reported the reaction mechanism of photo-oxidation of diols **3a-f**, sensitized by TiO₂ (as powder or colloid) in aerated CH₃CN, to give carbonylic compounds as C α -C β fragmentation products. On the basis of the reaction products, adsorption equilibrium constants, competitive kinetic experiments and quantum yields, the mechanism in Scheme 6 has been suggested.

The photoelectrochemical reaction of the considered diols has been performed (**3a-f**), both in deaerated and in aerated CH₃CN, always obtaining the same products observed in the presence of TiO₂ as powder or colloid in aerated medium. This study has confirmed the steps reported in Scheme 6 and has allowed the

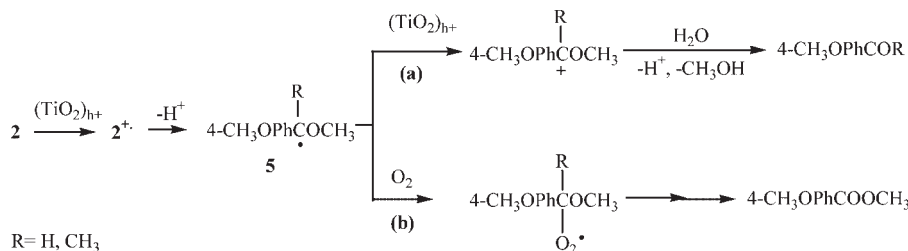
**Scheme 2.**



Scheme 4.

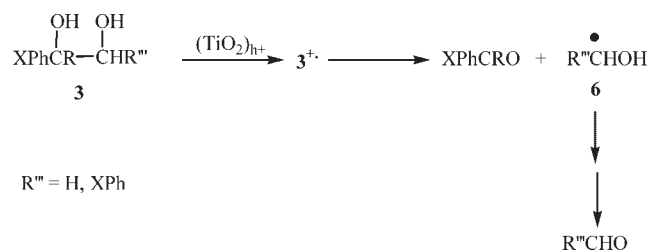
Table 2. Product yield and current efficiency in the photoelectrochemical oxidation of 4-methoxybenzyl methyl ethers **2a** and **2b** on TiO_2 (rutile)/Ti in CH_3CN

Substrate	R	Unreacted substrate (%)	Products (%)		Current efficiency (%) ^a	n_{C}^{b}	n_{E}^{c}
			C	E			
2a (O_2)	H	65	25	—	110	2	—
2a (O_2)	H	78	13	6	105	2	1
2b (O_2)	CH_3	76	9	6	110	2	1

^a Error = ± 20 .^b Electrons exchanged per molecule of carbonyl compound.^c Electrons exchanged per molecule of methyl benzoate.

Scheme 5.

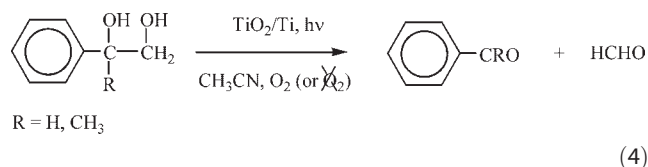
paths from the radical **6** to the corresponding carbonyl compound to be defined.



Scheme 6.

In particular, 1,2-diols **3a** and **3b** give $\text{C}_\alpha\text{—C}_\beta$ fragmentation products, the corresponding benzaldehyde or acetophenone, respectively, that were always accompanied by formaldehyde

(Eqn (4)).



As reported in Table 3, the material recovery (substrate + PhCRO) is nearly quantitative ($\geq 90\%$).

The c.e. determinations in Table 3 for the deaerated reactions of the diols **3a** and **3b** are quantitative for two electrons exchanged per molecule of aromatic carbonyl compound. Therefore, the first electron is captured from the substrate by the hole and a second electron must be involved for the oxidation of the α -hydroxyl radical intermediate **6** with $\text{R}''' = \text{H}$ (Scheme 6 and via **a** in Scheme 7).

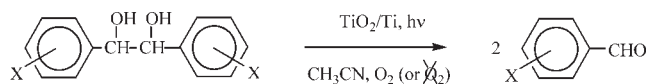
Table 3. Product yield and current efficiency in the photo-electrochemical oxidation on TiO₂ (rutile)/Ti of 1,2-diols **3a,b** in CH₃CN

Substrate	PhCRO (%)	Unreacted substrate (%)	Current efficiency (%) ^a	n ^b
3a (O_2)	18	78	81	2
3b (O_2)	26	60	93	2
3a (O_2)	27	80	80	1
3b (O_2)	20	70	95	1

^a Error = ± 20 .^b Electrons exchanged per molecule of aromatic carbonyl compound.

In contrast, the c.e. determined in aerated medium for the diols **3a** and **3b** (Table 3) are quantitative considering the exchange of only one electron. This means that one hole is involved in catching the electron from the substrate to give the cation radical, whereas the hydroxymethyl radical reacts with oxygen (Scheme 7, via **b**) and is not oxidized by the semiconductor (via **a**).

Regarding 1,2-diaryl-1,2-ethanediols **3c–f**, the corresponding benzaldehyde was obtained, both in deaerated and in aerated medium (Eqn (5)).

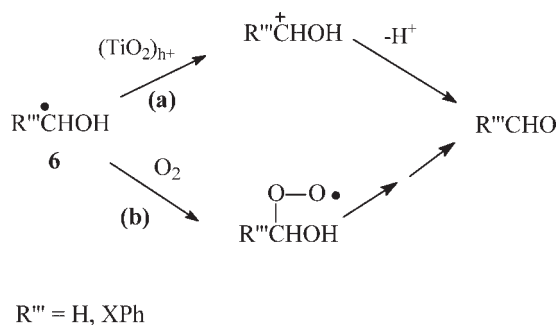
X = H, 4-CH₃O, 3-CH₃O, 4-CF₃

(5)

In all the photoelectrochemical experiments the material recovery was quantitative considering two moles of carbonyl product per mole of reacted substrate (Table 4).

As observed for **3a** and **3b**, the c.e. determinations in deaerated medium showed that two electrons are involved in the reaction. This is in line with Scheme 6 and via **a** in Scheme 7 (where the corresponding benzaldehyde is formed through the oxidation of the α -hydroxybenzylic radical **6**, with R''' = Ph, 4-CH₃O, 3-CH₃O, and 4-CF₃Ph, to the corresponding cation).

The c.e. measurements in the photo-oxidation of the diols **3c–e** in aerated medium showed that two electrons are again involved (Table 4); the corresponding ring-substituted benzylic radicals **6** (R''' = Ph, 4-CH₃O, 3-CH₃O) are oxidized to the

**Scheme 7.****Table 4.** Product yield and current efficiency in the photo-electrochemical oxidation of 1,2-diaryl-1,2-ethanediols **3c–f** on TiO₂ (rutile)/Ti in CH₃CN

Substrate	XPhCHO (%) ^a	Unreacted substrate (%)	Current efficiency (%) ^b	n ^c
3c (O_2)	28	70	90	2
3d (O_2)	13	75	82	2
3e (O_2)	8	94	94	2
3f (O_2)	20	71	85	2
3c (O_2)	15	70	83	2
3d (O_2)	16	73	91	2
3e (O_2)	21	71	85	2
3f (O_2)	16	75	70 (140)	2 (1)

^a According to the XPhCHO/substrate stoichiometry (2/1) the reported yield is half of the measured one.^b Error = ± 20 .^c Exchanged electrons with respect to the half of molecules of benzaldehyde.

corresponding cation (Scheme 7, via **a**) instead of being captured by oxygen (via **b**).

In this aerated medium, the current yield for **3f** is not quantitative when either two electrons (c.e. = 140%) or one are involved (70%). This result suggests that, in the case of benzylic radical **6** with R''' = 4-CF₃Ph, the oxidation to the corresponding cation by the hole (path **a** in Scheme 7) and the capture by oxygen (path **b**) are in competition. The different behaviour of the radicals **6** from **3c–e** with respect to that from **3f** can be ascribed to the lower oxidizability of the latter radical due to the presence of the electron-withdrawing ring substituent.

Finally, the c.e. data show that it is possible to evaluate, in these experimental conditions, the relative oxidizability of different α -hydroxy radicals **6** derived from diols **3a–f** that is: $\text{CH}_2\text{OH} < \text{CH}(4\text{-CF}_3\text{Ph})\text{OH} < \text{CH}(\text{XPh})\text{OH}$ (X = 4-OCH₃, 3-OCH₃, H).

EXPERIMENTAL

¹H-NMR spectra were run on a Bruker AC 200 (200 MHz) spectrometer, with solutions in CDCl₃ with TMS as internal standard. GC-MS analyses were performed on a Hewlett Packard 6890A gas-chromatograph (HP-Innovax capillary column, 15 m) coupled with a MSD-HP 5973 mass selective detector (70 eV). GC analyses were carried out on a HP Agilent Technologies 6850 gas-chromatograph using a HP capillary column, 30 m. HPLC analyses were performed with a liquid chromatograph HP 1100.

Starting materials

Titanium plates (CpG2 from Titania S.p.A. Terni Italy 2.5 $\times$ 8.0 cm, thickness = 0.5 mm containing N < 0.007%, C < 0.004%, H < 0.012%, Fe < 0.024% and O < 0.09%) were cleaned in acetone, then etched for 30 s in dilute Kroll's acid (4% w/w HF, 30% w/w HCl), rinsed in distilled water and then in acetone.^[3a] H₂SO₄, LiClO₄, Na₂CO₃ and CH₃CN (99.9%, HPLC grade, containing

0.02% water from Karl Fisher analysis) were analytical grade commercial products. 1(4-Methoxyphenyl)ethanol, 1-phenyl-1,2-ethanediol, 2-phenyl-1,2-propanediol, 1,2-diphenyl-1,2-ethanediol were commercial samples. 4-Methoxybenzyl methyl ether^[10], 4-methoxy- α -methylbenzyl methyl ether^[11], 1,2-bis(3-methoxyphenyl)-1,2-ethanediol^[12], 1,2-bis(4-methoxyphenyl)-1,2-ethanediol^[12], 1,2-bis[4-(trifluoromethyl)phenyl]-1,2-ethanediol^[13] were prepared and characterized as described in the literature.

Preparation and characterization of TiO₂/Ti electrodes

The titanium plates were subjected to constant current (25 mA cm⁻²) mild anodic oxidation (6443B DC HP power supply) in 1M H₂SO₄ using Pt (2 cm²) as the cathode up to 30 V (further surface cleaning) and then rinsed with distilled water. The plates were then heated in an oven at 700 °C for 2 h and 4 h.

The crystalline phase of the samples was identified by X-ray diffraction (Philips X'Pert APD diffractometer) using Cu K α radiation at Bragg angles 13.73° (rutile crystalline form).

The film thickness was determined by a LEO SUPRA 25 field emission scanning electron microscope, FESEM (Fig. 1).

Photoelectrochemical oxidation

The photoelectrochemical measurements were performed in an undivided cylindrical jacketed cell provided with Ti/TiO₂ anode (20 cm²), Pt cathode and SCE as reference connected to the AMEL potentiostat. The substrate (0.30 mmoles), LiClO₄ (7.5 mmoles) and Na₂CO₃ (4.7 mmoles) in CH₃CN (150 ml) were placed in the cell and magnetically stirred in the atmosphere (aerated medium) or under nitrogen bubbling (deaerated medium). The cell was externally irradiated by a 400 W high pressure Hg lamp (Helios Italquartz), cooled by a Pyrex water jacket ($\lambda \geq 300$ nm) positioned in front of Ti/TiO₂ electrode and the apparatus was covered by a closed aluminium cylinder. Current flowed only under irradiation and after 10–30' (depending of the substrate) it was practically constant. After 15–20 coulombs passed, the mixture was concentrated at room temperature, poured into a double volume of water and repeatedly extracted with diethyl ether. The organic layer was washed with NaCl-saturated water, dried on Na₂SO₄ and concentrated. The crude product was analysed by ¹H-NMR, HPLC and GC in the presence of suitable internal standards, and by GCMS.

Reaction product analysis

The reaction products were identified directly from the crude by comparison of ¹H-NMR and GC analysis data with those of the commercial samples (acetophenone, 4-methoxyacetophenone, methyl 4-methoxybenzoate, 4-methoxybenzaldehyde, 3-methoxybenzaldehyde, benzaldehyde and 4-trifluoromethylbenzaldehyde).

Formaldehyde was recognized as dimedone adduct [MS *m/z* (rel intensity) 292 M⁺, 191, 165(100), 124, 97, 83, 69, 55].

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