



Photoelectrocatalytic selective oxidation of 4-methoxybenzyl alcohol in water by TiO₂ supported on titanium anodes

Levent Özcan^{a,*}, Sedat Yurdakal^a, Vincenzo Augugliaro^b, Vittorio Loddo^b, Simonetta Palmas^c, Giovanni Palmisano^b, Leonardo Palmisano^{b,**}

^a Kimya Bölümü, Fen-Edebiyat Fakültesi, Afyon Kocatepe Üniversitesi, Ahmet Necdet Sezer Kampüsü, 03200 Afyon, Turkey

^b "Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'Informazione, e Modelli Matematici (DEIM), University of Palermo, Viale delle Scienze, 90128 Palermo, Italy

^c Dipartimento di Ingegneria Meccanica, Chimica e dei Materiali, Università degli Studi di Cagliari, Via Marengo 2, 09123 Cagliari, Italy

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ABSTRACT

The photoelectrocatalytic partial oxidation of 4-methoxybenzyl alcohol in aqueous solution irradiated by near-UV light was carried out in a three-electrode batch reactor. TiO₂ films were either deposited by dip-coating of a TiO₂ sol onto a Ti foil and subsequent calcination or generated on Ti plates by thermal oxidation in air at 400–700 °C. The effects of the anode preparation method and bias potential values on conversion and selectivity to the corresponding aldehyde were investigated. The photoelectrocatalytic results were compared with the photocatalytic and electrocatalytic ones. The results indicated that no reaction occurred during the electrocatalytic experiments, whereas the photocatalytic reactivity was positively influenced by the application of a small bias (0.75 V vs. saturated calomel electrode). By applying the previous bias the highest initial degradation rates, r_0 , and selectivities to 4-methoxybenzaldehyde, S , were obtained in photoelectrocatalytic experiments by using Ti plate calcined at 500 °C ($r_0 = 0.1507 \text{ mM h}^{-1}$, $S = 85\%$) or TiO₂ film prepared by dip-coating and calcined at 700 °C ($r_0 = 0.1339 \text{ mM h}^{-1}$, $S = 90\%$). In order to investigate the influence of the substituent groups on reactivity and selectivity, photoelectrocatalytic runs with benzyl alcohol, 2-methoxybenzyl alcohol, 3-methoxybenzyl alcohol, 2,4-dimethoxybenzyl alcohol, 2,3,4-trimethoxybenzyl alcohol, 4-nitrobenzyl alcohol and 4-hydroxybenzyl alcohol have been performed. The selectivity and reactivity values increased by increasing the electron-donor properties of the substituent groups. This positive effect, however, was obtained only if the electron-donor group is in para or ortho position with respect to the alcoholic group.

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1. Introduction

The selective oxidation of alcohols is an important reaction in organic chemistry. The resulting products, aldehydes and ketones, are extensively used as precursors and intermediates in pharmaceutical and fine-chemical industries [1–3]. Moreover they are particularly useful for the production of flavours, fragrances, and biologically active compounds. In the industrial practice aldehydes are synthesized from the corresponding alcohols in liquid phase in the presence of Co, Ce and Mn salts in acidic medium, through routes that are not atom efficient. The application of these methods, however, causes severe environmental problems owing to the generation of dangerous wastes and of undesirable byproducts [4–8].

From the standpoint of green and sustainable chemistry, the development of cleaner catalytic oxidation systems is desirable. Obviously, the choice of the "green" oxidant(s) determines the environmental impact of an oxidation process to a significant extent. In general, molecular oxygen is the ideal oxidant, and many processes have been developed under relatively mild reaction conditions with oxygen or air in the presence of transition-metal complexes as the catalysts [9–11].

The photocatalytic method has been successfully used for performing the partial oxidation of aromatic alcohols in aqueous suspensions of commercial and home-prepared anatase (HPA) [12–14]. Near-UV irradiated suspensions of P25-TiO₂ performed the partial oxidation of different alcohols (geraniol, citronellol, trans-2-penten-1-ol and 1-pentanol, dissolved in CH₃CN–H₂O mixture) with good selectivity (>70%) [15]. The selective photocatalytic oxidation of benzyl alcohol to benzaldehyde has been carried out in solvent-free system by using TiO₂ and Ir/TiO₂ photocatalysts [16] or in aqueous solution, under acidic conditions, through the TiO₂/Cu(II)/solar UV photocatalytic system [17].

* Corresponding author. Tel.: +90 272 228 1339/230; fax: +90 272 228 1235.

** Corresponding author. Fax: +39 09123860841.

E-mail addresses: leventozcan@aku.edu.tr (L. Özcan), leonardo.palmisano@unipa.it (L. Palmisano).

Visible-light-driven partial photocatalytic oxidation of alcohols was achieved over Pt nanoparticles supported on anatase TiO₂ [18], single-crystalline rutile TiO₂ nanorods [19] and over pure TiO₂ with selectivity of 99% [20]. It has been found that the addition of Brønsted acids [21] adsorbed onto TiO₂ dramatically accelerated the photocatalytic oxidation of alcohols without any loss of selectivity.

The textural, bulk and surface properties of HPA and commercial catalysts have been investigated [13,14] in order to explain their different performance. In particular ATR-FTIR studies indicated that the low crystallinity and the high surface density of hydroxyl groups of HPA catalysts may justify their higher selectivity with respect to the commercial ones. Both these properties induce an enhanced hydrophilicity of the TiO₂ surface, thus promoting desorption of the photo-produced aldehyde so that its further oxidation is hindered. However, the HPA catalysts showed lower photo-catalytic activity than most of the commercial samples.

The activity of a photocatalyst is mainly affected by the quantum efficiency that depends on the electron–hole recombination rate. The key point to improve the photocatalytic activity of TiO₂ is therefore to enhance the separation of electron–hole pairs inhibiting their recombination. A method for achieving that goal is to modify the TiO₂ intrinsic properties [22–24] by doping it with metal, non metal and ions or by improving the geometrical properties of the nanostructure. An alternative method for hindering the photo-generated pairs recombination consists in applying an external potential bias [25–31] to a thin TiO₂ layer deposited on a conductive support. The photoelectrocatalytic (PEC) method, i.e. combination of the heterogeneous photocatalysis (PC) with the electrocatalytic (EC) one, has shown to be an effective tool in order to improve the performance of mineralization reactions [32]. However, very few examples of synthetic reactions carried out by the PEC method are reported in the literature; in most cases the synthetic reactions were carried out in organic solvents [33,34].

Several methods can be used to prepare TiO₂ electrodes for PEC experiments. The anodizing method, widely used by several authors [35–38], allows to prepare Ti/TiO₂ electrodes by anodizing titanium metal in acidic [39–41] or alkaline [42] solution. The sol–gel method has been also used by many authors [31,43,44]; the Ti/TiO₂ electrode was prepared by coating a layer of TiO₂ sol onto the titanium substrate via repetitive heat treatments. The chemical deposition method is also able to prepare photoanodes with TiO₂ thin films. Sun et al. [45] deposited a 500 nm thick titanium film on nickel plates by means of arc ion plating. A TiO₂ film was deposited on pre-treated fibres coated with SnO₂:Sb by the electrophoretic deposition method [46].

Rutile and anatase TiO₂ films can be grown on Ti plates by thermal oxidation [33,47] in air or oxygen. A very important step in the preparation of the oxide layers, especially when applying short oxidation times, is the pre-treatment consisting in cleaning the Ti support with ethanol and etching it in acid prior to thermal oxidation.

In this work the PEC method has been used for performing the partial oxidation of 4-methoxybenzyl alcohol (4-MBA) to the corresponding aldehyde (p-anisaldehyde, PAA) in aqueous electrolyte. PAA is a compound used in sweet blossom and flavour compositions for confectioneries and beverages; moreover it is employed as an intermediate in the synthesis of pharmaceuticals (especially antihistamines), agrochemicals, dyes and plastic additives. In order to investigate the influence of the substituent groups on reactivity and selectivity, other benzyl alcohols were also tested. The 4-MBA oxidation to PAA has been recently carried out [27] by photosensitized electrochemical oxidation at a TiO₂/Ti anode obtained by constant current mild anodic oxidation of titanium plate and mesh and subsequent heating in air at 700 °C. By following the green chemistry criteria different cathodes, cell geometries,

media, supporting electrolytes and electrochemical methods were tested and optimized. In the best experimental conditions 4-MBA was quantitatively converted to PAA with a 23% conversion after 14 h at constant current with 40–50% of current efficiency.

In our case the photoanodes, contained in a three-electrode photoelectroreactor and irradiated by near-UV light, were rutile and anatase TiO₂ films. The films were either deposited by dip-coating of a TiO₂ sol onto a Ti plate or generated on Ti plate by thermal oxidation in air at temperature in the 400–700 °C range. The effects of the anode preparation method and of bias potential values on 4-MBA conversion and selectivity to PAA were investigated. The results obtained with the PEC method have been compared with those obtained with the PC and EC ones.

2. Experimental

2.1. Preparation and characterization of dip-coated and thermally oxidized anodes

- A TiO₂ precursor solution was obtained by adding drop wise under mixing 20 mL of TiCl₄ (purity >97%, Fluka) to 200 mL of deionized water contained in a 500 mL beaker put inside an ice bath. After that the beaker was sealed and the mixing was prolonged for 12 h at room temperature, eventually obtaining a clear solution. Ti foils (4.2 cm × 2.1 cm × 0.05 cm) were used as conductor supports. Ti foils were washed with water and ethanol, dried at 50 °C and finally immersed in the precursor solution at a rate of 60 mm min⁻¹. After keeping the foils inside the precursor for 2 min, they were dried at 100 °C for 5 min. This procedure was repeated from 1 to 10 times. Afterwards the foils were heated for 3 h at different temperatures in the 100–850 °C range. The obtained samples are hereafter labelled as TiO₂/Ti-X-YL where X indicates the thermal treatment temperature expressed in °C whereas Y indicates the number of dip-coated layers.
- TiO₂/Ti anodes were produced by oxidizing the surfaces of Ti foils by means of thermal treatment in air at temperatures ranging from 400 to 700 °C. The obtained samples are labelled as Ti-X where X indicates the thermal treatment temperature expressed in °C.

X-Ray diffractometry (XRD) patterns of the anodes were recorded by an Ital Structures APD 2000 powder diffractometer using the Cu K α radiation and a 2 θ scan rate of 2°/min. SEM images were obtained using a FEG microscope (Philips, Quanta 200F) operating at 20 kV.

2.2. Photoreactivity set up and procedure

The set up of the cylindrical reactor (diameter, 5 cm; height, 7 cm), used for all the experiments, is reported in Fig. 1. The irradiation source was a 500 W medium pressure mercury lamp (Helios Italquartz, Italy) externally positioned with respect to the reactor. The distance of the lamp from the anode was 7 cm. The radiation energy impinging on the TiO₂ sample had an average value of 5.0 mW cm⁻². It was measured in the wavelength range of 315–400 nm by using a radiometer Delta Ohm, DO 9721. The photocatalytic experiments have been performed at ca. 30 °C.

A magnetic stirrer set at 400 rpm guaranteed homogeneity of the aqueous solution. The initial concentration of the used substrate was 0.5 mM. The photocatalytic experiments were carried out at neutral pH (ca. 7).

Photoelectrochemical experiments were performed by using a potentiostat (CHI630B Electrochemical Workstation, CH Instruments) connected to working (anode), counter (cathode, Pt spiral

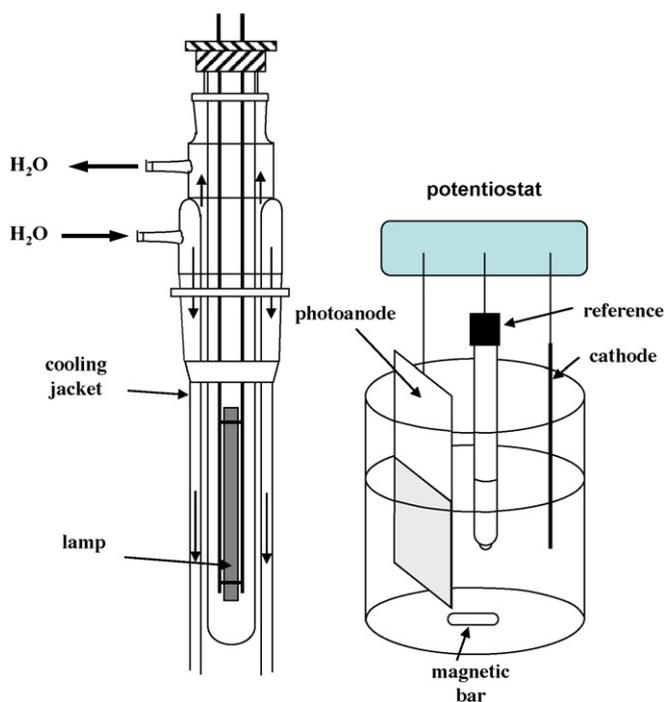


Fig. 1. Experimental set up.

wire) and reference (saturated calomel) electrodes. The reference electrode was positioned close to the anode (about 2 mm from its surface), so as to minimize the uncompensated solution resistance. Moreover, attention was paid to the position of the reference electrode in order to not affect the irradiation of the photoanode. The electrolyte was water with 50 mM Na_2SO_4 .

Before switching on the lamp, the solution was stirred for 30 min at room temperature to reach the thermodynamic equilibrium. Before and in the course of the runs the aqueous solution was in contact with the atmosphere, thus absorbing oxygen from the environment. Adsorption of the organic substrate under dark conditions was negligible. During the run, samples were withdrawn from the solution at fixed time intervals. The quantitative determination and identification of the species present in the solution was performed by means of a Beckman Coulter HPLC (System Gold 126 Solvent Module and 168 Diode Array Detector), equipped with a Dionex, 3 μm Acclaim polar advantage column (4.6 mm \times 150 mm) and working at room temperature. The eluent consisted of 20% acetonitrile and 80% 1 mM trifluoroacetic acid aqueous solution and its flow rate was 0.8 $\text{cm}^3 \text{min}^{-1}$. Retention times and UV spectra of the compounds were compared with those of standards. TOC analyses were carried out by using a 5000 A Shimadzu TOC analyser in order to evaluate the degree of mineralization. All the used chemicals were purchased from Sigma Aldrich with a purity >98.0%.

3. Results and discussion

3.1. Characterization of anodes

Figs. 2 and 3 show XRD patterns of dip-coated and thermally oxidized Ti foil samples, respectively. The allotropic crystalline phases of TiO_2 show peaks at $2\theta = 25.58^\circ$, 38.08° , 48.08° and 54.58° of anatase phase and at $2\theta = 27.5^\circ$, 36.5° , 41° , 44° , 54.1° and 56.5° of rutile one. Figs. 2 and 3, moreover, show the characteristic peaks of naked titanium at $2\theta = 34.95^\circ$, 38.25° , 40.05° and 52.90° .

Among dip-coated Ti foils (Fig. 2), only $\text{TiO}_2/\text{Ti-400-10L}$ showed pure anatase, $\text{TiO}_2/\text{Ti-550-10L}$ showed anatase–rutile phases (with anatase prevailing) whereas both $\text{TiO}_2/\text{Ti-700-10L}$ and

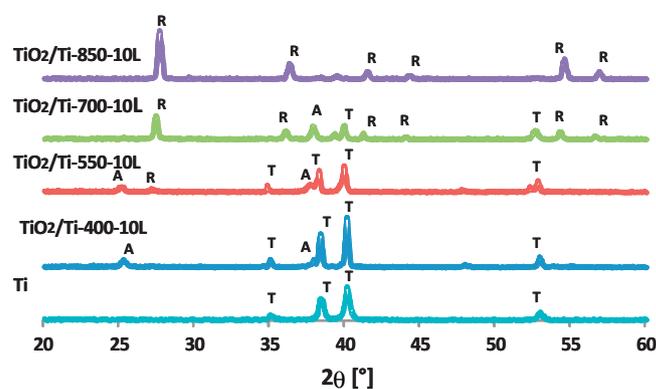


Fig. 2. XRD patterns of TiO_2 supported on Ti foil by dip-coating (A, anatase; R, rutile; T, titanium).

$\text{TiO}_2/\text{Ti-850-10L}$ showed rutile phase with traces of anatase. By increasing calcination temperature, peak intensities raised too, thus indicating an improvement of crystallinity.

Fig. 3 shows the XRD patterns of thermally oxidized Ti foils. Formation of TiO_2 was detected mainly in the rutile crystalline form. Increasing thermal treatment temperature results in better crystallization of TiO_2 . The rutile phase gets much more crystalline while anatase phase decreases by increasing the treatment temperature.

Fig. 4 shows some representative SEM images of both kinds of anodes prepared at different temperatures. It can be noticed that by increasing the temperature of the treatment a better crystallization is showed for thermally oxidized or dip-coated samples. From SEM images it is possible to approximately estimate the thickness value of the layer deposited by one dip-coating operation; this value is in the 300–1000 nm range.

3.2. Photocatalytic and photoelectrocatalytic performance of dip-coated samples

No oxidation of organic substrate was observed in the absence of TiO_2 , UV irradiation or oxygen. Bias alone was never capable to give rise to reactivity at any of the used voltage (–0.5 V to 3 V).

During the PC and PEC runs, the main products of 4-MBA oxidation were PAA and CO_2 . The absence of measurable amounts of other products was proved by HPLC analysis. The CO_2 concentration was evaluated by TOC measurements; owing to the fact that for the used experimental conditions volatile organic compounds are not produced [48], the difference between the TOC concentration values of the initial solution and that of the withdrawn sample was entirely attributed to CO_2 production. Carbon balance was carried out by adding the 4-MBA, PAA and CO_2 concentration values;

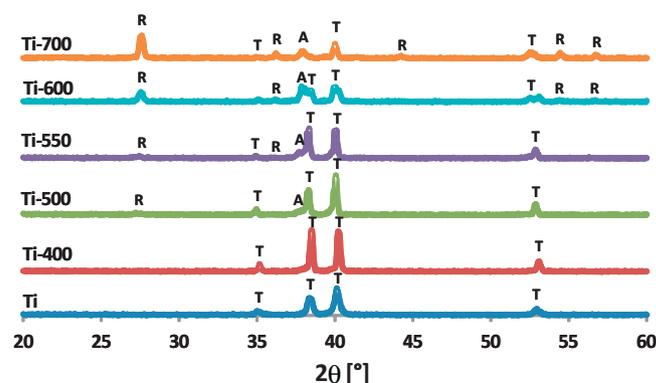


Fig. 3. XRD patterns of thermally oxidized Ti foils (A, anatase; R, rutile; T, titanium).

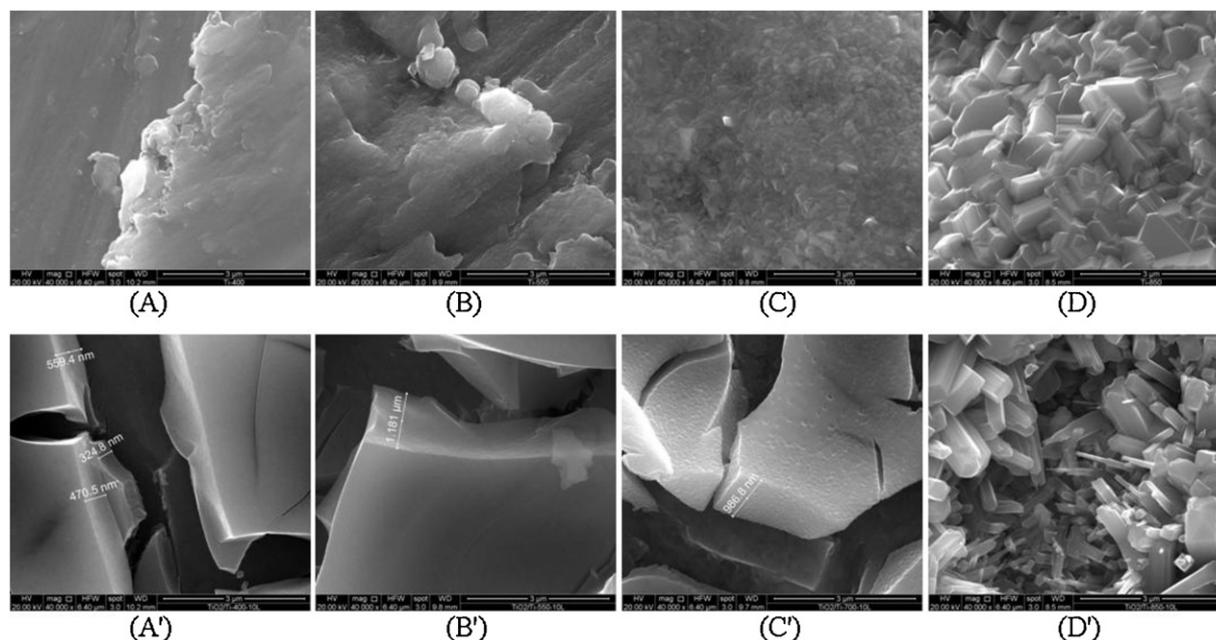


Fig. 4. SEM pictures of thermally treated and supported titanium sheets: (A) Ti-400; (A') TiO₂/Ti-400-10L; (B) Ti-550; (B') TiO₂/Ti-550-10L; (C) Ti-700; (C') TiO₂/Ti-700-10L; (D) Ti-850; (D') TiO₂/Ti-850-10L.

it was indeed satisfied at extents higher than 95% (for 25% conversion) in all the runs. Fig. 5 reports the experimental results obtained in a representative run of PEC oxidation by using TiO₂/Ti-700-1L sample with an applied bias of 0.75 V. PAA selectivity values show an almost constant value during the run. The CO₂ concentration values are quite low during the reported run showing that the predominant reaction is the 4-MBA partial oxidation to PAA. Carbon balance is satisfied for more than 98%, thus excluding the presence of relevant byproducts dissolved in water and of organic volatile species. Indeed HPLC analysis only detected peaks of alcohol and aldehyde. The parameters used for measuring the performance of the TiO₂ samples are the initial 4-MBA degradation rate, r_0 , and the selectivity to PAA, S . These parameters are reported in Table 1. The open circuit voltage (OCV) measured for each sample in the presence of irradiation in the course of the photocatalytic runs showed variation in the small range of -0.06 and $+0.03$ V.

Fig. 6 shows some examples of the amperometric tests carried out at three different samples. Data were recorded by turning light

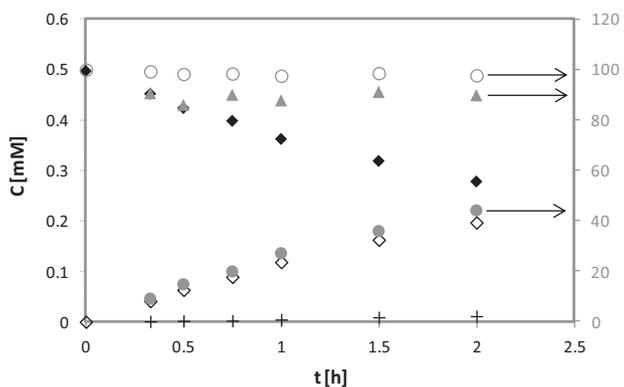


Fig. 5. Experimental results of PEC oxidation of 4-MBA with Ti-TiO₂-700-1L sample by applying a bias potential of 0.75 V. Conversion, selectivity and carbon balance values are quoted to the right ordinate axis. Symbols: concentration of (◆) 4-MBA, (○) PAA, and (+) CO₂, (●) conversion, (▲) selectivity, (○) carbon balance. CO₂ concentration values were divided by 8 for normalization.

Table 1

Results of photoelectrocatalytic and photocatalytic oxidation of 4-MBA by using TiO₂/Ti. Initial degradation rate, r_0 ; selectivity to aldehyde, S . Selectivity values were determined by considering 25% conversion. Initial 4-MBA concentration, 0.5 mM.

	Catalyst	Bias (V)	r_0 (mM h ⁻¹)	S (%)
A	TiO ₂ /Ti-400-10L	Open circuit	0.0336	63
	TiO ₂ /Ti-400-10L	-0.50	0.0332	68
	TiO ₂ /Ti-400-10L	-0.25	0.0985	43
	TiO ₂ /Ti-400-10L	0	0.1203	44
	TiO ₂ /Ti-400-10L	0.05	0.1208	42
	TiO ₂ /Ti-400-10L	0.25	0.1145	43
	TiO ₂ /Ti-400-10L	0.50	0.1196	44
	TiO ₂ /Ti-400-10L	0.75	0.1347	42
	TiO ₂ /Ti-400-10L	1	0.1333	42
	TiO ₂ /Ti-400-10L	2	0.1307	41
B	TiO ₂ /Ti-400-10L	3	0.1340	38
	TiO ₂ /Ti-100-10L	0.75	Negligible	-
	TiO ₂ /Ti-100-10L	Open circuit	Negligible	-
	TiO ₂ /Ti-200-10L	0.75	0.0098	43
	TiO ₂ /Ti-200-10L	Open circuit	Negligible	-
	TiO ₂ /Ti-300-10L	0.75	0.0416	43
	TiO ₂ /Ti-300-10L	Open circuit	0.0088	61
	TiO ₂ /Ti-400-10L	0.75	0.1347	42
	TiO ₂ /Ti-400-10L	Open circuit	0.0336	63
	TiO ₂ /Ti-550-10L	0.75	0.1654	31
C	TiO ₂ /Ti-550-10L	Open circuit	0.0272	60
	TiO ₂ /Ti-700-10L	0.75	0.1375	65
	TiO ₂ /Ti-700-10L	Open circuit	Negligible	-
	TiO ₂ /Ti-850-10L	0.75	Negligible	-
	TiO ₂ /Ti-850-10L	Open circuit	Negligible	-
	TiO ₂ /Ti-700-1L	0.75	0.1339	90
	TiO ₂ /Ti-700-4L	0.75	0.1563	70
	TiO ₂ /Ti-700-7L	0.75	0.1355	73
	TiO ₂ /Ti-700-10L	0.75	0.1375	65
	D	TiO ₂ /Ti-700-1L	-0.25	-
TiO ₂ /Ti-700-1L		0	0.0228	95
TiO ₂ /Ti-700-1L		0.25	0.0456	95
TiO ₂ /Ti-700-1L		0.75	0.1339	90
TiO ₂ /Ti-700-1L ^a		0.75 ^a	0.1330 ^a	85 ^a
TiO ₂ /Ti-700-1L		1.25	0.1446	86
TiO ₂ /Ti-700-1L		2	0.1432	84
TiO ₂ /Ti-700-1L		3	0.1496	86

^a Run carried out in the presence of bubbling O₂.

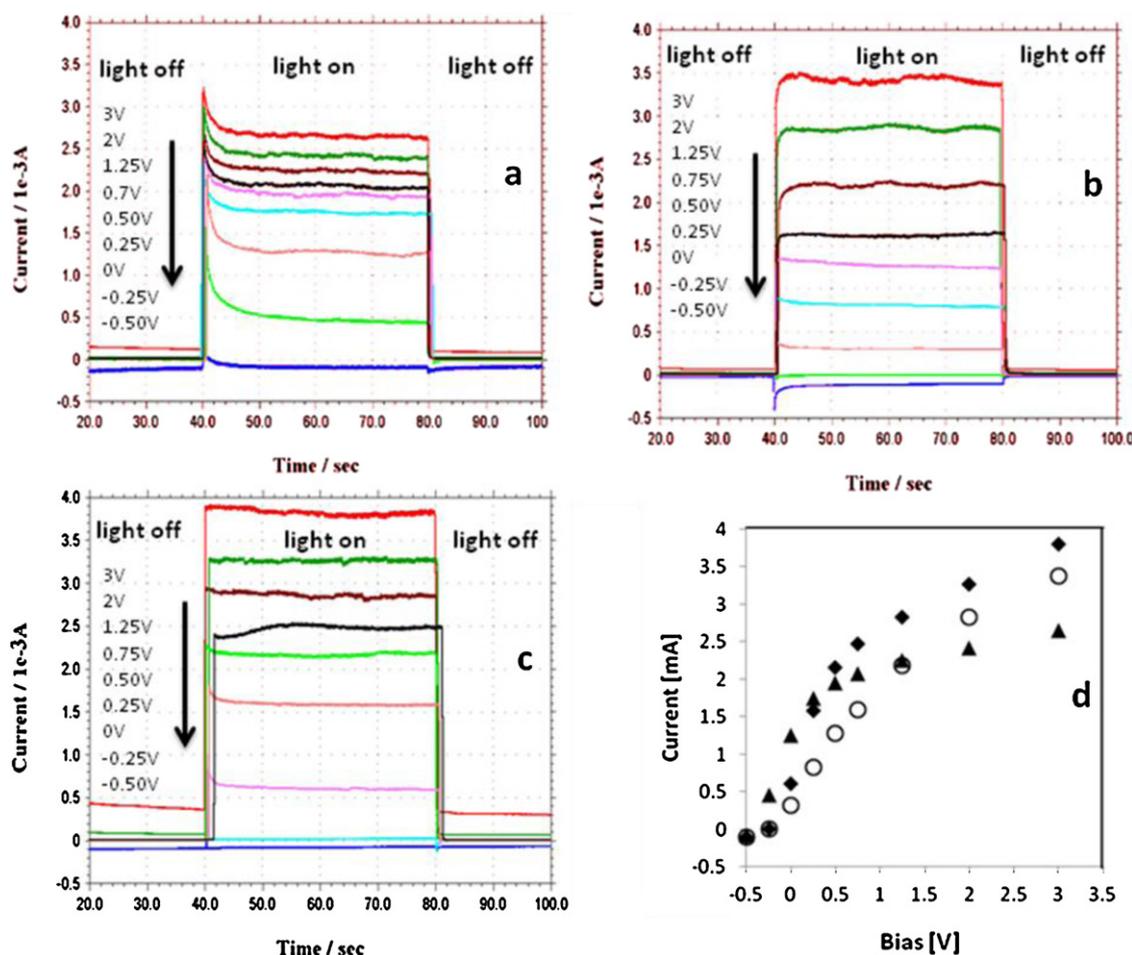


Fig. 6. Amperometries with intermitting light for 4-MBA PEC oxidation by using (a) TiO₂/Ti-400-10L, (b) TiO₂/Ti-700-1L and (c) Ti-500 samples. (d) Current versus bias values of TiO₂/Ti-400-10L (▲), TiO₂/Ti-700-1L (○) and Ti-500 (◆) samples obtained from (a), (b) and (c), respectively.

on and off in order to study the effect of irradiation on the current. It can be seen that the current values quickly increased when light was turned on, whereas they assumed their initial values upon turning light off. It is worth noting that the thick film TiO₂/Ti-400-10L (Fig. 6a) needs ca. 5 s before reaching a stable current value after turning light on (practically at any of the applied biases). This induction time is clearly due to the higher semiconducting pathway that charges have to cross before reaching the highly conductive titanium anode. Conversely the thinner TiO₂/Ti-700-1L (Fig. 6b) and Ti-500 (Fig. 6c) films reached an equilibrium current value very quickly. Fig. 6d shows the steady-state current values reached under UV irradiation read from Fig. 6a–c; accordingly to the amperometric trends, the thicker TiO₂/Ti-400-10L seemed to undergo a low influence of applied bias, so that photocurrent reaches a certain level of saturation; the two thinner films held similar behaviours, with a high sensitivity toward the applied bias, and in their I–V curves saturation is less evidenced.

The determination of the optimal voltage value to be imposed to the cell was firstly investigated, by using the dip-coated TiO₂/Ti-400-10L. An OCV value of -0.06 V was measured at this sample, under UV irradiation. The calculated values of reaction rate and selectivity to PAA, evaluated in a range of bias from -0.5 to 3 V, are shown in Table 1.

As the bias value was moved far from the OCV, the reactivity increased by reaching a plateau at 0.75 V and remaining almost constant at higher biases. Correspondingly, a decreasing trend of selectivity to PAA was measured at increasing bias, which tended to a nearly constant value of 42% at 0.75 V.

These results are in agreement with the photocurrent I–V trend (Fig. 6d) obtained at this sample, at which photocurrent saturates at about 0.75 V.

The data A of Table 1 allow to compare the reaction rate obtained with a 0.75 V bias with that obtained at open circuit, i.e. with that determined by only photocatalysis. PEC reaction rate was 4 times higher than the PC one, although with a lower selectivity (42% vs. 63%). The strong increase of reaction rate is due to the promotion of charge separation and hence to the decrease of the recombination rate of the photogenerated electron–hole pairs. The low selectivity measured at the higher reaction rate may indicate that photo-generated charges are able to accelerate not only the initial transformation of the reactant but also, and even in a more extent, the subsequent transformation of the intermediate product into CO₂, so avoiding the accumulation of PAA in the solution.

On the basis of results of Table 1A, a bias value of 0.75 V was applied in all the runs devoted to compare the anodes prepared by dip-coating and subsequent calcination at different temperatures. The reactivity and selectivity results are shown as B data in Table 1. For the runs carried out at open circuit, i.e. for the photocatalytic ones, the reaction rate is negligible for TiO₂ samples heated at temperatures less than 300 °C; for samples heated at higher temperature the rate increases and reaches a maximum at 400 °C. By further increase of temperature the reactivity decreases due to the anatase-to-rutile phase transformation that starts at ca. 550 °C. TiO₂ samples calcined at 700 °C or higher temperatures resulted to be completely inactive for PC experiments owing to the drastic dehydroxylation of the TiO₂ surface.

The PEC activity of samples heated at increasing temperatures increased and reached a maximum value for the sample heated at 550 °C for which both anatase and rutile phases are present. Besides that temperature the reactivity decreases and disappears for the sample heated at 850 °C. The highest selectivity, instead, was shown by the sample heated at 700 °C; its value was about 2 times higher than that of the fastest catalyst. Also in this case, the enhancement of the oxidizing power of TiO₂ may be claimed as responsible for the worsening of the selectivity for 4-MBA partial oxidation to PAA. However, it should be noted that samples heated at 400 °C and 700 °C, show the same reactivity, but have different values of selectivity. This could indicate that also the different distribution of the phases originated by the increasing of the temperature could be considered as a possible parameter which influences the reaction path and selectivity.

In order to study the influence of TiO₂ thickness, TiO₂/Ti samples covered with different layers (from 1 to 10) were prepared and calcined at 700 °C. The results of the PEC runs are reported as C data in Table 1. All the samples exhibited reaction rates quite similar, whereas selectivity was optimal by using the 1-layer sample, reaching the outstanding value of 90%. By using this last sample, a series of PEC runs were carried out by varying the bias potential applied to the photoanode. The results are reported as D data in Table 1. The results indicate that also the performance of this thin film is strongly affected by bias potential. In particular, it can be seen that the sample was inactive in the presence of a negative bias, and a higher bias is needed in order to activate the reaction path, indicating a major recombination at this sample. The high temperature used for this sample may have originated a defective sample at which recombination is favoured. Accordingly, a more sharply trend of the I–V response is obtained at this sample at the lowest bias.

As the bias is increased reaction rate obtained by using TiO₂/Ti-700-1L increases, reaching a plateau at 1.25 V with selectivities ranging from 86% to 95%.

In order to check if the oxidation reaction was controlled by the O₂ concentration in the liquid phase, a run was performed by continuously bubbling pure O₂ at atmospheric pressure in the reacting solution. In this way the dissolved oxygen concentration increased of about 5 times. The reactivity results, reported among the D data of Table 1, showed that the reaction rate and the selectivity do not substantially change by increasing the O₂ concentration, thus indicating that oxygen is not limiting the samples performance.

3.3. Photoelectrocatalytic performance of thermally oxidized anodes

Naked titanium anodes in 4-MBA solution were irradiated in order to observe a possible reactivity. In the absence of either light or bias no 4-MBA conversion was measured. The presence of both UV light and bias gave however rise to a very low reaction rate (A data of Table 2).

For the thermally oxidized anodes no reactivity was indeed observed in the absence of irradiation, oxygen, or bias. Bias alone was never capable to give rise to activity at any of the used voltage (–0.25 V to 3 V). The reason of this behaviour can be probably ascribed to the predominance of rutile crystalline phase with respect to anatase one (especially for Ti-600 and Ti-700). In all the runs carried out at open circuit, i.e. in photocatalytic conditions, the thermally oxidized anodes did not show any measurable activity (A data of Table 2).

As a bias value of 0.75 V was found to be the optimal one for dip coated samples, the same bias value was applied to the different samples prepared by thermal oxidation. The reactivity results are reported as A data in Table 2.

Table 2

Results of photoelectrocatalytic and photocatalytic oxidation of 4-MBA by using thermally oxidized Ti samples. Initial degradation rate, r_0 ; selectivity to aldehyde, S . Selectivity values were determined by considering 25% conversion. Initial 4-MBA concentration, 0.5 mM.

	Catalyst	Bias (V)	r_0 (mM h ⁻¹)	S (%)
A	Ti	0.75	0.0114	72
	Ti	Open circuit	Negligible	–
	Ti-400	0.75	0.0685	70
	Ti-400	Open circuit	Negligible	–
	Ti-500	0.75	0.1507	85
	Ti-500	Open circuit	Negligible	–
	Ti-550	0.75	0.1778	78
	Ti-550	Open circuit	Negligible	–
	Ti-600	0.75	0.2024	67
	Ti-700	0.75	0.0489	95
	Ti-700	Open circuit	Negligible	–
	Ti-500	–0.25	Negligible	–
	Ti-500	0	0.0504	84
	Ti-500	0.25	0.0703	95
B	Ti-500	0.75	0.1507	85
	Ti-500	1.25	0.1477	89
	Ti-500	2	0.1509	86

The low reactivity shown by Ti-400 sample can be justified by the fact that the TiO₂ layer produced on the Ti surface is very thin and, moreover, that TiO₂ is mainly present as amorphous phase. No anatase and rutile peaks were indeed detected in XRD analysis (Fig. 3). The increase of the temperature increases the reaction rate and the selectivity. However for samples treated at temperatures higher than 500 °C the selectivity starts to decrease. The sample treated at 700 °C shows a strong reaction rate decrease while the selectivity reaches its highest value (95%); in this sample anatase phase is mostly converted to the less active rutile one, as showed by the intensity decrease of anatase XRD peak at $2\theta = 36.5^\circ$ and the significant increase of the rutile peaks intensity (Fig. 3). It must be outlined that the data of Table 2 follow the same trend observed at deep-coated samples: higher selectivities are obtained only for lower reaction rate.

The Ti-500 sample, which shows both high reactivity and selectivity, has been used for studying the effect of the applied potential on selectivity and activity. The results are reported as B data in Table 2; the influence of applied bias on selectivity does not show a definite trend, whereas reactivity increased by reaching a plateau at potentials higher than 0.75 V.

3.4. Influence of substituent group

In order to investigate if the transformation of the alcoholic group to the aldehydic one is affected by the presence on the aromatic ring of groups different from the methoxy one, the reactivity and selectivity to the corresponding aldehyde of benzyl alcohol (BA), 2-methoxybenzyl alcohol (2-MBA), 3-methoxybenzyl alcohol (3-MBA), 2,4-dimethoxybenzyl alcohol (2,4-DMBA), 2,3,4-trimethoxybenzyl alcohol (2,3,4-TMBA), 4-nitrobenzyl alcohol (4-NBA) and 4-hydroxybenzyl alcohol (4-HBA) have been determined by performing photoelectrocatalytic runs with a bias of 0.75 V. The results obtained with the TiO₂/Ti-700-1L and Ti-500 samples are reported in Table 3.

By taking as reference the results obtained with the unsubstituted alcohol, i.e. the benzyl alcohol, from the data reported in Table 3 it may be noted that the presence of one electron donor group (EDG) in 2- or 4-position increases the reaction rate [49]. When both 2- and 4-positions are occupied by two EDG's, the reaction rate further increases. In 3-position the presence of an EDG has a small positive effect on the reaction rate if the 2- and 4-positions are free; however, the positive effect of two EDG's in 2- and 4-positions is strongly diminished if the same EDG is also in

Table 3

Results of photoelectrocatalytic (PEC) oxidations of substituted aromatic alcohols^a by using TiO₂/Ti-700-1L and Ti-500. Initial degradation rate, r_0 ; selectivity to aldehyde, S . Selectivity values were determined by considering 25% conversion. Initial aromatic alcohol concentration: 0.5 mM. Bias: 0.75 V.

Catalyst	Compound ^a	r_0 (mM h ⁻¹)	S (%) ^a
TiO ₂ /Ti-700-1L	4-MBA	0.1339	90
Ti-500	4-MBA	0.1507	85
TiO ₂ /Ti-700-1L	BA	0.0324	13
Ti-500	BA	0.0249	20
TiO ₂ /Ti-700-1L	2-MBA	0.1304	60
Ti-500	2-MBA	0.1643	70
TiO ₂ /Ti-700-1L	3-MBA	0.0469	9
Ti-500	3-MBA	0.0408	16
TiO ₂ /Ti-700-1L	2,4-DMBA	0.2884	54
Ti-500	2,4-DMBA	0.2883	50
TiO ₂ /Ti-700-1L	2,3,4-TMBA	0.1042	35
Ti-500	2,3,4-TMBA	0.1024	37
TiO ₂ /Ti-700-1L	4-NBA	0.0329	3
Ti-500	4-NBA	0.0469	2
TiO ₂ /Ti-700-1L	4-HBA	0.0435	11
Ti-500	4-HBA	0.0314	12

^a Benzyl alcohol, BA; 2-methoxybenzyl alcohol, 2-MBA; 3-methoxybenzyl alcohol, 3-MBA; 2,4-dimethoxybenzyl alcohol, 2,4-DMBA; 2,3,4-trimethoxybenzyl alcohol, 2,3,4-TMBA; 4-nitrobenzyl alcohol, 4-NBA, and 4-hydroxybenzyl alcohol, 4-HBA.

3-position. The presence of an electron withdrawing group (EWG) in 4-position improves the reaction rate that, however, remains lesser than that showed by the EDG substituted alcohols.

As to concern the selectivity to the corresponding aldehydes, the results of Table 3 indicate that the presence of one EDG in 2- or 4-position improves the selectivity, being the 4-position the most effective one. Because the EDG's are 2- and 4-orienting, the EDG in 2- or 4-position is able to activate the benzyl group thus favouring the alcohol-to-aldehyde transformation. In our case two substituent groups, such as CH₃O— and —CH₂OH, must be mutually in the 2- or 4-position in order for the alcoholic group to be selectively oxidized to the aldehydic one. When both 2- and 4-positions are occupied by two EDG's, while the degradation rate reaches its highest values, the selectivity increases but remains quite lower than that shown by the monosubstituted alcohols. The selectivity is negatively affected by the presence of an EDG in 3-position: in fact for 3-MBA it diminishes with respect to BA and also for 2,3,4-TMBA with respect to 2,4-DMBA. While the EDG in 3-position is able to increase the reaction rate, this increase is paid by the selectivity that decreases. The same behaviour is observed in the presence of an EWG in 4-position; it improves the reaction rate but it worsens the selectivity, being the NO₂ group that with the highest negative effect.

4. Conclusions

This study reports the preparation of TiO₂ supported on Ti anodes via two different methods. The performed reaction was the selective oxidation of 4-MBA to PAA. For both series of home-prepared photoanodes the influence of an applied positive bias on reactivity performance showed the same features: by increasing bias, reactivity increased to a certain value that did not change for higher biases.

The only application of a bias did not give rise to any reactivity, regardless of the used anode and the applied potential. The dip-coated samples at open circuit, i.e. in photocatalytic conditions, showed a very poor reactivity under UV irradiation; the thermally oxidized samples gave rise to a negligible photocatalytic activity probably due to the small amount of formed TiO₂ and its presence as mainly in rutile rather than in anatase phase.

The contemporary presence of light and bias (PEC oxidation) notably gave rise to an improvement of both selectivity and activity

with respect to the photocatalytic runs. In particular selectivity reached values as high as 95%. The study of thermal treatment temperatures of anodes indicated that an increase of crystallinity improves the activity in PEC oxidation without affecting the selectivity. Finally a positive effect on selectivity and reactivity values was observed for some benzyl alcohols bearing electron donor groups in 2- and/or 4-positions.

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