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Selective photocatalytic oxidation at TiO_2/Ti anodes of 4-methoxybenzyl alcohol to the corresponding benzaldehyde in “green” conditions

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ABSTRACT

The photosensitized electrochemical oxidation at a TiO_2/Ti anode is, in itself, a “green” chemical strategy as the semiconductor remains unchanged during the experiments, the metal is safe, low energies are involved and experimental conditions are mild. In this context, the oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde has been carried out on the light of further “green chemistry” requirements: water as medium, NaCl as supporting electrolyte, exclusion of the reference electrode, Ti cathode (less expensive than the traditional Pt one) and Ti mesh (to optimize the cell geometry). In this study some chemical (alcohol conversion to aldehyde and material recovery) and electrochemical (current efficiency and density) parameters have been used to select the reaction conditions that are more suitable for this purpose. As concern the cell, the best geometry was realized with an immersion lamp, coaxial with a mesh cylindrical TiO_2/Ti anode and a mesh Ti cathode.

1. Introduction

The photosensitized electrochemical technology, where a film of TiO_2 supported on Ti is used as the photoanode of an electrolytic cell, can present many advantages in the aim of realizing a “green” organic oxidation. In particular the semiconductor, immobilized at the electrode surface, photosensitizes the substrate oxidation remaining unchanged and, therefore, can be reused after each experiment. Moreover, the chemical material different from the substrate (water, TiO_2/Ti photoelectrodes and NaCl as supporting electrolyte) can be harmless, the energy amount can be reduced (low currents and solar energy are used), the experimental conditions are mild (room temperature and atmospheric pressure) and hazardous substances are not involved. It must be observed that this technology as “green process” in water presents some limitations due to the use of water and of a sufficiently soluble substrate. Moreover, to realize a selective process where the substrate is oxidized much more than the product, the substrate must be much more adsorbed onto the semiconductor surface and more electron reach (more oxidizable) than the product.

In this work we focus on the selective and stoichiometric TiO_2 sensitized photooxidation of 4-methoxybenzyl alcohol (**1**) to 4-methoxybenzaldehyde (**2**) in water, as a “green” process carried out with the photoelectrochemical technology, optimized on the light of the requirements previously reported. Moreover, **1**, a very electron reach benzylic substrate, is easily oxidizable while **2** is much less oxidizable in the reaction conditions.

It must be pointed out that the TiO_2 sensitized photooxidation of benzyl alcohols to the corresponding benzaldehydes has been studied by us in detail. In particular, it has been possible to acquire mechanistic informations in CH_3CN through product analysis, kinetic experiments and substrate adsorption measurements, considering TiO_2 as powder [1] and colloid [2]. The photoelectrochemical technology, through current yield and current density measurements, has allowed to confirm the stoichiometry (two exchanged electrons vs molecule of formed product) and the electron transfer mechanism (via radical cation intermediates) relative to the TiO_2 photosensitized oxidation of some benzyl alcohols in this organic medium [3]. Moreover, for these substrates it has been evidentiated that the same selective and stoichiometric reaction is realized also in water, with the same electron transfer mechanism [4]. Unfortunately, the above photoelectrochemical measurements are not reliable for mechanistic purposes in aqueous medium because water is competitively photooxidized.

Taking in mind these considerations, the optimization of the photoelectrochemical reaction of **1** to **2** in the light of the “green

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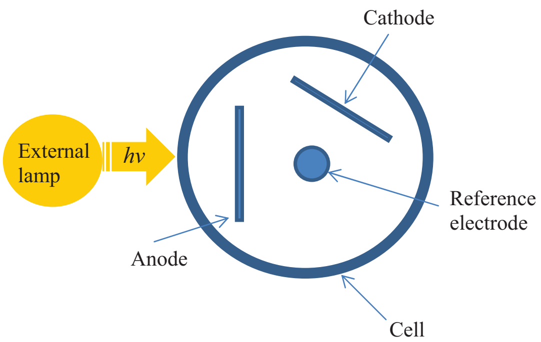

Fig. 1. Cell-geometry for potential controlled experiments with plate electrodes.

chemistry" requirements, has been realized through a preliminary study in CH_3CN, followed by a similar study in water, both based on the determination of some chemical (alcohol conversion to aldehyde and material recovery) and electrochemical (current efficiency and current density) parameters.

2. Experimental

GC analyses were carried out on a HP Agilent Technologies 6850 gas-chromatograph using a HP capillary column, 30 m.

2.1. Starting materials

Titanium plate (Grade 2 from Titania S.p.A. Terni, 2.5 cm × 8.0 cm, thickness = 0.5 mm containing $N < 0.007\%$, $C < 0.004\%$, $H < 0.012\%$, $Fe < 0.024\%$ and $O < 0.09\%$) and mesh (Grade 2 from TIG SRL, wire width: 0.6 mm, opening: 2.0 mm) 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]. 4-Methoxybenzyl alcohol, 4-methoxybenzaldehyde, H_2SO_4, $LiClO_4$, NaCl, Ag_2SO_4, Na_2CO_3 and CH_3CN (99.9%, HPLC grade, containing 0.02% water from Karl Fisher analysis) were analytical grade commercial products. Milli Q water (18 MΩ, pH 6.32).

2.2. Preparation and characterisation of TiO_2/Ti anodes

The titanium plate and mesh were subjected to constant current (25 mA/cm^2) mild anodic oxidation (6443B DC HP power supply) in 1 M H_2SO_4 using Pt (2 cm^2) as the cathode up to 30 V (further surface cleaning) and then rinsed with distilled water. Titanium plate and mesh were then heated in an oven at 700 °C for 4 h.

2.3. Photoelectrochemical oxidation in CH_3CN

The photoelectrochemical measurements were performed at controlled potential in an undivided cylindrical jacketed cell provided with TiO_2/Ti anode as plate (Fig. 1, with 10 cm^2 of immersed area) or mesh (Fig. 2, with 17 cm^2 of immersed area), Pt plate (Fig. 1) or Ti plate (Fig. 1) or mesh (Fig. 2) cathode and SCE as reference electrode, all connected to the potentiostat (AMEL, Model 552). The substrate (0.38 mmol), $LiClO_4$ (9.0 mmol) and Na_2CO_3 (4.5 mmol) in CH_3CN (150 ml) were placed in the cell and magnetically stirred. The cell was externally irradiated by a 500 W high pressure Hg lamp (Helios Italquartz), cooled by a Pyrex water jacket ((= 313, 366, 405/08, 436, 546, 577/79 nm) positioned in front of TiO_2/Ti anode and the apparatus was covered by a closed aluminium cylinder. Current flowed only under irradiation and it was practically constant during the reaction time. 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 Na_2SO_4 and concentrated. The crude product was analysed by GC, in the presence of suitable internal standard.

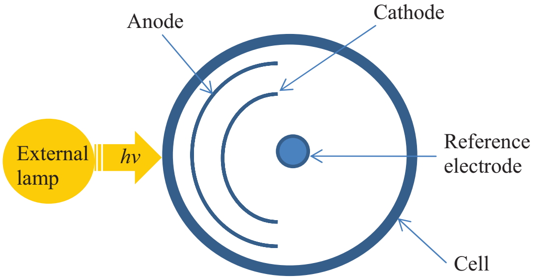

Fig. 2. Cell-geometry for potential controlled experiments with mesh electrodes.

2.4. Photoelectrochemical oxidation in H_2O

a) *At controlled potential*. The reaction was performed as above, with the following modifications: the experiments were performed only with TiO_2/Ti anode mesh and Ti cathode mesh; $LiClO_4$ (9.0 mmol) or NaCl (0.15 or 1.5 or 30 mmol) were used as supporting electrolyte.
b) *At constant current*. The reaction was performed as in a), without reference electrode and considering only NaCl (0.15 mmol) as supporting electrolyte.
c) *At constant current in large cell*. The experiments were performed in cell, as in Fig. 3, with TiO_2/Ti anode (immersed area: 85 cm^2), utilizing 580 ml of H_2O, by irradiation with a 500 or 125 W high pressure Hg lamp (Helios Italquartz), cooled by a Pyrex water jacket ($\lambda \geq 300$ nm).

2.5. Reaction product analysis

The reaction products were identified directly from the crude by comparison of GC analysis data with those of the commercial samples (4-methoxybenzaldehyde).

3. Results and discussion

In the past we have observed that in CH_3CN, both in the absence and in the presence of oxygen, **1** is photoelectrochemically oxidized (at a TiO_2/Ti anode) to **2** with a material recovery (**1** + **2**) ≥ 95% and the stoichiometry involves two electrons/molecule, according to the previously suggested mechanism (Scheme 1) [3].

More in detail, the substrate gives the first electron to the hole, $(TiO_2)_{h+}$, at the anode, furnishing a radical cation. The electron transfer step has been evidentiated through the relative reactiv-

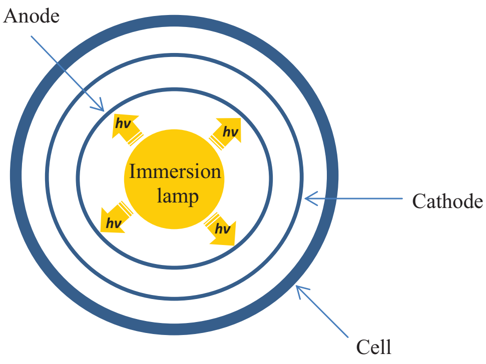

Fig. 3. Larger cell-geometry for constant current experiments with mesh electrodes.

$$\mathbf{1} \xrightarrow{(TiO_2)_{h+}} \mathbf{1}^{+\bullet} \xrightarrow{-H^+} 4\text{-}CH_3OPh\overset{\bullet}{C}HOH \xrightarrow{(TiO_2)_{h+}} 4\text{-}CH_3OPh\overset{+}{C}HOH \xrightarrow{-H^+} \mathbf{2}$$

Scheme 1.

Table 1
Photoelectrochemical oxidation at controlled anodic potential of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde at a TiO_2/Ti anode in CH_3CN.[a]

Entry	Anode[b]	Cathode	Unreacted alcohol (%)	Aldehyde (%)	Current density (mA/cm^2)[c]	Current efficiency (%)[d]
1	Ti plate	Pt plate	60	30	0.23	95
2	Ti plate	Ti plate	64	25	0.21	93
3	Ti mesh	Ti mesh	60	27	0.10	88

[a] [alcohol] = 2.5×10^{-3} M; [$LiClO_4$] = 0.06 M; [Na_2CO_3] = 4.5 mmol; reaction time ≅ 4 h; anodic bias, $\Delta V = 1$ V (vs SCE).
[b] The anode was obtained heating the Ti plate or mesh in an oven at 700 °C for 4 h.
[c] Medium value during the reaction.
[d] Calculated considering two exchanged electrons for aldehyde molecule.

ity kinetic data of a series of benzyl alcohols (linear correlation between k_{rel} vs E_p data [1a]). The cation radical, through deprotonation, produces a benzylic radical (evidence obtained by the absence of primary kinetic deuterium isotope effect at the benzylic hydrogen [2]); the second electron, is captured from the benzylic radical to yield **2** (evidence obtained by current efficiency measurements) by a second hole (or by the conduction band of TiO_2 if the phenomenon of "current doubling" is involved [5]).

Taking in account previous literature data [6–12], we have observed [3a] that, among the rutile anodes prepared by annealing Ti plates in an oven for two hours at temperatures from 500 to 800 °C, the one calcined at 700 °C showed the best efficiency, measured as current intensity for surface area (current density). Later [5] we reported that current density further increases on going, at 700 °C, from 2 h to 4 h of thermal treatment. This photocatalytic material (Ti/TiO_2 rutile) has a thickness of 2.3 μm, determined by field emission scanning electron micrography (FESEM) [5]. It must be observed that the selected method to prepare films of TiO_2 on Ti is easily realizable and not much expensive.

To satisfy the "green" requirements to be involved in this work, some suitable changes have been gradually introduced to the system, considering, as reference experiment, the one reported in Table 1 (Entry 1). This experiment is realized in CH_3CN, in the previously reported conditions [3]; the cell (containing 150 ml of solution), with the anode described above and a Pt cathode, is schematized in Fig. 1 (see also Section 2).

The current efficiency, defined as previously reported [5], is quantitative considering two exchanged electrons for molecule of aldehyde [3].

The experimental modifications introduced in the following experiments have been evaluated on the basis of current density and efficiency.

As first, considering the same cell, the cathodic material, Pt plate, has been substituted with a less expensive material, that is a Ti plate, without significative differences in both electrical parameters (compare Entry 2 with Entry 1 in Table 1).

Subsequently, we have considered a TiO_2/Ti anode and a Ti cathode, both as mesh, with the aim to easily change the geometry of the cell (in the perspective of the larger cell, see later). The covering of Ti mesh with TiO_2 has been previously reported to prepare anodes for both photoelectrocatalytic oxidations [13–16] and for all-Ti dye-sensitized solar cells [17]. In particular, it has been considered the cell-geometry reported in Fig. 2 where the anode is positioned near the external light source.

As observed in Table 1, Entry 3, the material recovery, the aldehyde selectivity and the current efficiency are practically unchanged, even if the current density is lower. In fact, the malleability of the Ti mesh material allows to adapt anodes with higher surface of the metal (17 cm^2 with the mesh vs 10 cm^2 with the plate) in the same cell and this allows to obtain similar percent of product also with a lower current density.

The change of the reaction medium from CH_3CN to water is surely a significative step toward "green chemistry" conditions. The substrate **1** is oxidized to **2** with a material recovery of 91–102% (see Table 2), a quantitative material recovery within the experimental error.

We have showed that also in this solvent the mechanism in Scheme 1 holds. In particular, a similar kinetic behaviour of the same series of benzyl alcohols (the k_{rel} vs E_p plot shows the same linear correlation with a similar slope) [4] has been observed. Moreover, through laser photolytic experiments, the absorption spectrum of $\mathbf{1}^{\bullet +}$ in this aqueous medium has been detected [4]. Unfortunately, in photoelectrochemistry the competitive anodic oxidation of water drastically reduces the current efficiency. In particular (see Table 2, Entry 1), the reaction carried out in the last solvent, realized in the same experimental conditions of Entry 3 in Table 1, shows a decrease of nearly 1/5 of current efficiency. However, the aldehyde amount is only three times lower probably due to the faster substrate discharge in water. The higher current density (from 0.10 in CH_3CN to 0.14 mA/cm^2 in water) could be due to the higher mobility of the supporting electrolyte in this medium.

We have also observed that, lowering the anodic polarization (ΔV), the alcohol discharge is advantaged with respect to the water.

Table 2
Photoelectrochemical oxidation at controlled anodic potential of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde at a TiO_2/Ti anode in water.[a]

Entry	ΔV (V, vs SCE)[b]	Unreacted alcohol (%)	Aldehyde (%)	Supporting electrolite (M)	Current density (mA/cm^2)[c]	Current efficiency (%)[d]
1	1	90	10	$LiClO_4$ (0.06 M)	0.14	18
2	0.5	83	13	$LiClO_4$ (0.06 M)	0.14	23
3	0.5	90	7	NaCl (0.001 M)	0.065	25
4	0.5	94	8	NaCl (0.01 M)	0.095	20
5	0.5	83	8	NaCl (0.2 M)	0.093	23

[a] Anode and cathode as Ti mesh in an oven at 700 °C for 4 h; [alcohol] = 2.5×10^{-3} M; reaction time ≅ 4 h.
[b] Anodic polarization.
[c] Medium value during the reaction.
[d] Calculated considering two exchanged electrons for aldehyde molecule.

Table 3
Photoelectrochemical oxidation at controlled current of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde at a TiO_2/Ti anode in water.[a]

Entry	Cell	Lamp power (W)	Unreacted alcohol (%)	Aldehyde (%)	Current intensity (mA)	Current density (mA/cm^2)	Current efficiency (%)[b]
1	Fig. 2	500	84	8	1.5	0.09	19
2	Fig. 2	500	70	23	3.0	0.18	27
3	Fig. 3	500	56	7	3.0	0.04	43
4	Fig. 3	125	86	7	3.0	0.04	52

[a] Anode and cathode as Ti mesh in an oven at 700 °C for 4 h; [alcohol] = 2.5×10^{-3} M; [NaCl] = 0.001 M; reaction time ≅ 4 h.

[b] Calculated considering two exchanged electrons for aldehyde molecule.

In fact, changing the ΔV from 1 to 0.5 V (vs SCE) the alcohol is more converted, as observed from the increase of the aldehyde percent and the current efficiency (compare Entry 1 and 2 in Table 2).

As concern the current density, we observed the same value both in Entry 1 and 2; the different behaviour from that in CH_3CN, where a decrease of ΔV corresponds to a decrease of the above electrical parameter [3a,18–21], can be explained considering that the discharge of both **1** and water contribute to the overall anodic current.

A further modification toward green reaction conditions is the choice of a less expensive supporting electrolyte. As reported in previous works, a possible choice could be NaCl [22,23]. In particular, the experiments performed at the more favourable ΔV (0.5 V) with this salt, both at lower and higher concentration respect to that of $LiClO_4$, show a similar current efficiency but a lower aldehyde conversion due to the lower observed current density. As the higher NaCl concentration do not produce significant difference in the aldehyde conversion (Entry 3, 4 and 5 in Table 2), in the following experiments (Table 3) we have considered NaCl as the electrolyte at the lower concentration (0.001 M).

We have also performed experiments at controlled current (Table 3, Entry 1) considering the same cell (see Fig. 2 without the reference electrode). Selecting the same current (I = 1.5 mA) measured in the potential controlled experiment, nearly similar current efficiency and aldehyde conversion, as expected, have been observed (compare Entry 1 in Table 3 with Entry 3 in Table 2).

It has been also observed (Table 3, Entry 2) that the current intensity doubling (I = 3.0 mA) produces an increase of both aldehyde conversion and current efficiency. It must be noted that, also operating at constant current, the material recovery (**1** + **2**) is quantitative within experimental error.

The last experimental parameters have been considered as optimal experimental conditions and have been used to realize the next experiment (Table 3, Entry 3), involving a larger cell, that allows to use a volume nearly four times higher of the same solution as in Entry 2 (see Section 2); in particular the same lamp (500 W) is immersed in the solution, coaxially with respect to the TiO_2/Ti mesh cylindric anode, surrounded by a Ti-mesh cylindric cathode (see Fig. 3). This photoelectrochemical configuration of the cell could allow to convert an higher amount of the substrate.

Unfortunately, in these experimental conditions we have not observed a quantitative material recovery (**1** + **2** = 63%). Probably, this result could be ascribed to a much higher amount of photons collected at the larger photoanode from the closer coaxial source. Therefore, both **1** and **2** could react until mineralization (no other products are obtained) [24]. In particular, in a control experiment involving 4-methoxybenzaldehyde (1.0×10^{-3} M) as substrate we observed that in the same time 55% of **2** is photodegraded.

As a confirmation, a photoelectrochemical experiment with a 125 W immersion lamp showed material recovery (Table 3, Entry 4). It is noteworthy to observe that the measured current efficiency is significantly higher with respect to the above experiments in the aqueous medium with the cell in Fig. 2 and this fact should be principally attributed to a suitable cell geometry. In particular, an important role should be due to the location of the lamp (coaxial to the TiO_2/Ti cylindric anode). In fact, we have observed that it is necessary a more powerfull lamp (500 W) to obtain a similar result in the same conditions of Entry 4 with external irradiation (9% of aldehyde, with 58% current efficiency and with a quantitative material recovery, was formed).To investigate the potentiality of this reaction, the aldehyde conversion and the current efficiency have been evaluated at different times in the experimental conditions of Entry 4 in Table 3. In particular, from the plot of formed aldehyde (%) vs time (h), a linear correlation until nearly 14 h (corresponding to 23% of aldehyde) was observed (Fig. 4, □); moreover the current efficiency is practically constant (40–50%) in the time (Fig. 5, □).

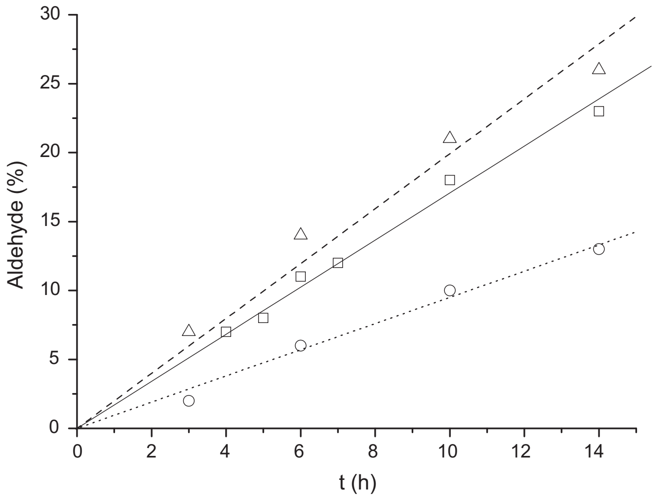

Fig. 4. Plot of obtained 4-methoxybenzaldehyde (**2**) vs time in the TiO_2 photoelectrochemical oxidation of **1** at 1.5 (○ ···), 3.0 (□ —) and 6.0 mA (△ - - -) constant current.

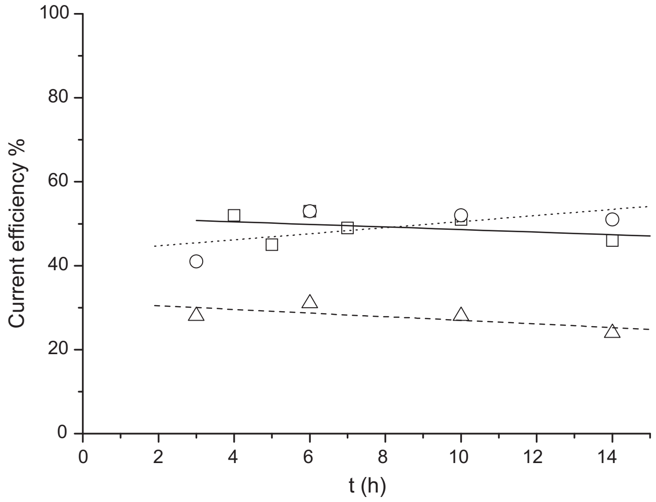

Fig. 5. Plot of current efficiency vs time in the TiO_2 photoelectrochemical oxidation of **1** at 1.5 (○ ···), 3.0 (□ —) and 6.0 mA (△ - - -) constant current.

As concern the current intensity, this approach allows to confirm $I = 3.0$ mA as an optimal value; in fact, with a double current intensity ($I = 6.0$ mA), the aldehyde per cent is similar at a parity of time (Fig. 4, △), but the current efficiency is always lower (nearly 30%, △ in Fig. 5). At half current intensity ($I = 1.5$ mA) the current efficiency is always similar (40–50%, ○ in Fig. 5), but the aldehyde per cent, at the same reaction time, is lower (Fig. 4, ○).

4. Conclusions

In this work the TiO_2 photosensitized electrochemical oxidation at a TiO_2/Ti anode of 4-methoxybenzyl alcohol (**1**) to 4-methoxybenzaldehyde (**2**) has been realized with the purpose of satisfying the requirements of "green chemistry". Keeping as reference the reaction in CH_3CN in the experimental conditions that previously allowed us to know the stoichiometry and the mechanism, we have gradually modified the above conditions as follows: i) cathode, from Pt to Ti (less expensive); ii) the electrodes, from plate to mesh (for cell geometry optimization); iii) the medium, from CH_3CN to water; iv) the supporting electrolyte from $LiClO_4$ to NaCl (less toxic and expensive); v) the electrochemical method, from controlled potential to controlled current (reference electrode elimination).

The best experiment involves an immersion 125 W high pressure Hg lamp, coaxial with a mesh cylindrical TiO_2/Ti anode and a mesh Ti cathode, where **1** quantitatively gives 23% of **2** after 14 h at constant I (3.0 mA) with 40–50% of current efficiency.

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References

[1] (a) L. Amori, T. Del Giacco, C. Rol, G.V. Sebastiani, J. Chem. Res. (S) (1998) 644–645;
(b) M. Bettoni, T. Del Giacco, C. Rol, G.V. Sebastiani, J. Chem. Res. (S) (2003) 415–417;
(c) M. Bettoni, T. Del Giacco, C. Rol, G.V. Sebastiani, J. Photochem. Photobiol. A: Chem. 163 (2004) 481–487.
[2] T. Del Giacco, M. Ranchella, C. Rol, G.V. Sebastiani, J. Phys. Org. Chem. 13 (2000) 745–751.
[3] (a) R. Palombari, M. Ranchella, C. Rol, G.V. Sebastiani, Sol. Energy Mater. Sol. Cells 71 (2002) 359–368;
(b) M. Ranchella, C. Rol, G.V. Sebastiani, J. Chem. Res. (S) (2002) 239–241.
[4] M. Bettoni, T. Del Giacco, F. Elisei, C. Rol, G.V. Sebastiani, Phys. Chem. Chem. Phys. 12 (2010) 5425.
[5] M. Bettoni, C. Rol, G.V. Sebastiani, J. Phys. Org. Chem. 21 (2008) 219.
[6] J.J. Ramsden, R. Toth-Boconadl, J. Chem. Soc. Faraday Trans. 86 (1999) 1527.
[7] G. Haas, Vacuum 2 (1952) 331.
[8] S.E. Lindquist, A. Lindgren, Y. Zhu, J. Electrochem. Soc. 132 (1985) 623.
[9] S.E. Lindquist, A. Lindgren, C. Leygraf, Sol. Energy Mater. 15 (1987) 367.
[10] Y. Matsumoto, J. Kurimoto, Y. Amagasaki, E. Sato, J. Electrochem. Soc. 127 (1980) 2148.
[11] P. Kofstad, K. Hauffe, H. Kjollesdal, Acta Chem. Scand. 12 (1958) 239.
[12] M. Dechamp, P. Lehr, J. Less-Common Met. 56 (1977) 193.
[13] X.Z. Li, P.T. Yue, C.L. Mak, Water Sci. Technol. 42 (2000) 181–188.
[14] X.Z. Li, H.L. Liu, P.T. Yue, Environ. Sci. Technol. 34 (2000) 4401–4406.
[15] R.T. Pelegrini, R.S. Freire, N. Duran, R. Bertazzoli, Environ. Sci. Technol. 35 (2001) 2849–2853.
[16] X.Z. Li, F.B. Li, C.M. Fan, Y.P. Sun, Water Res. 36 (2002) 2215–2224.
[17] Y. Wang, H. Yang, Y. Liu, H. Wang, H. Shen, J. Yan, H. Xu, Prog. Photovoltaics Res. Appl. 18 (2010) 285–290.
[18] K. Vinodgopal, P.V. Kamat, Sol. Energy Mater. Sol. Cells 38 (1995) 401.
[19] K. Vinodgopal, P.V. Kamat, Chemtech 26 (1996) 18.
[20] I.R. Bellobono, B. Barni, F. Gianturco, J. Membr. Sci. 102 (1995) 139.
[21] K. Vinodgopal, P.V. Kamat, Environ. Sci. Technol. 29 (1995) 841.
[22] Z. Zainal, C.Y. Lee, M.Z. Hussein, A. Kassim, N.A. Yusof, J. Photochem. Photobiol. A: Chem. 172 (2005) 316–321.
[23] S. Crawford, E. Thimsen, P. Biswas, J. Electrochem. Soc. 156 (5) (2009) H346–H351.
[24] S. Yurdakal, G. Palmisano, V. Loddo, O. Alagoz, V. Augugliaro, L Palmisano, Green Chem. 11 (2009) 510–526.