



## Letter to the Editor

**Turning lipophilic phthalocyanines/TiO<sub>2</sub> composites into efficient photocatalysts for the conversion of CO<sub>2</sub> into formic acid under UV–vis light irradiation**


## ARTICLE INFO

## Keywords:

Heterogeneous photocatalysis  
Phthalocyanines  
Metallo phthalocyanines  
TiO<sub>2</sub>  
CO<sub>2</sub> photo-reduction

## ABSTRACT

Metal-free, Cu(II)- or Zn(II) tetrakis [4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)]phthalocyanines loaded over TiO<sub>2</sub> (anatase) proved to be active in the photoreduction of CO<sub>2</sub> to formic acid (HCO<sub>2</sub>H) in water under UV–vis light. CuPc/TiO<sub>2</sub> is catalyst of choice, allowing to reach a maximum yield of HCO<sub>2</sub>H, unequalled by any other similar catalytic systems. Because of their low environmental impact, low potential cost, and efficient power conversion, these multipurpose materials show promise in the setup of sustainable methods for CO<sub>2</sub> valorization.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is the simplest alternative feedstock which attracted the interest of scientists [1–4]. The impossibility of its continuous storage, has led to the development of new technologies devised to produce chemicals from CO<sub>2</sub>. In particular, several studies have been focused on the efficient and selective heterogeneous photocatalytic reduction of CO<sub>2</sub> to CH<sub>4</sub> in water [5,6] as well as to formic acid (HCO<sub>2</sub>H) and its derivatives, specially devoted to industrial-scale operation [7,8]. On the other hand, these types of photocatalytic processes could be considered as an interesting alternative of analogous processes [9], for example in electrochemical condition [9a].

In 1979, for the first time, Inoue et al. reported the photocatalytic reduction of CO<sub>2</sub> in aqueous solution to HCO<sub>2</sub>H along with other organic molecules by using various semiconductors, such as tungsten trioxide (WO<sub>3</sub>), titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), cadmium sulfide (CdS), gallium phosphide (GaP), and silicon carbide (SiC) [10].

In recent years, TiO<sub>2</sub> has acquired prominence in various fields of technology, including photocatalysis. Although TiO<sub>2</sub> suffers from a relatively large band gap as well as from a massive recombination of photogenerated charge carriers, which limit its overall photocatalytic efficiency, modification of its band gap has become a well-established strategy that provides the additional benefit of conducting reactions under visible or solar light irradiation [11–13].

In this direction, strategies include the coupling with a narrow band gap semiconductor, the metal ion/non-metal ion doping, co-doping with two or more foreign ions, surface sensitization by organic dyes like phthalocyanines (Pcs), their metallo derivatives (MPcs), or metal complexes, and noble metal deposition [14,15].

Recently, we have fruitfully employed lipophilic metallo-phthalocyanine (MPcs)-sensitized TiO<sub>2</sub> in the efficient photodegra-

dation of pollutants in water [15]. Herein, we put forward the possibility to employ such composites in the photoreduction of CO<sub>2</sub> in aqueous medium and under UV–vis irradiation. Experiments carried out using TiO<sub>2</sub> sensitized with metal-free, Cu(II)- or Zn(II) tetrakis [4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)] phthalocyanine (H<sub>2</sub>Pc, CuPc ZnPc, respectively; Fig. 1) revealed that these composites are able to convert CO<sub>2</sub> into HCO<sub>2</sub>H, surpassing other similar catalytic systems [16,17] in efficiency and product yield. Moreover, the strongly alkaline media and the use of organic additives (e.g., hole scavengers) that are normally necessary for successful catalytic performance, are not required here [16,17], thus marking an additional step forward towards the sustainable CO<sub>2</sub> transformation.

## 2. Experimental

## 2.1. Material and method

<sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Varian-400 Inova at room temperature. Formic acid analysis was performed by Ion Chromatograph Dionex DX120 (Ion Pac ICE-AS6 Analytical Column); 0.8 mM heptafluorobutyric acid (Sigma–Aldrich) was used as eluent (flow 1.00 ml/min) and 5.0 mM tetrabutylammonium hydrate (Sigma–Aldrich) as regenerating eluent (flow 4.5 ml/min). Formic acid 99% (Sigma Aldrich) was employed as standard for building IC calibration curves. The analyses were carried out by using a sample loop of 25 μl, with a column pressure less than 640 PSI and a background of 35–40 μS. UV spectra of sensitizers were obtained by using a Shimadzu UV 2401PC spectrometer dissolving the samples in Chloroform (CHCl<sub>3</sub>). Commercial phosphoric acid 95% (H<sub>3</sub>PO<sub>4</sub>) (Carlo Erba) and sodium hydroxide (NaOH) (Carlo Erba) were used for the preparation of the solutions. Titanium dioxide (pure anatase phase, specific surface area 8 m<sup>2</sup>/g) was kindly

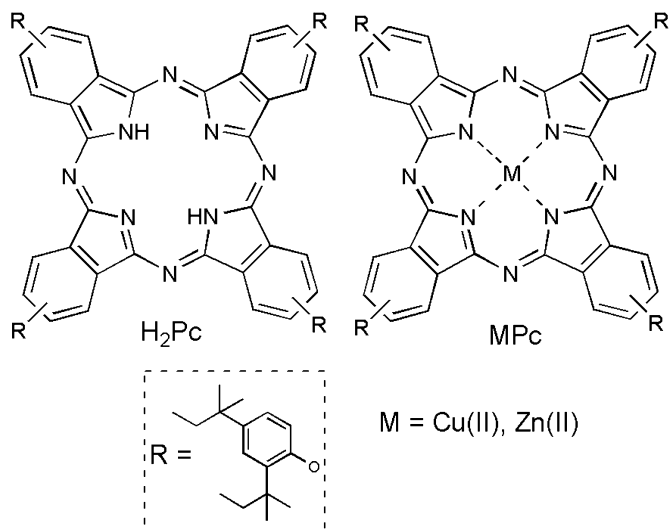


Fig. 1. Structure of H<sub>2</sub>Pc and MPcs.

provided by Tioxide Huntsman. Formic acid, 2,4-bis-(1,1-dimethylpropyl)-phenol, 4-nitrophthalonitrile and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) were purchased from Sigma–Aldrich and were used without further purification.

## 2.2. Synthesis of the

### 4-[2,4-bis-(1,1-dimethylpropyl)-phenoxy]-phthalonitrile

4-[2,4-Bis-(1,1-dimethyl-propyl)-phenoxy]-phthalonitrile was prepared following a procedure reported in literature [15]. 2.75 g (0.02 mol) of finely ground anhydrous K<sub>2</sub>CO<sub>3</sub> was added gradually (0.55 g at intervals of 0.5–1 h) under N<sub>2</sub> atmosphere and by stirring to a dry DMSO solution (100 ml) containing 3.5 g (0.015 mol) of 2,4-bis-(1,1-dimethyl-propyl)-phenol and 2.6 g (0.015 mol) of 4-nitrophthalonitrile. The reaction mixture after 1 day of stirring was filtered, added to 60 ml of water, extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried on anhydrous sodium sulfate.

The crude product of the reaction, obtained after evaporation of the solvent, was purified by column chromatography (silica, CHCl<sub>3</sub>) and recovered in 80% yields; mp = 89–90 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.72 (d, J = 8.6 Hz, 1H), 7.40–7.15 (m, 4H), 6.75 (d, J = 8.4 Hz, 1H), 1.68 (q, J = 7.5 Hz, 2H), 1.65 (q, J = 7.4, 2H), 1.31 (s, 6H), 0.70 (t, J = 7.4, 3H), 0.64 (t, J = 7.5, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 161.9, 149.8, 146.8, 139.0, 135.3, 127.1, 125.2, 121.5, 121.4, 120.7, 117.4, 115.4, 115.0, 108.2, 38.4, 37.8, 36.9, 34.2, 28.4, 28.1, 9.3, 9.0 ppm.

## 2.3. Synthesis of the Cu(II)

### tetrakis[4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)]phthalocyanine (CuPc)

The preparation of the Cu(II) tetrakis[4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)] phthalocyanine (CuPc) was previously reported [15]. A solution of 4-[2,4-bis-(1,1-dimethyl-propyl)-phenoxy]-phthalonitrile (1.8 g, 0.005 mol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.75 g, 0.0049 mol), and CuCl<sub>2</sub> (0.239 g, 0.0014 mol) in 12.5 ml of absolute ethanol was refluxed for 24 h under N<sub>2</sub> atmosphere. The organic layer enabled the separation of a blue solid which was purified by chromatography (silica, toluene) and gave a mixture of isomers of the Cu(II)-tetrakis [4-(2,4-bis-(1,1-dimethyl-propyl)-phenoxy)] phthalocyanine in 60% yields. Their structure was consistent with the following characterizations: UV–vis (CHCl<sub>3</sub>) λ<sub>max</sub> 287, 339, 391, 617, 686 nm.

## 2.4. Synthesis of the Zn(II) tetrakis[4-(2,4-bis-(1,1-dimethyl-propyl)-phenoxy)]phthalocyanine (ZnPc)

A solution of 4-[2,4-bis-(1,1-dimethyl-propyl)-phenoxy]-phthalonitrile (300 mg, 0.83 mmol), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (124 mg, 0.81 mmol), and Zn(OAc)<sub>2</sub> (33 mg, 0.25 mmol) in 5 ml of absolute ethanol (previously distilled from Mg) was refluxed for 24 h under N<sub>2</sub> atmosphere. The organic layer enabled the separation of a blue-green solid, which was purified by chromatography (silica, ethyl acetate/hexane 1:9) and gave a mixture of isomers of the Zn(II)-tetrakis [4-(2,4-bis-(1,1-dimethyl-propyl)-phenoxy)] phthalocyanine in 50% yields. Their structure was consistent with the following characterizations: UV–vis (CHCl<sub>3</sub>) λ<sub>max</sub>: 679, 615, 347, 284.5, 248.

## 2.5. Synthesis of the

### tetrakis[4-(2,4-bis-(1,1-dimethyl-propyl)phenoxy)] phthalocyanine (H<sub>2</sub>Pc)

The (H<sub>2</sub>Pc) was prepared by following a procedure similar to that reported in literature [18].

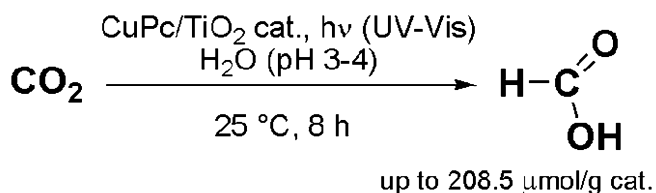
ZnPc (126 mg, 0.08 mmol) was dissolved in 10 ml of Pyridine and HCl (in molar ratio 4:1). The solution was continuously stirred for 36 h at 120 °C and monitored by TLC (thin-layer chromatography). The reaction mixture was extracted by CH<sub>2</sub>Cl<sub>2</sub> and the crude product of the reaction, obtained after evaporation of solvent, purified by chromatography (silica, ethyl acetate/hexane 0.5:9.5). A dark green solid (H<sub>2</sub>Pc) was recovered in 40% yield.

## 2.6. Preparation of TiO<sub>2</sub>-H<sub>2</sub>Pc, TiO<sub>2</sub>-ZnPc, TiO<sub>2</sub>-CuPc composites

The composite materials used as photocatalysts for the photoreactivity experiments were prepared by impregnating TiO<sub>2</sub> (Tioxide, anatase phase) with 6.65 μmol of sensitizers (CuPc, H<sub>2</sub>Pc or ZnPc) per gram of TiO<sub>2</sub>. Typically, the opportune amount of sensitizers were dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> and 500 mg of finely ground TiO<sub>2</sub> (previously sonicated for 30 min) was added to this solution. The mixture was stirred for 6 h and the solvent was removed under vacuum.

## 2.7. Photoreactivity experiments

The apparatus used for the photocatalytic experiments (Fig. S1, SupplInfo), consisted of a three necked Pyrex batch photoreactor of cylindrical shape containing 50 ml of aqueous suspension at various pH. The photoreactor was provided with a jacket for cooling water circulation and ports in its upper section for the inlet and outlet of gases, for sampling and for pH and temperature measurements. A HRC UV-VIS lamp 300 W (Sanolux) and Xe-Halogen lamp 400 W (Radium) (the emission spectra are reported in Fig. S2 SupplInfo) were placed in proximity (5–6 cm) of the reactor. CO<sub>2</sub> was bubbled into the suspensions for approximately 0.5 h before switching on the lamps to saturate the reaction mixture. The amount of catalyst used for the optimization of the reaction was between 50 and 300 mg. The amount of catalyst used to study of effect of the pH, the macrocycle, the metal and the quantity of sensitizers on the formation of formic acid was 50 mg. The initial pH, except in the basic (0.1 M NaOH) and neutral solution, was adjusted to 2.8 by addition of H<sub>3</sub>PO<sub>4</sub>. The temperature inside the reactor was held at approximately 300 K by a continuous circulation of water in the jacket around the photoreactor. The photoreactivity runs lasted 8.0 h and formic acid was detected by Ion Chromatography as reported in Fig S3 (SupplInfo).



**Scheme 1.** Photocatalytic reduction of CO<sub>2</sub>.

### 3. Results and discussion

All photoreduction experiments were routinely conducted by bubbling CO<sub>2</sub> into a suspension of solid catalyst in distilled water for approximately 0.5 h to saturate the reaction mixture, upon which irradiation was initiated and the suspension vigorously stirred for 8 h at room temperature (for details, see Supporting Information). Attempts to detect HCO<sub>2</sub>H by UV-vis [16] proved to be unsuccessful because of the interference of the HCO<sub>3</sub><sup>-</sup>, detectable even at the acidic pH values adopted. Therefore, the reaction progress and HCO<sub>2</sub>H quantitation were more conveniently estimated by ion chromatography (IC).

Because TiO<sub>2</sub>-CuPc system gave the best performance in the photo-oxidative degradation of pollutants [15], our investigations began with the optimization of the amount of TiO<sub>2</sub>-CuPc that gave a maximum HCO<sub>2</sub>H yield. Experiments run in the range of 0.05–0.30 g of catalyst, under the conditions specified in Scheme 1, showed a maximum HCO<sub>2</sub>H yield (208.5  $\mu\text{mol/g cat}^{-1}$ ) in the presence of 0.05 g of catalyst; this value is several times higher than those obtained by Ishitani et al. [19], Hirano et al. [20] and Kaneco et al. [21] (e.g. 8.8  $\mu\text{mol/g cat}^{-1}$  for 5 h irradiations with supercritical CO<sub>2</sub> and bare TiO<sub>2</sub> as photocatalyst).

Under the optimized conditions described above, a “hot filtration test” was also carried out in order to learn whether leaching of the catalytic material into the aqueous reaction medium occurred during the photocatalytic process. Accordingly, after 4 h reaction, the solid catalyst was removed by filtration and the solution saturated with CO<sub>2</sub> for 0.5 h and then irradiated for additional 8 h. IC analysis revealed no further progress in the reaction, suggesting that no appreciable loss of sensitizer took place under the reaction conditions adopted. Indeed, a noteworthy feature of this catalytic material is that the supported lipophilic phthalocyanines (completely insoluble in water) can be easily and quantitatively recovered from the TiO<sub>2</sub> surface by carefully washing the composite material with chloroform. This allowed us, on the other hand, to easily ascertain the structural integrity of the recovered sensitizers on the basis of their analytical and spectral data.

Having gathered evidence for the catalytic activity of TiO<sub>2</sub>-CuPc composites in the photoreduction of CO<sub>2</sub> to HCO<sub>2</sub>H, we turned to inspect the effect of a few selected reaction parameters on the efficiency of HCO<sub>2</sub>H production, namely the nature and role of sensitizer and of the central metal, the pH of the reaction medium, and the irradiation source. Results are collected in Table 1.

As shown in Table 1, the TiO<sub>2</sub>-CuPc catalyst (entry 3) was found to be more active than both the bare TiO<sub>2</sub> (entry 1) and the TiO<sub>2</sub>-H<sub>2</sub>Pc (entry 2). In this last instance, it seems that the presence of the dye appears even detrimental to the intrinsic photocatalytic activity of TiO<sub>2</sub> itself. On the other hand, the effect of replacing Cu(II) with Zn(II) results in a sizeable decrease in HCO<sub>2</sub>H yield (entry 4). A similar “metal effect” was also observed in oxidative photodegradation studies [15].

Entries 7–9 of Table 1 show the effect of the irradiation conditions on the HCO<sub>2</sub>H yield. To study this effect, the photocatalytic reactor was purposefully equipped with two light sources, consisting of a Vis lamp (RADIUM Xe-Halogen lamp 400 W) and UV source (SANOLUX HRC UV-VIS lamp 300 W), with the latter producing also

**Table 1**

Effect of sensitizer, pH of the medium and light source on the yield of formic acid produced by photocatalytic reduction of CO<sub>2</sub>.

| Entry | Catalyst <sup>a</sup>               | pH | Light source <sup>b</sup> | HCO <sub>2</sub> H yield               |                            |
|-------|-------------------------------------|----|---------------------------|--|----------------------------|
|       |                                     |    |                           | mg l <sup>-1</sup> g cat <sup>-1</sup> | $\mu\text{mol g cat}^{-1}$ |
| 1     | TiO <sub>2</sub>                    | 3  | S/H                       | 120.5                                  | 131.0                      |
| 2     | TiO <sub>2</sub> -H <sub>2</sub> Pc | 3  | S/H                       | 69.0                                   | 75.0                       |
| 3     | TiO <sub>2</sub> -CuPc              | 3  | S/H                       | 191.8                                  | 208.5                      |
| 4     | TiO <sub>2</sub> -ZnPc              | 3  | S/H                       | 81.5                                   | 88.5                       |
| 5     | TiO <sub>2</sub> -CuPc              | 7  | S/H                       | 58.3                                   | 63.4                       |
| 6     | TiO <sub>2</sub> -CuPc              | 13 | S/H                       | 60.0                                   | 65.2                       |
| 7     | TiO <sub>2</sub> -CuPc              | 3  | S                         | 30.0                                   | 32.6                       |
| 8     | TiO <sub>2</sub> -CuPc              | 3  | H                         | 48.6                                   | 52.2                       |
| 9     | TiO <sub>2</sub> -CuPc              | 3  | –                         | –                                      | –                          |

<sup>a</sup> Catalyst loading is 0.05 g and the amount of sensitizer 6.65  $\mu\text{mol/g TiO}_2$  (Tioxide Huntsman).

<sup>b</sup> S=SANOLUX HRC UV-VIS lamp 300 W; H=RADIUM Xe-Halogen lamp 400 W. Irradiation time 8 h.

a limited Vis component (see Supporting Information for detailed lamp emission spectra). It is seen that, while in the dark no HCO<sub>2</sub>H could expectedly be detected (entry 9), the maximum HCO<sub>2</sub>H production was achieved when both UV and Vis components were provided to the catalytic system (entry 3). A similar trend was also observed in the photocatalytic degradation of 4-nitrophenol in water by Copper porphyrins and phthalocyanines-TiO<sub>2</sub> composites [1522]. Taken together, these findings reinforce the view that both the semiconductor and the sensitizer component should be properly photoexcited to achieve maximum photocatalytic efficiency. According to what previously hypothesized [22–24], it appears likely that the beneficial effects on the photoreactivity is probably due to cooperative mechanisms induced by appropriate wavelengths.

Because the pH of the reaction medium is crucial for the efficient photoreduction of CO<sub>2</sub> [25], it was necessary to identify the appropriate pH value that allowed for the best HCO<sub>2</sub>H. To this purpose, three independent reactions were run under acidic, neutral, and alkaline conditions, respectively (Table 1, entries 3, 5, 6, respectively) and the initial pH values were not changed or checked throughout the process. Data in Table 1 suggest that yield in photosynthesized formic acid doubles on lowering the pH of the medium from neutral (and alkaline) to moderately acidic values. This may be ascribed to a favourable protonation and subsequent desorption of the formed species from the TiO<sub>2</sub> surface [2,25], which should then be able to get engaged in successive catalytic runs. On the other hand, under neutral or alkaline conditions, it is likely that HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> ions interfere with the photoreduction process, both ions being able to behave as radical scavengers [26].

### 4. Conclusions

In this work, we have shown that metal-free, Cu(II)- or Zn(II) tetrakis [4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)]-phthalocyanines loaded over TiO<sub>2</sub> (anatase), already known for their high photocatalytic activity in the photodegradation of organic pollutants in water, catalyze as much efficiently the reduction of CO<sub>2</sub> to formic acid in water under UV-vis irradiation. Cu(II)Pc/TiO<sub>2</sub> shows the best catalytic performance in terms of formic acid yields, surpassing in efficiency other similar catalytic systems.

Additional benefits are the high stability of composites, the mild conditions under which reactions are run (room temperature, moderate acidic pH), and the avoidance of organic additives (e.g., radical scavengers) that are usually necessary to increase the catalytic efficiency [17].

In view of their low environmental impact, low potential cost, and efficient power conversion, these multipurpose materials show

promise in the search for sustainable methods for CO<sub>2</sub> valorization. It is obviously needed to widen the study to other different MPCs supported on TiO<sub>2</sub> for the sake of comparison and to try to clarify the mechanistic aspects in the light of these surprising experimental results.

### Acknowledgements

L. P. and G. M. wish to acknowledge MIUR for economical support (PON01\_02257); G. V. and G. M. wish to thank to PONA3\_00334 “2HE” for financial support. L. D., C. F. and C. A. wish to thanks CNR /CCOM for economical support. D. Benedetti is acknowledged for his technical assistance. Regione Puglia MIUR PON Ricerca e Competitività 2007–2013 Avviso 254/Ric. del 18/05/2011, Project PONA3 00369 “Laboratorio SISTEMA”.

### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2014.05.008>.

### References

- [1] M. Poliakoff, J.M. Fitzpatrick, T.R. Farren, P.T. Anastas, *Science* 297 (2002) 807–810.
- [2] (a) L. Schmidt-Mende, J.K. Stolarczyk, S.N. Habisreutinger, *Angew. Chem. Int. Ed.* 52 (2013) 7372–7408; (b) M. Aresta, A. Dibenedetto, *Dalton Trans.* 28 (2007) 2975–2992.
- [3] V. Jeyalakshmi, R. Mahalakshmy, K.R. Krishnamurthy, B. Viswanathan, *Mater. Sci. Forum* 734 (2013) 1–62.
- [4] M.A. Henderson, *Surf. Sci. Rep.* 66 (2011) 185–297.
- [5] F. Jo, *ChemSusChem* 1 (2008) 805–808.
- [6] M. Grasmann, G. Laurenczy, *Energy Environ. Sci.* 5 (2012) 8171–8181.
- [7] P.G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* 99 (1999) 475–493.
- [8] W. Leitner, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2207–2221.
- [9] (a) T.V. Magdesieva, T. Yamamoto, D.A. Tryk, A. Fujishima, *J. Electrochem. Soc.* 149 (2002) D89–D95; (b) M. Aresta, A.A. Dibenedetto, *Angelini Chem. Rev.* 113 (2013) 1709–1742.
- [10] T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature* 277 (1979) 637–638.
- [11] (a) V. Jeyalakshmi, K. Rajalakshmi, R. Mahalakshmy, K.R. Krishnamurthy, B. Viswanathan, *Res. Chem. Intermed.* 39 (2013) 2565–2602.
- [12] V. Jeyalakshmi, R. Mahalakshmy, K.R. Krishnamurthy, B. Viswanathan, *Indian J. Chem. Sect. A* 51 (2012) 1263–1283.
- [13] C. Wang, R. Thompson, J. Baltrus, C. Matranga, *J. Phys. Chem. Lett.* 1 (2010) 48–53.
- [14] S. Girish Kumar, L. Gomathi Devi, *J. Phys. Chem. A* 115 (2011) 13211–13241 (see also references therein).
- [15] G. Mele, G. Ciccarella, G. Vasapollo, E. García-López, L. Palmisano, M. Schiavello, *Appl. Catal. B* 38 (2002) 309–319.
- [16] (a) Z. Zhihuan, F. Jimin, W. Zhizhong, *J. Clean. Prod.* (15) (2007) 1894–1897; (b) Z. Zhihuan, F. Jimin, W. Zhizhong, *J. Clean. Prod.* 17 (2009) 1025–1029.
- [17] J.R. Premkumar, R. Ramaraj, *Chem. Commun.* (1997) 343–344.
- [18] J. Alzeer, P.J.C. Roth, *Chem. Commun.* (2009) 1970–1971.
- [19] O. Ishitani, C. Inoue, Y. Suzuki, T. Ibusuki, *J. Photochem. Photobiol. A: Chem.* 72 (1993) 269–271.
- [20] K. Hirano, K. Inoue, T. Yatsu, *J. Photochem. Photobiol. A: Chem.* 64 (1992) 255–258.
- [21] (a) S. Kaneco, H. Kurimoto, Y. Shimizu, K. Ohta, T. Mizuno, *Energy* 24 (1999) 21–30.
- [22] G. Mele, R. Del Sole, G. Vasapollo, E. García-López, L. Palmisano, M. Schiavello, *J. Catal.* 217 (2003) 334–342.
- [23] K.T. Ranjit, I. Willner, S. Bossman, A. Braun, *J. Phys. Chem. B* 102 (1998) 9397.
- [24] G. Mele, E. García-López, L. Palmisano, G. Dyrda, R. Słota, *J. Phys. Chem. C* 111 (2007) 6581–6588.
- [25] A. Piscopo, D. Robert, J.V. Weber, *Appl. Catal., B* 35 (2001) 117–124.
- [26] N.M. Dimitrijevic, B.K. Vijayan, O.G. Poluektov, T. Rajh, K.A. Gray, H.Y. He, P. Zapol, *J. Am. Chem. Soc.* 133 (2011) 3964–3971.

Giuseppe Mele<sup>a,\*</sup>

Cosimo Annese<sup>c</sup>

Alberto De Riccardis<sup>a,b</sup>

Caterina Fusco<sup>c</sup>

Leonardo Palmisano<sup>d</sup>

Giuseppe Vasapollo<sup>a</sup>

Lucia D'Accolti<sup>b,c</sup>

<sup>a</sup> Dipartimento di Ingegneria dell'Innovazione  
Università del Salento, Via Arnesano, 73100, Lecce,  
Italy

<sup>b</sup> Dipartimento di Chimica, Università degli Studi di  
Bari “Aldo Moro”, via Orabona 4, 70126 Bari, Italy  
<sup>c</sup> CNR-Istituto di Chimica dei Composti  
Organometallici (ICCOM), Bari Section, via Orabona  
4, 70126 Bari, Italy

<sup>d</sup> Dipartimento di Energia, Ingegneria  
dell'Informazione e Modelli Matematici, DEIM  
Università di Palermo Viale delle Scienze, Ed. 6, 90128  
Palermo, Italy

\* Corresponding author at: Dipartimento di  
Chimica, Università degli Studi di Bari “Aldo Moro”,  
via Orabona 4, 70126 Bari, Italy.  
Tel.: +39 0805442068.

26 September 2013

8 May 2014

10 May 2014

Available online 17 May 2014