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Photocatalytic degradation of 4-nitrophenol in aqueous suspension by using polycrystalline TiO_2 impregnated with functionalized Cu(II)–porphyrin or Cu(II)–phthalocyanine

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Abstract

The photocatalytic activity of polycrystalline TiO_2 samples impregnated with functionalized Cu(II)- or metal-free porphyrins has been investigated. A probe reaction, i.e., 4-nitrophenol (4-NP) photodegradation in aqueous suspension, has been used. The results indicated that the presence of the sensitizers is beneficial for the photoactivity and suggest an important role of Cu(II). A comparison with similar samples impregnated with modified Cu(II)- and metal-free phthalocyanines showed that the presence of porphyrin is more beneficial both for the decomposition rate of 4-nitrophenol and for the disappearance of nonpurgeable organic carbon (NPOC). Experiments were carried out by using cutoff and interference filters and a cooperative mechanism involving the photoactivation of both TiO_2 and sensitizer is proposed.

Keywords: Porphyrin; Cu(II)–porphyrin; Phthalocyanine; Cu(II)–phthalocyanine; TiO_2 photocatalysts; 4-Nitrophenol photodegradation

1. Introduction

Photodegradation of organic compounds in water by means of economically advantageous and environmental friendly processes is a topic of growing interest and much attention has been devoted in recent years to TiO_2-based photocatalysts for the oxidative degradation of various kinds of organic pollutants [1–5].

A goal of both academic and industrial researches is to obtain new catalytic systems having an enhanced activity compared with the simply TiO_2-catalyzed processes.

Phthalocyanines (Pcs) and porphyrins (Pps) have been used as photocatalysts for a large variety of oxidation reactions of phenol derivatives and some mechanistic aspects have also been investigated [6–9]. Metal–phthalocyanines (MPcs) are efficient photosensitizers and catalysts for many reactions [10] and, due to their high photostability and ability to absorb light, offer many advantages in comparison to the more popular methylene blue and rose Bengal dyes.

Few papers concern their use associated which polycrystalline TiO_2 samples as efficient photocatalytic systems used for the degradation of organic pollutants in water [11–14]. These combined systems showed an improved activity compared to the well-known and widely studied bare TiO_2 samples.

Although phthalocyanines and metal–phthalocyanines in oxidative media are reported to be more resistant than porphyrins [15], both of them present real perspectives as (photo)-catalysts because their relative stability depends on their molecular structure, reaction conditions, irradiation time, temperature, light intensity, pH, and whether they are supported or not. The chemistry of porphyrin derivatives has played an important role especially during the past 10 years in particular branches of new material science and many researchers have on-going projects on the synthesis of variously substituted compounds aimed to obtain new "functional materials." The latter have found an application for the construction of solar cells as light absorbents in organic dyes displaying notable stability and unique chemical, physical, and spectroscopic properties.

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Moreover, studies on the capability of porphyrins and metal–porphyrins to give rise to photoinduced electron transfer processes and to present gas sensors properties have been also reported [16–20].

In a recent paper [21] Héquet and co-workers compare the photocatalytic activity of an hemine (which is an iron porphyrin) with an iron sulfophthalocyanine and with a bare TiO_2 (anatase) sample affording the degradation of atrazine by using a mercury UV lamp. TiO_2 showed better degradation performance compared with the iron porphyrin and iron porphyrin derivatives. However, all the catalyzed processes are reported to be more efficient than the uncatalyzed ones.

The preparation of polycrystalline TiO_2 samples impregnated with different Cu(II)–phthalocyanines (TiO_2–CuPc) for the photocatalytic degradation of 4-nitrophenol (4-NP) has recently been performed [22]. The presence of modified CuPc was found to be beneficial especially for the photoactivation of TiO_2 (anatase), while in only few cases a slightly enhanced photoactivity for TiO_2 (rutile) was observed.

In this paper some Cu(II)–porphyrins opportunely functionalized with sterically hindered alkyl groups were prepared in order to obtain substrates soluble in organic solvents and hence suitable for their impregnation onto the TiO_2 surface. The peripheral substitution in such molecules and the possibility of coordinating different metals is important for the design of functional dyes and molecular devices. Moreover, a very recent paper [23] reports that the modification of the structure of a porphyrin dye caused a variation of the recombination rate between injected electrons in the TiO_2 and the anchored oxidized dye.

It is worth noting that many molecular analogies exist between phthalocyanines and porphyrins, such as a characteristic macrocyclic structure with extended π-electron systems and the presence of metal ions (or alternatively two hydrogen atoms) in the middle of the macrocycle.

Consequently the photocatalytic activity of polycristalline TiO_2 samples impregnated with a functionalized Cu(II)–porphyrin was compared with that of some selected samples impregnated with a functionalized Cu(II)–phthalocyanine for a probe reaction, i.e., 4-NP photodegradation [24]. In this paper, consequently, in order to investigate the role of the metal some TiO_2 samples impregnated with the corresponding metal-free porphyrin and metal-free phthalocyanine were prepared and tested.

2. Experimental

2.1. NMR, IR, and LC-MS measurements

The water used was purified by a Milli-Q/RO system (Millipore) resulting in a resistivity, ρ, of more than 10 $M\Omega$ cm. Melting points were determined on an electrothermal apparatus. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 at room temperature and chemical shifts are reported in ppm units with respect to the reference frequency of tetramethylsilane, Me_4Si.

IR and MS spectra were performed on Perkin-Elmer 683 and Hewlett-Packard GC/Mass MSD 5971 instruments, respectively.

Mass spectrometry analyses were carried out by using a LC mass spectrometer 1100 Series (Agilent) equipped with an atmospheric pressure chemical ionization (APCI) interface. The samples, dissolved in chloroform, were introduced into the mass spectrometer injected by an autosampler spraying a methanol solution at a flow rate of 0.5 mL/min. A heated nebulized spray was continuously introduced into a point corona discharge region using nitrogen to nebulize and sheath the liquid inlet.

Ions were extracted via a heated capillary to a skimmer lens arrangement at reduced pressure and transferred by an octapole to the main analytical quadrupole assembly. The instrumental conditions were as follow: drying gas (nitrogen) 13 L/min, nebulizer pressure 60 psi, drying gas temperature 350 °C, vaporizer temperature 500 °C, capillary voltage 3000 V, corona current 4.0 µA, mass range 500–2000 amu.

2.1.1. Synthesis of the [5,10,15,20-tetra(4-tert-butylphenyl)]porphyrin (H_2Pp)

4-*tert*-butylbenzaldehyde (1.622 g, 10 mmol), pyrrole (0.67 g, 10 mmol), and $BF_3 \cdot OEt_2$ (0.160 g, 1.2 mmol) were dissolved in 200 mL of chloroform and stirred in a 250-mL round-bottom flask at room temperature under nitrogen atmosphere. After 2 h 1.816 g (0.8 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added and the solution was stirred for 2 h more.

After solvent evaporation the crude of reaction was purified by column chromatography (silica, CH_2Cl_2/hexane, 7/3) and product was recovered in 40% yields and characterized by LC-MS, FT-IR, ^1H NMR, ^{13}C NMR, and UV–vis analyses. The melting point of H_2Pp solid was $>$ 350 °C. LC-MS (APCI interface) observed ($M - H^+$): 839 ($M + 1$) amu, calculated M: 838 amu. FT-IR: 3313, 2953, 2920, 2851, 1736, 1461, 1262, 1105, 964, 803, 789, 734, 713 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ: 8.87 (s, 8H), 8.14 (d, $J = 8.2$ Hz, 8H), 7.75 (d, $J = 8.2$ Hz, 8H), 1.61 (s, 36H), -1.4 (s, br, 2H). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 150.4, 139.2, 134.5, 129, 128.2, 123.6, 120.1, 24.9, 31.7.

UV–vis (nm) $\lambda = 423$ (Soret band); 518, 554, 591, 648 (Q bands).

2.1.2. Synthesis of the Cu(II)[(5,10,15,20-tetra(4-tert-butylphenyl)]porphyrin (CuPp)

An excess of $CuCl_2$ (5.0 mmol) was added to a solution obtained dissolving 0.840 g (1.0 mmol) of H_2Pp in 200 mL of dichloromethane. The mixture was stirred for 2 h and monitored by TLC (thin-layer chromatoghaphy) analysis until the complete disappearance of the starting material. The crude of reaction was filtered to remove the unreacted solid salt and further purified by column chromatography (silica,

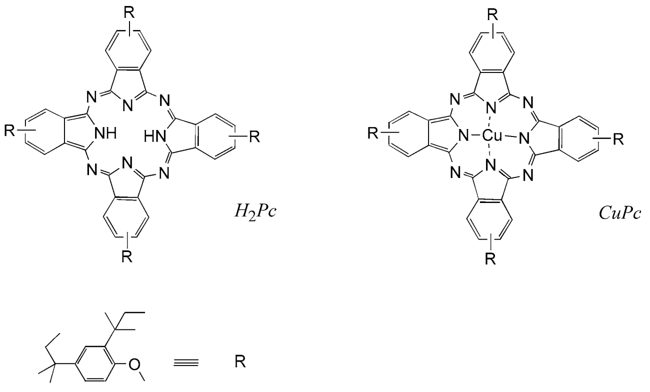


Fig. 1. Molecular structure of H_2Pc and CuPc.

CH_2Cl_2/Hexane, 7/3). CuPp was recovered in 90% yields and characterized by LC-MS, FT-IR, UV–vis analyses. The melting point of CuPp solid was $> 350\,^\circ C$. LC-MS (APCI interface) observed $(M - H^+)$: 900 $(M + 1)$ amu, calculated M: 899 amu. FT-IR: 2953, 2922, 2852, 1731, 1461, 1344, 1265, 1108, 1070, 997, 809, 802, 741, 720 cm^{-1}. UV–vis (nm) $\lambda = 417$ (Soret band); 540, 576 (Q bands).

2.1.3. Synthesis of the Cu(II) tetrakis[4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)]phthalocyanine (CuPc) and of the tetrakis[4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)]-phthalocyanine (H_2Pc)

The molecular structures of H_2Pc and CuPc are shown in Fig. 1 and their preparation has been previously reported [22].

2.1.4. Preparation of TiO_2–CuPc, TiO_2–H_2Pc, TiO_2–CuPp, and TiO_2–H_2Pp samples

TiO_2 (anatase) and TiO_2 (rutile) were kindly provided by Tioxide Huntsman. The loaded samples used as photocatalysts for the photoreactivity experiments were prepared by impregnating TiO_2 (Tioxide, anatase phase, specific surface area 8 m^2/g) with various amounts of CuPp (3.30, 5.55, 6.65, 8.35, 11.10, and 13.30 μmol/g TiO_2); H_2Pp (6.65 and 11.10 μmol/g TiO_2); CuPc (6.65 μmol/g TiO_2), H_2Pc (6.65 and 11.10 μmol/g TiO_2), and TiO_2 (Tioxide, rutile phase, specific surface area 7 m^2/g) with various amounts of CuPp (3.90, 6.65 and 11.10 μmol/g TiO_2); H_2Pp (6.65 and 11.10 μmol/g TiO_2). The sensitizers were dissolved in 10 mL of $CHCl_3$ (or CH_2Cl_2) and 2 g of finely ground TiO_2 was added to this solution. The mixture was stirred for 3–4 h and the solvent was removed under vacuum.

The code used for the samples is the following: the figure indicates the micromoles of sensitizer used for the impregnation of 1 g of TiO_2, A or R the anatase or rutile phases, CuPp and CuPc the copper porphyrin and the copper phthalocyanine, and H_2Pp and H_2Pc the metal-free porphyrin and the metal free phthalocyanine. For instance 6.65-TiO_2(A)–H_2Pp represents the sample prepared by using 6.65 μmol of metal-free porphyrin to impregnate 1 g of TiO_2 (anatase).

2.2. X-ray diffraction (XRD)

X-ray powder diffraction analysis of all of the samples was carried out at room temperature by a Philips PW 1130 generator and PW 1050 goniometer using Ni-filtered Cu-K_α radiation.

2.3. Specific surface area determination (BET)

The specific surface areas were measured by the single-point BET method using a Flow Sorb 2300 apparatus (Micromeritics International Corp.).

2.4. Diffuse reflectance spectroscopy (DRS)

The spectra were obtained in air at ca. 300 K in the wavelength range 250–800 nm using a Shimadzu UV-2401 PC spectrophotometer with $BaSO_4$ as the reference material.

2.5. Photoreactivity experiments

A Pyrex batch photoreactor of cylindrical shape containing 0.5 L of aqueous suspension was used. 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 125 W medium pressure Hg lamp (Helios Italquartz, Italy) was immersed within the photoreactor and the photon flux emitted by the lamp was $\Phi_i = 13.5\ mW/cm^2$. It was measured by using a UVX Digital radiometer (300–400 nm) leaned against the external wall of the photoreactor containing only pure water. O_2 was bubbled into the suspensions for ca. 0.5 h before switching on the lamp and throughout the occurrence of the photoreactivity experiments. The initial 4-NP (BDH) concentration was 20 mg/L and the amount of catalyst used for all the experiments was 0.8 g/L. The transmitted light in the presence of this quantity, measured by using the UVX Digital radiometer as reported before in the case of pure water, was negligible, indicating that most of the radiation was absorbed. The initial pH of the suspension was adjusted to 4.0 by the addition of H_2SO_4 (Carlo Erba RPE), and the temperature inside the reactor was held at ca. 300 K, due to a continuous circulation of water in the jacket around the photoreactor. The photoreactivity runs lasted 6.0 h. Samples of 5-mL volume were withdrawn from the suspensions every 3 or 5 min during the first 30 min of irradiation and subsequently every 30 or 60 min. The catalysts were separated from the solution by filtration through 0.45-μm cellulose acetate membranes (HA, Millipore). The quantitative determination of 4-NP was performed by measuring its absorption at 315 nm with a spectrophotometer Shimadzu UV-2401 PC. Finally, nonpurgeable organic carbon (NPOC) determinations were carried out by using a Shimadzu total organic carbon analyzer 5000-A. An additional set of selected experiments was carried out in the setup sketched in Fig. 2 consisting of an arc lamp supply (8540 Oriel Corp., USA)

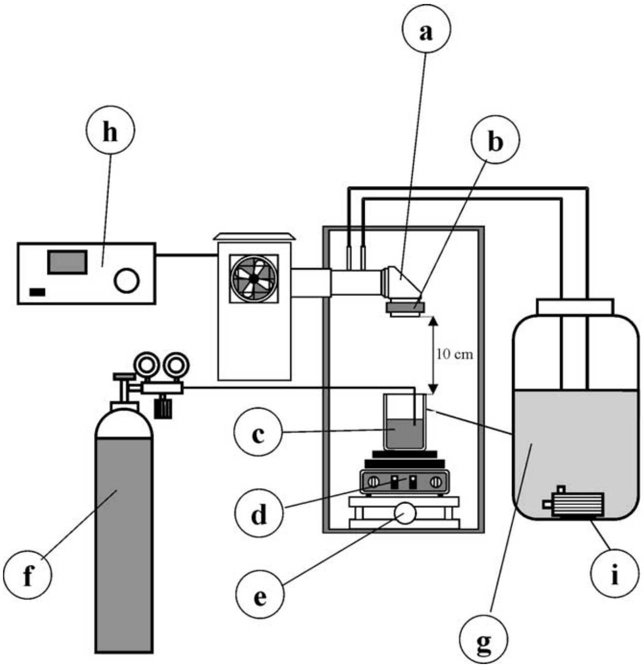


Fig. 2. Setup of the runs carried out by using filters: (a) illuminator–collimator, (b) position for filters, (c) photoreactor, (d) magnetic stirrer, (e) elevator, (f) oxygen cylinder, (g) water reservoir, (h) power supply, and (i) pump.

equipped with a 1000 W Hg–Xe lamp (Hanovia) and with a system of collimating lenses. A 50-mL batch photoreactor was used and some experiments were performed by using a 420-nm cutoff filter (Oriel Corp.) or a 370-nm interference filter (Oriel Corp., bandwidth of 20 nm). The initial 4-NP (BDH) concentration was 20 mg/L and the amount of catalyst used for all the experiments was 0.8 g/L. The catalyst also in this case was separated by filtration through 0.45-μm cellulose acetate membranes (HA, Millipore). The duration of the experiments was 1 h and the UV analyses of 4-NP were carried out by using 1-mL samples withdrawn every 3 or 5 min.

In order to obtain the quantum efficiencies (reported in Table 1) for the runs carried out in the 0.5-L photoreactor, the ferrioxalate actinometer method was used for measuring the photon flow inside the photoreactor [25]. The absorbance of the actinometer sample was measured at 510 nm. The value of the photon flow was 0.635×10^{-5} einstein/(s L).

3. Results and discussion

3.1. Synthesis of H_2Pp and CuPp

The synthesis of the metal-free porphyrin (5,10,15,20-tetra(4-*tert*-butylphenyl)porphyrin, H_2Pp, reported in Scheme 1, was performed according to the procedure similar to that reported in the literature [26,27] reacting 4-*tert*-butylbenzaldehyde with pyrrole (1:1 molar ratio) in chloroform at room temperature for 2 h in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). More de-

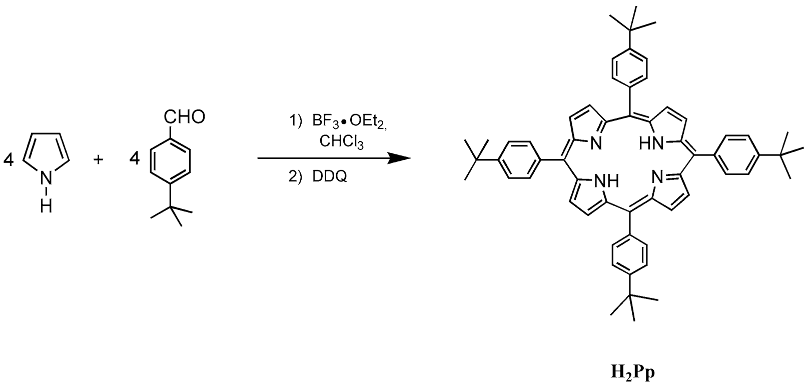
Table 1
List of the samples used together with the BET specific surface areas, the total coverage areas due to the porphyrin molecules, the initial photoreaction rates, and the quantum efficiencies determined by using the 0.5-L batch photoreactor

Samples[a]	BET specific surface areas SSA (m^2/g)	Calculated total areas[b] (m^2)	$r_0 \times 10^{10}$ (mol/(s L))	$r'_0 \times 10^{10}$ (mol/(s L m^2))	Quantum efficiencies η (%)
TiO_2(A)	8		467	146	0.7
6.65-TiO_2(A)–H_2Pp	8	9	606	189	0.9
11.10-TiO_2(A)–H_2Pp	8	15	569	178	0.9
3.30-TiO_2(A)–CuPp	8	4.5	595	190	0.9
5.55-TiO_2(A)–CuPp	8	7.5	1225	383	1.9
6.65-TiO_2(A)–CuPp	8	9	1162	363	1.8
8.35-TiO_2(A)–CuPp	8	11	1087	352	1.7
11.10-TiO_2(A)–CuPp	8	15	950	315	1.5
13.30-TiO_2(A)–CuPp	8	18	854	271	1.3
6.65-TiO_2(A)–CuPc	8	9	755	236	1.2
6.65-TiO_2(A)–H_2Pc	8	9	454	142	0.7
11.10-TiO_2(A)–H_2Pc	8	15	359	122	0.5
TiO_2(R)	7		16	6	0.02
3.90-TiO_2(R)–CuPp	7	5	30	10.7	0.04
6.65-TiO_2(R)–CuPp	7	9	17	6.1	0.02
11.10-TiO_2(R)–CuPp	7	15	16	5.7	0.02
6.65-TiO_2(R)–H_2Pp	7	9	13	4.6	0.02
11.10-TiO_2(R)–H_2Pp	7	15	7	2.5	0.01

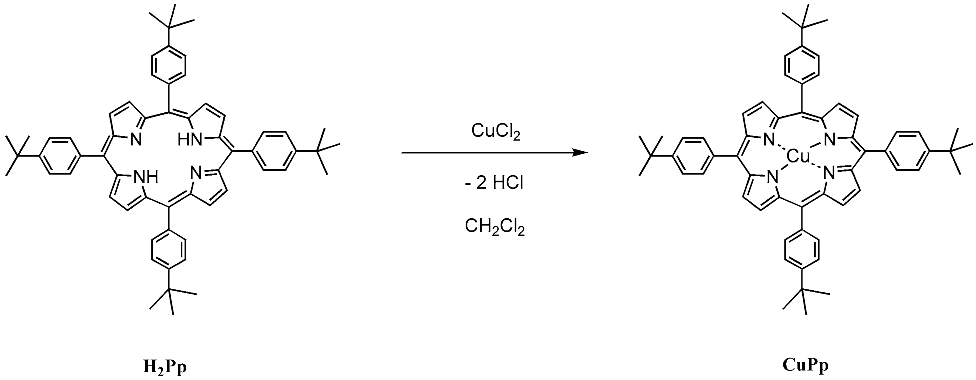
Lamp: 125 W medium pressure Hg lamp. Photocatalyst: 0.8 g/L. Initial 4-NP concentration: 20 mg/L. $T = 300$ K. The values reported in the table are the average of three measurements.

[a] TiO_2(A) and TiO_2(R) used for these experiments were provided by Tioxide Huntsman.

[b] The calculated areas refer to 1 g of TiO_2. The surface area for a single porphyrin molecule was approximate to 2.25 nm^2/molecule. The porphyrins were supposed flat onto the TiO_2 surface.



Scheme 1. Scheme of reaction for the synthesis of (5,10,15,20-tetra(4-*tert*-butylphenyl)porphyrin (H_2Pp).



Scheme 2. Scheme of reaction for the synthesis of the porphyrin metal complexes.

tails on the preparation and purification of H_2Pp have been previously reported (see Section 2).

The isolated porphyrin derivative was characterized by spectral data. UV–vis spectra showed a characteristic strong band centered at $\lambda = 423$ nm (Soret band) and the absorptions, respectively, at 518, 554, 591, and 648 nm (Q bands).

The liquid mass spectra showed the positively charged $M - H^+$ adduct at 839.6 $(M + 1)$ amu, as expected by using the APCI interface. ^1H NMR, ^{13}C NMR and FT-IR spectra were also consistent with the structure of the isolated compound.

H_2Pp was successively used as ligand to coordinate the Cu(II) ion for the synthesis of the porphyrin metal complex, CuPp, through the general protocol of metal complexation as shown in Scheme 2 and described under Section 2. The coordination of the metal by the metal-free porphyrin ligand in solution was easily monitored by TLC analyses. Spectral data for the isolated compound were consistent with the structure of the Cu(II)–porphyrin complex.

3.2. *X-ray diffraction and diffuse reflectance spectroscopy*

The X-ray diffractograms of all of the loaded samples indicated that no modification of the starting anatase or rutile phases of the bare TiO_2 supports occurred after the impregnation treatments.

Fig. 3 shows the diffuse reflectance spectra in air of the bare TiO_2(A) and some TiO_2(A)–CuPp and TiO_2(A)–H_2Pp catalysts recorded in the range 250–800 nm.

It is worth noting that no shift of the band gap edge of TiO_2 can be observed for all the loaded samples. Nevertheless they reflect light less significantly than the bare support and their absorption increases by increasing the loading.

DR spectra of TiO_2(A)–CuPp and TiO_2(A)–H_2Pp samples present shapes, relative intensities and maximum absorption values that are similar to those observed for CuPp and H_2Pp in $CHCl_3$ solution (see Fig. 3, inset).

As a consequence of this comparison, we could presume that there is only a negligible molecule–molecule dye aggregation onto the TiO_2 particles both for the least heavily loaded samples and for the most heavily ones, for which some molecule–molecule interactions cannot be excluded.

TiO_2(A)–CuPp samples showed a characteristic strong absorption band centered at 417 nm (Soret band) and at 540, and 576 nm (Q bands).

A strong absorption at $\lambda = 423$ nm (Soret band) and absorptions decreasing in intensity at 518, 554, 591, and 648 nm (Q bands) can be found, instead, in the spectra of TiO_2(A)–H_2Pp samples.

Similar DR spectra, not shown for the sake of brevity, were observed when the sensitizers used in this work were supported onto rutile TiO_2. DR spectra of the samples impregnated with the phthalocyanine derivatives are also not

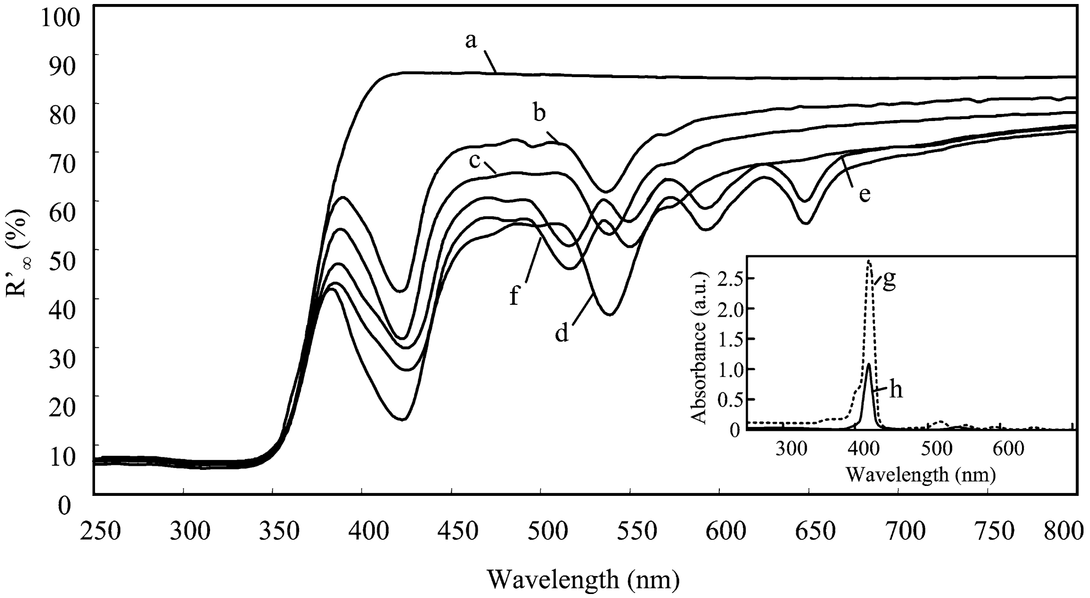


Fig. 3. Diffuse reflectance spectra of bare TiO_2 and differently loaded samples obtained by impregnation of TiO_2 with CuPp or H_2Pp. TiO_2(A) (a); 5.55-TiO_2(A)–CuPp (b); 6.65-TiO_2(A)–CuPp (c); 11.10-TiO_2(A)–CuPp (d); 6.65-TiO_2(A)–H_2Pp (e); 11.10-TiO_2(A)–H_2Pp (f). Inset: spectra in $CHCl_3$ of TiO_2(A)–H_2Pp (g) and TiO_2(A)–CuPp (h).

reported because they do not differ significantly from those reported in a previous paper for similar samples [22].

3.3. Photoreactivity experiments

A preliminary investigation was carried out in order to establish if the CuPp and H_2Pp supported onto TiO_2 were photostable, i.e., if some decomposition or chemical modification of the supported CuPp and H_2Pp took place under the same conditions used during the photocatalytic experiments. NPOC determinations in the absence of 4-NP indicated no significant release of organic degradation compounds even after long irradiation times (5–7 h). Moreover the supported sensitizers can be recovered quantitatively (and unchanged) from the TiO_2 surface by extraction with chlorinated solvents ($CHCl_3$ or CH_2Cl_2). The absence of structural modifications was confirmed by analytical and spectral data (TLC, UV–vis, ^1H NMR).

The list of the used samples is reported in Table 1 along with the BET specific surface areas, the calculated areas due to the porphyrin molecules, the initial reaction rates for 4-NP disappearance, and the quantum efficiencies. A straight line fits the data collected during the first 30 min of irradiation and consequently the results are reported as zero-order initial rates. No significant induction period for 4-NP concentration decrease was seen. No analyses of intermediates was performed because it was out of the aim of this work, and the 4-NP photodegradation was chosen only as a probe reaction [24]. Dihydroxynitrobenzene isomers were found initially as the intermediates and these compounds absorb mainly in the visible range, not interfering at 315 nm [24].

It can be seen that the samples impregnated with Cu(II)–porphyrins exhibited the highest photoactivity; in particular the best samples appear to be 5.55-TiO_2(A)–CuPp and 6.65-TiO_2(A)–CuPp. The 6.65-TiO_2(A)–CuPc sample is less photoactive than the corresponding 6.65-TiO_2(A)–CuPp sample, and this finding indicates that the beneficial effect of porphyrin as sensitizer is more significant than that showed by phthalocyanine. Moreover the metal-free porphyrin showed a photoactivity slightly higher than the corresponding bare TiO_2, indicating that the porphyrinic macrocycle is photocatalytically active even in the absence of the metal. As far as the loaded TiO_2(R) samples are concerned, no significant improvement of the photoreaction rate was observed for all of the samples compared to bare TiO_2(R) with the exception of the 3.90-TiO_2(R)–CuPp. Nevertheless the reaction rates were in all cases more than one order of magnitude lower than those observed for the loaded TiO_2(A) samples.

As far as the quantum efficiencies values are concerned (see Table 1), their trend is equal to that of the initial reaction rates, and it is worth noting that they are less than the true ones because they were calculated by taking into account the photons impinging on the reacting system.

Nonpurgeable organic carbon concentration versus irradiation time is reported in Fig. 4 for some selected samples. A complete disappearance of organic carbon can be observed after ca. 4 h for the 6.65-TiO_2(A)–CuPp sample. TiO_2(A) appears to be the worst sample, while 6.65-TiO_2(A)–H_2Pp showed a behavior similar to that of 6.65-TiO_2(A)–CuPc in the final steps.

In Table 2 the results of some selected experiments carried out in the setup shown in Fig. 2 in the absence and in the presence of 370 nm interference and 420-nm cutoff filters are reported with the aim of comparing the initial reaction rates of the samples for each kind of irradiation.

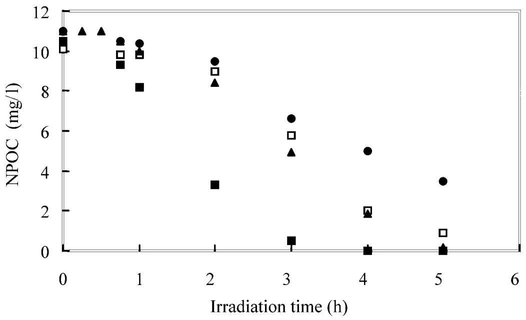


Fig. 4. Nonpurgeable organic carbon concentration (NPOC) versus irradiation time: TiO_2(A) (●); 6.65-TiO_2(A)–CuPp (■); 6.65-TiO_2(A)–H_2Pp (□); 6.65-TiO_2(A)–CuPc (▲).

Table 2
Initial photoreaction rates of the samples used with the setup shown in Fig. 2, without filtered light and by using a 420-nm cutoff and a 370-nm interference filters

Sample[a]	$r_0 \times 10^8$ (mol/(s L))		
	Without filter	370-nm interference filter	420-nm cutoff filter
TiO_2(A)	9.0	2.4	Negligible
6.65-TiO_2(A)–CuPp	14.1	3.9	Negligible
6.65-TiO_2(A)–CuPc	11.9	3.7	Negligible
6.65-TiO_2(A)–H_2Pp	10.8	2.0	Negligible
6.65-TiO_2(A)–H_2Pc	9.6	1.3	Negligible

Lamp: 1000 W Hg–Xe. Photocatalyst: 0.8 g/L. Initial 4-NP concentration: 20 mg/L. $T = 300$ K. The values reported in the table are the average of three measurements.

[a] TiO_2(A) used for these experiments was provided by Tioxide Huntsman.

It can be seen that a negligible photoactivity was observed for all of the samples when the cutoff filter was used. This indicates that the photoexcitation of TiO_2 is essential for inducing the photodegradation of 4-NP. The runs carried out in the absence of filters confirm the results obtained by using the other setup, i.e., both CuPp- and CuPc-loaded samples are more photoactive than the bare TiO_2 sample, but the presence of CuPp as sensitizer was more beneficial.

The two samples impregnated with the metal-free sensitizers were more active than TiO_2(A) and this fact appears to be relevant also because the experiments carried out by using the 370-nm interference filter indicated lower photoactivities of the 6.65-TiO_2(A)–H_2Pp and the 6.65-TiO_2(A)–H_2Pc samples in comparison to TiO_2(A). Moreover, both corresponding samples containing the metal were much more photoactive than the bare TiO_2, although the highest values of reaction rate were obtained always in the absence of filter, due to the higher light intensity impinging on the reacting system.

In light of the above results it can be suggested that it is necessary to photoexcite both the components of the system, i.e., TiO_2 and the sensitizer, in order to obtain substantial improvement of the photodegradation rate of 4-NP.

It appears likely that the beneficial effect on the photoreactivity is due to a cooperative mechanism, according to that hypothesized for TiO_2 impregnated with Fe(III)–phthalocyanine [11].

A tentative set of reactions explaining the observed photoreactivity behavior is reported below.

3.3.1. Role of TiO_2

$$TiO_2[Cu(II)Sens] \xrightarrow{h\nu\ (<394\text{ nm})} TiO_2[Cu(II)Sens]\left(e^-_{CB} + h^+_{VB}\right). \tag{1}$$

3.3.2. Role of electrons

$${}^3O_2 + e^-_{CB} \rightarrow {}^{\cdot}O_2{}^-, \tag{2}$$

$${}^1O_2\left({}^1\Delta\right) + e^-_{CB} \rightarrow {}^{\cdot}O_2{}^-, \tag{3}$$

$$H_2O_2 + e^-_{CB} \rightarrow {}^{\cdot}OH + OH^-, \tag{4}$$

$$TiO_2[Cu(II)Sens] + e^-_{CB} \rightarrow TiO_2[Cu(I)Sens]. \tag{5}$$

3.3.3. Role of holes

$$OH^- + h^+_{VB} \rightarrow {}^{\cdot}OH, \tag{6}$$

$$H_2O + h^+_{VB} \rightarrow {}^{\cdot}OH + H^+, \tag{7}$$

$$H_2O_2 + h^+_{VB} \rightarrow HO_2{}^{\cdot} + H^+, \tag{8}$$

$$HO_2{}^{\cdot} + h^+_{VB} \rightarrow O_2 + H^+, \tag{9}$$

$$TiO_2[MSens] + h^+_{VB} \rightarrow TiO_2[MSens]^+. \tag{10}$$

3.3.4. Role of sensitizer

$$[MSens] \xrightarrow{h\nu} {}^1[MSens]^* \xrightarrow{\overset{\text{intersystem crossing}}{\text{(isc)}}} {}^3[MSens]^*, \tag{11}$$

$${}^3[MSens]^* + {}^3O_2 \rightarrow [MSens] + {}^1O_2\left({}^1\Delta\right), \tag{12}$$

$${}^3[MSens]^* + {}^3O_2 \rightarrow [MSens]^+ + {}^{\cdot}O_2{}^-, \tag{13}$$

$$TiO_2{}^{3\text{ or }1}[MSens]^* \rightarrow TiO_2[MSens]^+ + e^-_{CB}, \tag{14}$$

$$TiO_2[MSens]^+ + OH^- \rightarrow TiO_2[MSens] + {}^{\cdot}OH, \tag{15}$$

$$TiO_2[MSens]^+ + 4\text{-NP} \rightarrow TiO_2[MSens] + \text{oxidation products}. \tag{16}$$

3.3.5. Role of some reactive intermediates in aqueous phase

$${}^{\cdot}O_2{}^- + H_2O \rightleftarrows HO_2{}^{\cdot} + OH^-, \tag{17}$$

$${}^{\cdot}O_2{}^- + H^+ \rightleftarrows HO_2{}^{\cdot}, \tag{18}$$

$$2HO^{\cdot} \rightarrow H_2O_2, \tag{19}$$

$$2HO_2{}^{\cdot} \rightarrow H_2O_2 + O_2, \tag{20}$$

$$H_2O_2 + {}^{\cdot}O_2{}^- \rightarrow HO^{\cdot} + OH^- + O_2, \tag{21}$$

$$2HO_2{}^{\cdot} + {}^{\cdot}O_2{}^- \rightarrow HO^{\cdot} + OH^- + 2O_2. \tag{22}$$

3.3.6. *Role of metal*

$$TiO_2[Cu(I)Sens] + {}^3O_2 \rightarrow TiO_2[Cu(II)Sens] + {}^{\cdot}O_2{}^{-}, \quad (23)$$

$$TiO_2[Cu(I)Sens] + {}^1O_2({}^1\Delta) \rightarrow TiO_2[Cu(II)Sens] + {}^{\cdot}O_2{}^{-}, \quad (24)$$

$$TiO_2[Cu(I)Sens] + H_2O_2 \rightarrow TiO_2[Cu(II)Sens] + HO^{\cdot} + OH^{-}. \quad (25)$$

3.3.7. *Oxidation reactions in aqueous phase*

$${}^1O_2({}^1\Delta) + \text{4-NP} \rightarrow \text{oxidation products}, \quad (26)$$

$$HO_2{}^{\cdot} + \text{4-NP} \rightarrow \text{oxidation products}, \quad (27)$$

$${}^{\cdot}HO + \text{4-NP} \rightarrow \text{oxidation products}. \quad (28)$$

As reported in Eq. (1), the photoinduced process of charge separation promoted by UV radiation represents the key step of the main process, and the presence of the sensitizer onto TiO_2 does not influence appreciably this process.

In the above set of reactions we have tried to distinguish the roles played by conduction band electrons, valence band holes, and metal-free or copper-coordinated organic sensitizers in the production of reactive intermediates effective for the photodegradation of 4-NP in water.

Analogous to that reported by Wöhrle and co-workers [28], both metal and metal-free porphyrin and phthalocyanine samples can produce ${}^1O_2({}^1\Delta)$ or ${}^{\cdot}O_2{}^{-}$ under irradiation [see Eqs. (11)–(13)] and quantum yields of this process are generally reported to be higher for porphyrin.

Some runs were carried out by using TiO_2(A) or 6.65-TiO_2(A)–CuPp in the presence of furfuryl alcohol [29] with the aim of demonstrating the presence of ${}^1O_2({}^1\Delta)$ in our system. Unfortunately, they were unsuccessfully because the photoreactivity decreased significantly in the presence of furfuryl alcohol for both samples, suggesting that this compound did not react selectively with singlet oxygen in our heterogeneous system and/or a competition with 4-NP on the surface sites could occur.

Literature reports that the route via ${}^1O_2({}^1\Delta)$ is the predominant process in both photodynamic therapy of cancer and photooxidation of many biological and environmental substrates [28,30].

Frackowiak and co-workers [31] report that the yields of triplet state formation of some metal phthalocyanine via i.s.c. (inter system crossing) producing ${}^1O_2({}^1\Delta)$ were higher than for the investigated free phthalocyanine.

Moreover it is known that aggregation and dimerization reduce the lifetimes of the excited state of metal phthalocyanines, due possibly to enhanced radiationless excited state dissipation and, therefore, quantum yields of the singlet oxygen generation [32]. When this kind of sensitizer is supported and well dispersed onto TiO_2 surfaces it is likely that the above phenomena do not play a significant role. Consequently, a monomolecular distribution of the dye onto the TiO_2 surface represents a favorable condition for obtaining an improved photocatalytic activity.

In Table 1 we have reported in the third column, the calculated total areas due to the porphyrin molecules, considering the surface area occupied by a single porphyrin molecule, supposed flat onto the TiO_2 surface, approximately equal to 2.25 nm^2, as reported for a similar compound [33]. Interestingly, we observed the maximum of photocatalytic activity when the molecular coverage was comparable with BET specific surface areas measured for TiO_2 samples.

In the system studied in this work Cu(II) could be reduced to Cu(I) [see Eq. (5)] by electrons of the conduction band of TiO_2 where additional electrons are injected, due to the presence of the sensitizer [11,34]. Subsequently the reoxidation of Cu(I) to Cu(II) not only by ${}^3O_2$ and ${}^1O_2({}^1\Delta)$ [see Eqs. (23) and (24)] but also by hydrogen peroxide produced in solution (25) in the presence of the sensitizer could improve significantly the kinetics of the process due to the higher oxidant properties of ${}^1O_2({}^1\Delta)$ and H_2O_2 on respect to ${}^3O_2$.

${}^{\cdot}O_2{}^{-}$ production along with Eqs. (6)–(8) is essential for inducing the formation of $HO_2{}^{\cdot}$ and ${}^{\cdot}OH$ radicals responsible for oxidant attacks in photocatalytic reactions.

As far as holes are concerned, they can be delocalized in the macrocyclic structure of the sensitizers [see Eq. (10)] contributing to increase the lifetime of the photoproduced pairs and/or to react with surface OH and water according to well-known photocatalytic steps.

It is worth noting that hole transport in p-type organic semiconductors has been also reported [33]: when smooth TiO_2 (anatase) films coated with an amorphous thin film of zinc tetra(4-carboxyphenyl)porphyrin molecules acting as sensitizer are optically excited, the porphyrin stimulates the injection of electrons into the conduction band of TiO_2 while the remaining holes migrate toward the back electrode where they are collected.

This phenomenon could be not important for the most photoactive samples because the dye presumably is not agglomerated onto the surface of TiO_2 particles and it does not form a definite solid. On the other hand, when the dye is present as a layer of an agglomerate solid, occupying the entire surface, no space is left for surface hydroxyl groups and the photoactivity would be lower.

Finally, it should also be taken into account a possible additional oxidation pathway in the homogeneous phase involving a direct interaction between ${}^1O_2({}^1\Delta)$ [see Eq. (26)] or other radical species and the substrate [see Eqs. (27) and (28)].

4. Conclusions

TiO_2 (anatase) samples impregnated with functionalized Cu(II)–porphyrine and Cu(II)–phthalocyanine were more efficient catalysts compared to bare TiO_2 for the photodegradation of 4-nitrophenol with Cu(II)–porphyrine showing a more significant beneficial effect.

The photocatalytic activities of samples impregnated with metal-free porphyrin and metal-free phthalocyanine were always less significant than those of the corresponding samples impregnated with the Cu(II) complexes.

A tentative mechanism based on the formation of $^1O_2(^1\Delta)$, due to the presence of the sensitizers on the TiO_2 surface, is proposed. The rate of electron transfer to this very oxidant-adsorbed species (in addition or alternative to $^3O_2$) from the conduction band of TiO_2 and/or from Cu(I) species possibly produced under irradiation is hypothesized to be mainly responsible for the enhancement of the reaction rate of the global photocatalytic process.

A contribution of a homogeneous oxidative process due to the presence of $^1O_2(^1\Delta)$ and/or other radical species cannot be excluded.

Interestingly, we observed the maximum photocatalytic activity when the molecular coverage was comparable with BET specific surface areas measured for TiO_2 samples.

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