

TRMC, XPS, and EPR Characterizations of Polycrystalline TiO₂ Porphyrin Impregnated Powders and Their Catalytic Activity for 4-Nitrophenol Photodegradation in Aqueous Suspension

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Received: December 17, 2004; In Final Form: April 18, 2005

Characterization of polycrystalline TiO₂ bare or porphyrin impregnated powders, used as photocatalysts for the degradation of 4-nitrophenol (4-NP) in aqueous suspension, was performed by time-resolved microwave conductivity (TRMC) measurements and electronic paramagnetic resonance (EPR) and X-ray photoelectron (XPS) spectroscopies. The presence of porphyrin sensitizers, as the metal-free or Cu [5,10,15,20-tetra (4-*tert*-butylphenyl)] porphyrin, impregnated onto the TiO₂ surface improved the photocatalytic activity of the bare TiO₂. TRMC measurements indicate that the number and lifetime of the photoinduced excess charge carriers increase in the presence of the macrocycles, and EPR and XPS spectroscopies support the mechanistic hypotheses based on the photoreactivity experiments.

Introduction

Phthalocyanines and porphyrins are considered to be very attractive photo- and radiosensitizers that can find extensive application in chemical technology, ecology, medicine, and electronics. In recent years, they have also received increasing attention because of their biological implications for many photocatalytic reactions.

On the other hand, there is nowadays a growing interest in the development of a new class of TiO₂ based hybrid organic/organometallic/inorganic materials where porphyrins, phthalocyanines, and their metal complexes are used as surface modifiers of TiO₂ in various morphologies and crystalline forms.^{1–5}

At the same time, photodegradation of organic pollutants in aqueous media is of topical importance especially in view of the possible development of environmentally sustainable processes and deserves the attention of both academic and industrial research.

The photoactivity of phthalocyanine and porphyrin compounds as sensitizers for a variety of oxidation reactions of phenol derivatives is known, and some mechanistic aspects have been also investigated.^{6,7} In particular, metal phthalocyanines have been shown to be efficient photosensitizers and catalysts for many reactions.⁸

It is also well-known that polycrystalline TiO₂ powders represent a class of innovative photocatalysts widely used for the oxidative degradation of various organic pollutants in water.^{9–13}

Moreover, the modified TiO₂ systems, doped or loaded with some metallic or organometallic species, can present an enhanced photoactivity compared with the corresponding bare TiO₂ samples, depending on the type of metal, reaction, and experimental conditions used.^{14–17}

Recently, the photocatalytic activity of TiO₂ powders impregnated with lipophilic metal-free or Cu porphyrins used as sensitizers for the decomposition of 4-nitrophenol (4-NP) has been investigated.^{18,19} 4-NP photocatalytic degradation was chosen as a probe reaction because it is well-known in the literature.^{13,20}

The presence of the sensitizers was to be found beneficial, and in particular, the Cu porphyrin complex was shown to be the best one.^{18,19}

The main aim of the present paper is to establish through X-ray photoelectron spectroscopy (XPS) and electronic paramagnetic resonance (EPR) techniques the role of copper related to its oxidation state when the Cu porphyrin TiO₂ impregnated samples were used as photocatalysts for the above photoreaction and to justify the beneficial role that different copper species could play in these processes.

Indeed, XPS studies on Cu(II) macrocyclic compounds including copper phthalocyanines and copper porphyrins show Cu2p spectra consisting of two doublets separated by ~20 eV due to the spin–orbit splitting.^{21–25} The presence of a high binding energy satellite accompanying each component of the most intense doublet distinguishes Cu(II) species from the Cu(I) one, and consequently, this technique is suitable to obtain information on the oxidation states of copper.

Similarly, EPR spectroscopy, on the other hand, has been widely used for the study of Cu(II) porphyrins, since this

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technique can provide valuable information about the electronic structure and magnetic properties of these species.^{26,27}

Moreover, TRMC measurements were performed in addition to XPS and EPR studies in order to give useful information on the lifetime of the photoproduced e^- – h^+ pairs on the surfaces of both bare and impregnated TiO_2 samples.

Experimental Section

I. Preparation of the Photocatalysts and Photoreactivity Experiments. TiO_2 (anatase) was kindly provided by Tioxide Huntsman. The loaded samples used as the photocatalysts for the photoreactivity experiments were prepared by impregnating TiO_2 (Tioxide, anatase phase, BET specific surface area $8 \text{ m}^2\cdot\text{g}^{-1}$) with [5,10,15,20-tetra (4-*tert*-butylphenyl)] porphyrin (H_2Pp) or Cu(II) [5,10,15,20-tetra (4-*tert*-butylphenyl)] porphyrin (CuPp) which were prepared as previously reported.¹⁸

TiO_2 (anatase) was impregnated with H_2Pp or with CuPp according to the following procedure: The sensitizer was 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 removed under vacuum.

The code used for the identification of the samples is the following: the figure indicates the micromoles of sensitizer used for the impregnation of 1 g of TiO_2 , (A) the crystalline anatase phase, CuPp the copper porphyrin, and H_2Pp the metal-free porphyrin. For instance, 6.65- $\text{TiO}_2(\text{A})$ - H_2Pp represents the sample prepared by using $6.65 \mu\text{mol}$ of metal-free porphyrin to impregnate 1 g of TiO_2 (anatase).

The photoreactivity experiments for 4-NP degradation were carried out by using a Pyrex batch photoreactor of cylindrical shape containing 0.5 L of aqueous suspension. The photoreactor was provided with a jacket for the cooling water 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 $\Phi_i = 13.5 \text{ mW}\cdot\text{cm}^{-2}$. 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 ~ 0.5 h before switching on the lamp and throughout the occurrence of the photoreactivity experiments. The initial 4-NP (BDH) concentration was $20 \text{ mg}\cdot\text{L}^{-1}$, and the amount of catalyst used for all the experiments was $0.8 \text{ g}\cdot\text{L}^{-1}$. The transmitted light in the presence of this quantity, measured by using the UVX Digital radiometer as before reported 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 1 M H_2SO_4 (Carlo Erba RPE), and the temperature inside the reactor was ~ 300 K. The photoreactivity runs lasted 6.0 h. Samples of 5 mL in 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 $0.45 \mu\text{m}$ cellulose acetate membranes (HA, Millipore). The quantitative determination of 4-NP was performed by measuring its absorption at 315 nm with a Shimadzu UV-2401 PC spectrophotometer.

To check the photochemical stability of the impregnated catalysts, nonpurgeable organic carbon (NPOC) determinations were carried out ad hoc in an aqueous suspension of stirred photocatalysts in the absence of 4-NP and under irradiating conditions similar to those used for the photoreactivity experiments. These analyses did not show any significant release and/or dissolution of organic compound even after 5–7 h of

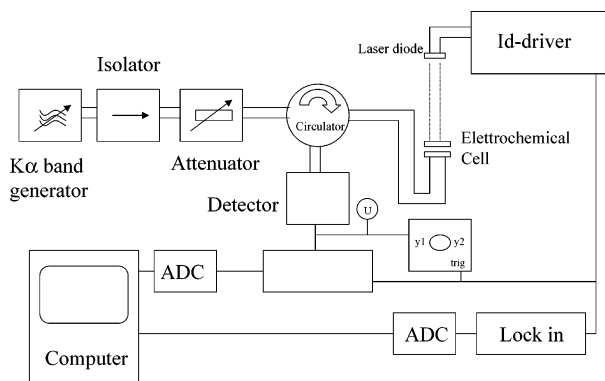


Figure 1. Setup for the time-resolved microwave conductivity (TRMC) experiments.

irradiation times. The absence of any chemical modification or degradation for H_2Pp and CuPp , recovered almost quantitatively from the TiO_2 surface by extraction with CH_2Cl_2 after their use in the photocatalytic experiments, was confirmed by comparison of the analytical and spectral data (TLC, UV–vis, NMR, and LC-MS) that were found to be the same of the freshly synthesized samples.¹⁸

II. Lifetimes of Photoinduced Excess Charge Carrier Measurements. The lifetimes and amount of charge carriers produced during the course of an excitation experiment were measured by the time-resolved microwave conductivity (TRMC) technique.^{28,29} The experimental setup is reported in Figure 1.

This technique is based on measurements of the relative change of the microwave power reflected from the sample. The different reflection of microwave is due to a change of the conductivity of the sample. In these experiments, an excess of charge carriers was produced by illumination with 20 ns pulses of a Nd:YAG laser (JK lasers) at 355 nm. The microwaves were generated by a gun diode (Ka bands 28.5–40 GHz equipment were used) and directed via a circulator to the sample. The reflected microwaves were directed from the sample, via a circulator, to a detector connected to a transient digitizer. Among the prepared samples, 6.65- $\text{TiO}_2(\text{A})$ - H_2Pp and 6.65- $\text{TiO}_2(\text{A})$ - CuPp were studied without any previous treatment. The reference sample was TiO_2 Tioxide anatase ($\text{TiO}_2(\text{A})$).

III. XPS Measurements. XPS measurements were performed with a Leybold LHS10 spectrometer upgraded by a PHOIBOS 100 analyzer/detector system (SPECS, Berlin, Germany) and equipped with a twin anode (Mg $\text{K}\alpha/\text{Al K}\alpha$) non-monochromatized source (operating at 280 W). The base pressure in the instrument was 10^{-9} mbar.

Survey scans (kinetic energy range 200–1500 eV, CRR mode, retarding ratio 30) and high resolution detail spectra (spectral range 50 eV, CAE mode, pass energy 30 eV) were recorded for each sample. The binding energy (BE) spectrometer scale was calibrated by assigning $\text{BeCu}_{2p_{3/2}} = 923.6$ eV and $\text{BeAu}_{4f_{7/2}} = 84.0$ eV. Charging correction was performed by adventitious carbon calibrant ($\text{BeC}_{1s} = 284.8$ eV). Specslab software was employed for analyzing spectra.

XPS characterization of the CuPp/TiO_2 system was performed on samples with a CuPp loading higher than the 6.65- $\text{TiO}_2(\text{A})$ - CuPp sample, since in the latter it was not possible to detect a significant copper signal. In particular, $\text{TiO}_2(\text{A})$ - CuPp was obtained by impregnating TiO_2 powders pressed in the form of a circular self-supporting pellet ($\phi = 13$ mm) with a chloroform (or CH_2Cl_2) solution of CuPp ($10 \text{ mg}\cdot\text{mL}^{-1}$).

Nevertheless, we are confident that they share qualitative features, since important catalytic activity was observed on XPS samples, too.

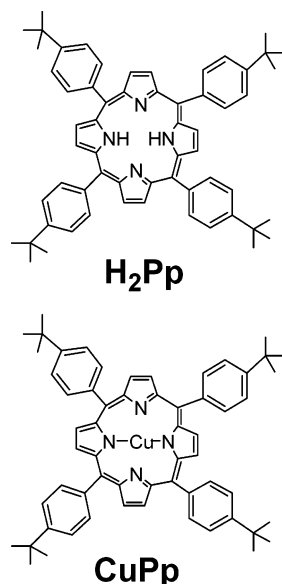


Figure 2. Molecular structures of [5,10,15,20-tetra (4-*tert*-butylphenyl)] porphyrin (H₂Pp) and Cu(II) [5,10,15,20-tetra (4-*tert*-butylphenyl)] porphyrin (CuPp).

IV. EPR Measurements. EPR measurements were carried out at 77 K with a Bruker ER200D spectrometer provided with a T-type double cavity and operating in the X-band (9.55 GHz). Frequency calibration was performed using a 2,2-diphenyl-1-picrylhydrazine (DPPH) standard ($g = 2.0036$). All of the spectra were recorded at 77 K using a microwave power of 19 mW. Computer simulations were used when necessary to check spectral parameters. Aliquots of the catalyst (30–40 mg) were placed into a quartz cell with greaseless stopcocks. Irradiation treatments at 77 K were carried out by placing the cell in a quartz Dewar flask filled with liquid N₂ for 15 min and employing four UV fluorescent lamps (Sylvania F6WBLB-T5, 6 W, maximum at 365 nm). Oxygen adsorption experiments were performed in a conventional high vacuum line made of Pyrex, which is able to achieve dynamic pressures lower than 2×10^{-2} Pa. A fixed dose (about 100 mmol/g of sample) of gas (L'Air Liquide; 99.9%) was admitted in the cell at 77 K, and subsequently, the sample was evacuated at the same temperature for 30 min in order to remove physisorbed oxygen, which could lead to the broadening of the signals.

Results and Discussion

I. Photocatalysts and Photoreactivity Experiments. Recently, the photocatalytic degradation of 4-nitrophenol (4-NP) in aqueous suspension by using polycrystalline TiO₂ impregnated with functionalized metal-free or Cu(II) porphyrin has been reported, the structures of which are reported in Figure 2.¹⁸ Moreover, the diffuse reflectance spectra in air of TiO₂/CuPp and TiO₂/H₂Pp recorded in the range 250–800 nm were also reported. Weak interactions with the surface of TiO₂ can be envisaged because the spectra present shapes, relative intensities, and absorption maxima similar to those observed for CuPp and H₂Pp in CHCl₃ solution. It is reported that appreciable differences in the UV–vis spectra can be observed when porphyrins having polar groups are dissolved in solution or they are loaded onto the surface of polycrystalline TiO₂, due to the occurrence of strong interactions. The spectra of tetra (4-carboxyphenyl) porphyrin, adsorbed onto the surface of nanoparticulate TiO₂, for instance, show evident shifts (5–10 nm) with respect to those of the same compound present in solution.³⁰

TABLE 1: Initial Photoreaction Rates per Used Mass (r_0) and per Unit Surface Area (r_0') of the Catalysts and Photonic Efficiencies (ξ , %) Determined by Using the 0.5 L Batch Photoreactor

| sample ^a | $r_0 \cdot 10^{10}$ ^b (mol·L ⁻¹ ·s ⁻¹) | $r_0' \cdot 10^{10}$ ^b (mol·L ⁻¹ ·s ⁻¹ ·m ⁻²) | $\xi^{b,c}$ (%) |
|---|---|---|--------------------|
| TiO ₂ (A) | 467 | 146 | 0.7 |
| 6.65-TiO ₂ (A)-H ₂ Pp | 606 | 189 | 0.9 |
| 6.65-TiO ₂ (A)-CuPp | 1162 | 363 | 1.8 |

^a The BET specific surface area of the samples used is 8 m²·g⁻¹.

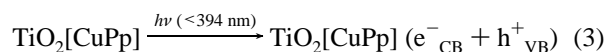
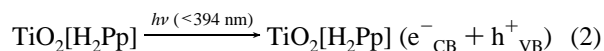
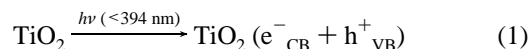
^b The data are the average of three measurements. ^c Photonic efficiency was determined by dividing the initial rate of the photoreaction by the rate of incident photons at 365 nm.

The photocatalytic activity was evaluated by carrying out the degradation of 4-NP for selected runs performed by using bare TiO₂ and some TiO₂ samples impregnated with metal-free and Cu(II) porphyrin.

Although the porphyrinic macrocycle is photocatalytically active even in the absence of the metal, the samples impregnated with Cu(II) porphyrin exhibited the highest photoactivity; in particular, the most photoactive one appeared to be the 6.65-TiO₂(A)-CuPp sample. This finding derived from a systematic investigation aimed to demonstrate the existence of an optimum photoreactivity, due to an optimum for the number of supported Cu porphyrin species (presumably not aggregated and forming a monomolecular distribution) and not engaged surface sites available for 4-NP adsorption.¹⁸

Some selected values of initial reaction rates (zero-order kinetics) are reported in Table 1 for 4-NP disappearance per used mass of the sample (r_0) and per square meter (r_0') of powder. A more significant photoactivity for the sample 6.65-TiO₂(A)-CuPp with respect to both TiO₂(A) and 6.65-TiO₂(A)-H₂Pp can be noticed. Moreover, the photon efficiency for this sample is also the highest.

II. Lifetimes of Photoinduced Excess Charge Carriers. The lifetimes and amount of charge carriers produced during the course of excitation experiments by the time-resolved microwave conductivity (TRMC) technique have been investigated. As reported in eqs 1–3, the photoinduced process of charge separation promoted by UV radiation represents the key step of the main process. The presence of the sensitizer onto TiO₂ influences the lifetime of the recombination hole–electron process.



The results of the lifetime of the charge carriers for the studied samples are reported in Figure 3.

As can be observed in Figure 3, the amount of generated charge is always higher in the case of the loaded samples.

In particular, the 6.65-TiO₂(A)-CuPp sample shows the most significant charge generation and the highest amount of hole–electron pairs available to participate in surface redox reactions with adsorbed species. This finding is in accord with the photoreactivity results, as the above sample appeared to be the most photoactive for the studied reaction.¹⁸

Moreover, a slower recombination rate can be noticed for the 6.65-TiO₂(A)-CuPp sample with respect to the bare TiO₂(A) when the time scale used is larger (see inset of Figure 2).

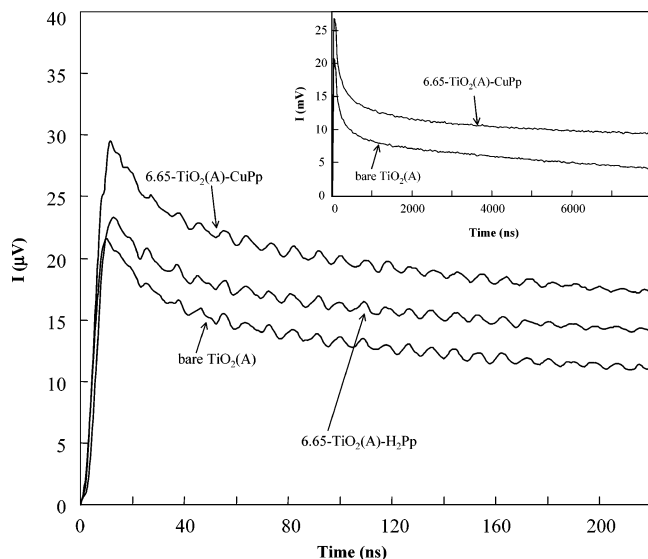
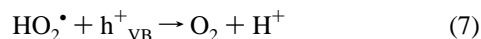
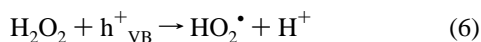
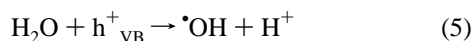
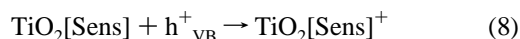


Figure 3. Time-resolved microwave conductivity (TRMC) experiments for bare $\text{TiO}_2(\text{A})$, 6.65- $\text{TiO}_2(\text{A})\text{-H}_2\text{Pp}$, and 6.65- $\text{TiO}_2(\text{A})\text{-CuPp}$. Inset: bare $\text{TiO}_2(\text{A})$ and 6.65- $\text{TiO}_2(\text{A})\text{-CuPp}$.

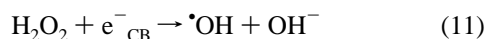
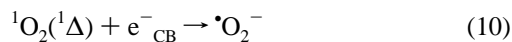
The higher lifetime of holes onto the sensitizer modified TiO_2 surface could give rise to an enhancement of oxidation reactions with adsorbed species, as shown in eqs 4–7.



The holes can be delocalized in the macrocyclic structure of the sensitizers (Sens = H_2Pp or CuPp), as shown in eq 8, contributing to an increase of the lifetime of the photoproducted pairs and/or to react with surface OH and water according to well-known photocatalytic steps.



As far as the electrons are concerned, eqs 9–11 show some possible reactions producing reactive intermediates effective for the photodegradation of 4-NP.



$\cdot\text{O}_2^-$ production along with eqs 4–6 are essential steps to induce the formation of the $\text{HO}_2\cdot$ and $\cdot\text{OH}$ radicals responsible for oxidant attacks in photocatalytic reactions.

The formation of singlet oxygen [$^1\text{O}_2(^1\Delta)$] and hydrogen peroxide, consumed respectively in eqs 10 and 11, cannot be excluded because the production of singlet oxygen in the presence of porphyrin samples has been reported^{31–33} and the formation of H_2O_2 onto a catalyst surface is well-known in TiO_2 heterogeneous photocatalysis.

In the system studied in this work, Cu(II) could be reduced to Cu(I) (see eq 12) by electrons of the conduction band of

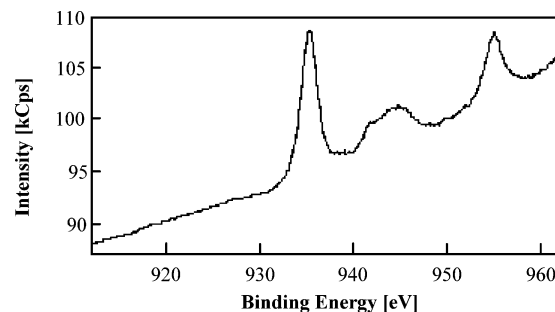
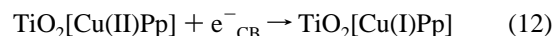


Figure 4. High resolution XP spectrum of the $\text{Cu}2\text{p}$ region recorded on $\text{TiO}_2(\text{A})\text{-CuPp}$ (the spectrum has been subtracted of source satellites).

TABLE 2: XPS Results for TiO_2 , CuPp , and $\text{TiO}_2(\text{A})\text{-CuPp}$ Samples

| sample | $\text{Ti}2\text{p}_{3/2}$ (eV) | $\text{Cu}2\text{p}_{3/2}$ (eV) | $\text{N}1\text{s}$ (eV) |
|---------------------|---------------------------------|---------------------------------|--------------------------|
| TiO_2 | 458.4 | | |
| CuPp | | 935.3 | 398.5 |
| CuPp/TiO_2 | 458.5 | 935.2 | 398.7 |

TiO_2 where additional electrons are injected, due to the presence of the sensitizer:



It is worth noting that, although the photocatalytic reaction rates are generally some order of magnitude lower than those for the generation and recombination of electron–hole pairs, TRMC measurements provide essential information on the intrinsic electronic properties of the samples studied. The results related to the photodegradation of 4-NP in an aqueous heterogeneous environment suggest that the $\text{Cu(II)}\text{--Cu(I)}$ photocatalytic redox cycle plays the main beneficial role for the occurrence of the whole process.

III. XPS Study. It was essential in this work to establish the oxidation state of copper in CuPp used as the starting material in order to give valid experimental support to the mechanism reported in eq 12. In fact, it is known that the oxidation state of copper in nitrogen square planar complexes such as porphyrin or phthalocyanine derivatives could depend on the molecular structure and aggregation of the complex.²⁵

To this purpose, copper speciation was evaluated by using pure CuPp and the purposely prepared pellet of $\text{TiO}_2(\text{A})\text{-CuPp}$. Indeed, the amount of copper in the 6.65- $\text{TiO}_2(\text{A})\text{-CuPp}$ was too low to enable its detection (see the Experimental Section).

Figure 4 shows the $\text{Cu}2\text{p}$ XP spectrum for this catalyst: the presence of satellites establishes the Cu(II) nature of the copper species. The same finding is observed for CuPp . Table 2 collects selected binding energy values for the investigated systems. The findings are in good agreement with literature data^{25,34} for pure materials and confirm copper speciation. Weak interactions between CuPp and TiO_2 are likely responsible for catalyst loading on support, since no significant shift of XP signals is observed. Fine analysis of the $\text{Cu}2\text{p}$ region shows the presence of very minor Cu(I) species accounting for less than 5% of the total copper both on $\text{TiO}_2(\text{A})\text{-CuPp}$ (Figure 5) and on CuPp . In the present stage of investigation, it cannot be excluded that a Cu(I) species was originally present, although it has been reported that other copper porphyrin species are reduced under XPS experimental conditions (as other Cu(II) species do), and consequently, the detected Cu(I) species could be an artifact.

IV. EPR Studies. EPR as XPS measurements support a possible photoreduction of Cu(II) to Cu(I) reported in eq 12 as well as the subsequent reoxidation of Cu(I) to Cu(II) by

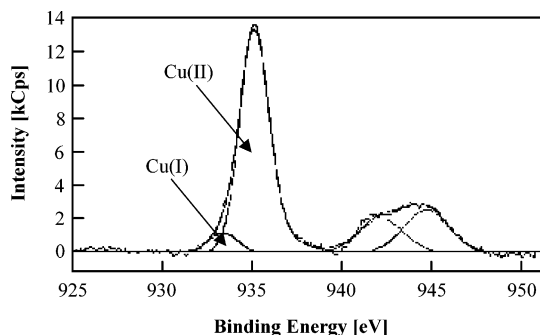


Figure 5. Cu2p curve-fitted region of the TiO₂(A)-CuPp.

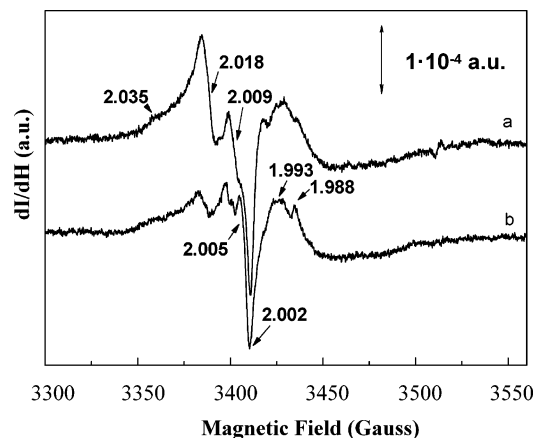
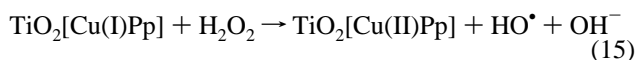
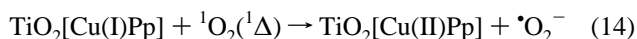
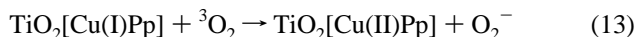


Figure 6. EPR spectra of the samples (a) TiO₂(A) and (b) 6.65-TiO₂(A)-H₂Pp UV-irradiated in the presence of O₂ at 77 K. The background spectrum of each sample recorded in a vacuum was subtracted.

dioxygen species and/or by hydrogen peroxide produced in solution (see eqs 13–15):



The EPR spectra of the TiO₂(A) sample following UV irradiation in the presence of oxygen are displayed in Figure 6a.

A background signal (not shown), which is akin to those previously ascribed to Cr³⁺ impurities in other commercial anatase samples of low surface area,³⁵ is observed in the spectrum of the untreated TiO₂. Since this feature is basically unaffected by either the UV irradiation or the adsorption of gases, it has been subtracted to the spectra of Figure 6 for the sake of simplicity.

The remaining signals are similar to those previously obtained for TiO₂(A) submitted to similar treatments,^{35,36} and they can be attributed to the stabilization of both photogenerated electrons and holes. The broad axial feature with $g_\perp = 1.993$ can be assigned to Ti³⁺ centers, which are very likely located in the bulk of the solid, as they are not affected by the presence of oxygen. Nevertheless, some electrons are transferred to the oxygen molecules which subsequently are protonated to yield hydroperoxyl radicals, HO₂[•], characterized by an orthorhombic signal with the parameters $g_1 = 2.035$, $g_2 = 2.009$, and $g_3 = 2.002$. On the other hand, holes are trapped by surface oxide anions to form O^{•−}, which produce an orthorhombic signal with $g_1 = 2.028$, $g_2 = 2.018$, and $g_3 = 2.002$.³⁶

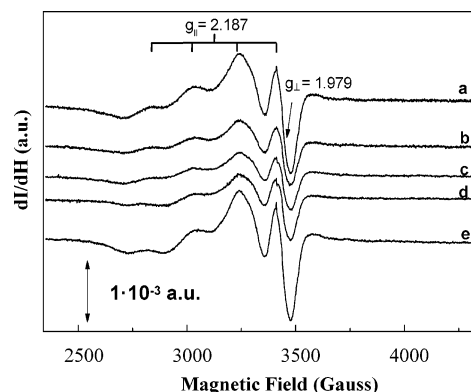


Figure 7. EPR spectra of the samples 6.65-TiO₂(A)-CuPp (a) outgassed for 1 h at RT, (b) UV-irradiated at 77 K, (c) contacted with O₂, (d) irradiated at the same temperature, and (e) warmed at RT.

The spectrum of the sample 6.65-TiO₂(A)-H₂Pp UV-irradiated in the presence of oxygen at 77 K is shown in Figure 6b, after subtraction of the background signal. The main effect of the impregnation of H₂Pp on the TiO₂ is an overall decrease in the concentration of oxygenated radicals. This effect is more evident in the case of the signal corresponding to the O^{•−} radicals, whose intensity is considerably lower than that for bare TiO₂. In addition, a new signal, apparently symmetric with $g = 2.005$, can be observed. This feature is similar to those characteristics of other organic radicals, and it could correspond to the capture of a hole by the porphyrin molecules to yield a H₂Pp^{•+} species (see eq 8).¹⁸ On the other hand, the line at $g = 1.988$ could be associated with the change in the coordination of some Ti³⁺ centers due to the adsorption of the porphyrin molecules, although small variations in the background signal of the TiO₂ impurities could also cause this feature.

Figure 7 displays the spectra of the sample 6.65-TiO₂(A)-CuPp recorded after different treatments. Following 1 h of outgassing at room temperature (RT), a very intense signal with the characteristic hyperfine structure of copper (nuclear spin $I = 3/2$) is observed (Figure 7a). The parameters of the signal are $g_{||} = 2.187$, $g_\perp = 1.979$, and $A_{||} = 20 \times 10^{-3} \text{ cm}^{-1}$, which are very close to those found for other pseudoplanar Cu²⁺ complexes that mimic porphyrin, although in the present case the superhyperfine coupling with the ¹⁴N is not resolved.³⁷

UV irradiation under vacuum at 77 K leads to a remarkable decrease in the intensity of the Cu(II) signal (Figure 7b). This finding could be interpreted as a result of the capture of photogenerated electrons by the Cu(II)Pp to yield Cu(I)Pp complexes (eq 12), which presents a closed-shell configuration, and consequently, they cannot be detected by ESR.^{18,38} Subsequent oxygen adsorption at 77 K (Figure 7c) does not modify the spectrum of the adsorbed Cu(II)Pp complexes. However, if UV irradiation is carried out in the presence of oxygen, a slight modification to the spectrum is apparent at low field (Figure 7d). This could be interpreted as a small change in the coordination of the adsorbed copper complexes, which could be related to the adsorption of oxygen. On the other hand, if the sample is heated to RT in the presence of oxygen, the initial intensity of the Cu(II)Pp complexes is recovered (Figure 7e), due to the oxidation of the Cu(I) species (eqs 13–15). However, some modification in the low field wing of the signal suggests that some changes in the coordination sphere of Cu are not totally reversible. In any case, since these processes do not occur at 77 K, it can be deduced that the electron transfer from the Cu(I)Pp complexes to the oxygen molecules is thermally activated. Because the intensity of the signals corresponding to Cu(II) species is about 2 orders of magnitude larger than those

of the radicals photogenerated on TiO₂ (note the different scales of Figures 6 and 7), the simultaneous variations in the concentration of these last species are extremely difficult to ascertain. Nevertheless, extensive formation of $\cdot\text{O}_2^-$ or $\cdot\text{O}_2\text{H}$ radicals on the TiO₂ surface is not observed upon UV irradiation of the 6.65-TiO₂(A)-CuPp sample. Therefore, EPR results suggest that the main role of CuPp complexes is the capture of photogenerated electrons, which can be subsequently transferred to oxygen molecules. XPS and EPR measurements, in particular, evidenced the important role of copper, due to the redox Cu(II)/Cu(I)/Cu(II) loop, activated under irradiation conditions.

They, along with findings derived from TRMC, are in accord with the hypothesis that the beneficial effect on the photoreactivity is due to a cooperative mechanism linked to the photoexcitation of both TiO₂ and the sensitizer, as hypothesized also for TiO₂ impregnated with Fe(III) phthalocyanine.³⁹

Conclusions

Time-resolved microwave conductivity measurements and electronic paramagnetic resonance and X-ray photoelectron spectroscopies have been used for the characterization of polycrystalline TiO₂ porphyrin impregnated powders.

Polycrystalline TiO₂ powders—bare or impregnated with metal-free or Cu [5,10,15,20-tetra (4-*tert*-butylphenyl)] porphyrin as sensitizers—were used as photocatalysts for the degradation of 4-nitrophenol in aqueous suspension.

The TRMC, XPS, and EPR techniques adequately support some mechanistic hypotheses allowing justification of the improved photocatalytic activity observed in the presence of the porphyrin impregnated TiO₂ samples.

Acknowledgment. The authors wish to thank the “Ministero dell’Istruzione, Università e Ricerca” (MIUR) for financial support. G.M. wishes to thank the DAAD (Deutscher Akademischer Austausch Dienst) for the supply of a fellowship to carry out the measurements on the lifetimes of photoinduced excess charge carriers at Hahn Meitner Institut, Berlin, Germany, and Prof. H. Tributsch for his encouragement and very helpful discussions. J.M.C. wants to thank the financial support from the “Ramón y Cajal” program. XPS measurements were performed at CIS-Università degli Studi di Bari.

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