# Quantum Efficiency of Hydroxyl Radical Formation in a Composite Containing Nanocrystalline TiO₂ e Zinc Phthalocyanine, and the Nature of the Incident Radiation

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## Abstract

In this study, we investigate the generation of hydroxyl radicals mediated by a composite containing TiO₂ and 1.6% m/m of zinc phthalocyanine (TiO₂/ZnPc) in aqueous suspensions containing methanol as oxidisable substrate. The composite features a specific surface 20% less than the value estimated for TiO₂ P25, probably due to the covering of the surface of the oxide by ZnPc and the pH of the isoelectric point of this composite equal of 5.5, about two units of pH lower than the value estimated for TiO₂ P25, are probably related to the difference in photocatalytic activity found for these materials. To assess the influence of different spectral bands of electromagnetic radiation on the production of hydroxyl radicals, we used different sources of radiation in experiments conducted to estimate the quantum efficiency of hydroxyl radical formation (HO•), via photocatalytic oxidation of methanol. The association between zinc phthalocyanine and TiO₂ has allowed the formation of a light absorber material with absorption spectral range extended to the visible region. Our results suggest that, despite the higher values of $\Phi_{HO•}$ for TiO₂ P25, the combination of visible and ultraviolet radiation furnished by a high pressure mercury lamp without the protective bulb, or solar radiation, causes the composite to present good values for the same parameter.

## Notation

DRS = Diffuse reflectance spectrometry.

EDX = Energy dispersive X-ray.

HP = Heterogeneous photocatalysis.

IEP = Isoelectric point.

SEM = Scanning electron microscopy.

TEM = Transmission electron microscopy.

TiO₂ = Titanium dioxide.

UV-Vis-NIR = Ultraviolet visible and near infrared absorption.

ZnPc = Zinc phthalocyanine.

$(\Phi_{HO•})$ = Quantum yield of the production of hydroxyl radicals.

(P/P0) = Relative pressure.

## 1. Introduction

Titanium dioxide ($TiO_2$) is a chemically stable material in a large pH range, showing very low toxicity and that can be obtained by different synthetic routes. The suitable control of the synthesis method employed for the particle production can influence the surface area, crystalline phase and size, morphologic structure, optical absorption and other physical and chemical properties (Anpo & Takeuchi, 2003; Carp et al., 2004; Linsebigler et al., 1995; Mills & Le Hunte, 1997). Although, new $TiO_2$ bulk materials have been employed for UV protection and in advanced oxidative processes (AOPs) (Fox & Dulay, 1993; Wold, 1993), for many years, this kind of material was mainly employed as a white pigment. At present days, composites (Machado et al., 2008; Khalid, Ahmed, E., Hong, Sana, & Ahmed, M., 2013) and doped materials based on $TiO_2$ are also used in photocatalysis (Ahmad et al., 2013) and recent investigations have shown its potential for applications in DSC (dye solar cells) and DSSC (dye sensitised solar cells) (Dozzi & Selli, 2013; Giannakas et al., 2013; Niu et al., 2013). Furthermore, the investigation of new processes to obtain renewable energy, based on $TiO_2$ properties is under development. In special, the conversion of solar radiation in electricity and hydrogen production by water splitting as methods to obtained "green" fuels (Zhong et al., 2012), were encouraged by the seminal research of Fujishima and Honda occurred many decades ago (Fujishima & Honda, 1972).

The absorption of radiation with photon energy equal to or higher than the band gap of the semiconductor material generates charge carriers, which are fundamental to the mediation of photocatalytic processes ( Linsebigler et al., 1995; Diebold, 2003; Carp et al., 2004). However, such process competes directly with the recombination of the charge carriers, usually a very fast process (Diebold, 2003). Thus, the photoactive material performance relies on the net effect of the generation and recombination of charge carriers (Joshi et al., 2013; Liu et al., 2013). Furthermore, recent advances in studies on semiconductor particle are closely related to the development of new synthetic methods to obtain bulk and film materials. Using such methods, materials with structural defects, promoted by doping agents (Chen & Lu, 2013), oxide mixtures and its phases (Khalid, Ahmed, E., Ikram, Ahmad, M., Phoenix, Elhissi, & Jackson, 2013; Ohno et al., 2003), and more recently, composite materials, can be obtained with the aim to extend the limits of UV absorption (Anpo & Takeuchi, 2003; Malato et al., 2003; Vyacheslav & Serprone, 2006). In fact, these materials are currently undergoing experimental tests to evaluate their potential for applications in solar photocatalytic processes (Kim et al., 2013; Machado et al., 2008) and conversion of luminous radiation into electricity (Garcia-Segura et al., 2013). Consequently, the evaluation of how the composition and nature of electromagnetic radiation can influence the driving of photoprocesses in $TiO_2$ composite, e.g. generation of hydroxyl radicals, is a keystone study.

In the present work, the commercial $TiO_2$ (P25) and a composite material constituted by $TiO_2$ P25 and zinc phthalocyanine ($TiO_2$/ZnPc), were studied using different forms of characterization and the role of the radiation wavelength on the efficiency of hydroxyl radical formation induced by $TiO_2$ P25 and the composite $TiO_2$/ZnPc is evaluated.

## 2. Experimental

### 2.1 Material

Methanol (Spectroscopic grade), acetyl acetone and ammonium acetate were purchased from LabSynth and used without previous treatment. Barium sulphate (Vetec) was used as reference in DRS experiments. Commercial P25 $TiO_2$ was kindly provided by Ph.D. Christian Sattler (Institute of Technical Thermodynamics, Solar Research, DLR, Köln, Germany), and the composite $TiO_2$ P25/Zinc Phthalocyanine (P25/ZnPc) was prepared in our laboratory by dissolution of ZnPc in dimethyl sulfoxide, impregnation of the $TiO_2$ surface and posterior solvent removal. Ultrapure water (Milli-Q degree) was employed in all experiments.

### 2.2 Characterisation of the Composite

The light absorption of the composite was estimated by diffuse reflectance spectrometry (DRS), using a UV-2501PC/SHIMADZU spectrophotometer, equipped with an integrating sphere, reflectance module (ISR 240A) and a computer interface. The spectra were recorded along UV-Vis-NIR spectral range, from 300 nm to 800 nm. Barium sulphate and $TiO_2$ P25 were used separately as reference materials in the spectra acquisition. To follow the surface behaviour of P25 associated to zinc phthalocyanine, the specific surface area of P25/ZnPc and porosity was estimated from BET isotherm experiments based on the adsorption of gaseous nitrogen. Such measurements were performed in an ASAP 2020 (Micrometrics) instrument. The evaluation of the zero point charge (ZPC) of P25 and composite, in zeta potential measurements, was carried out in a disperse suspension using a Zetasizer Nano ZS90 (Malvern Instruments). The aqueous suspensions (50.0 mL) containing P25 or P25/ZnPc (100.0 mg/L) were dispersed through the use of an ultrasonic probe for 1 minute. The estimation of particle zeta potential change was done from pH 4 to 10, using 0.01 mol/L solutions of HCl and NaOH to adjust

the pH of the samples. The thickness of ZnPc coating, homogeneity, and aggregation of the TiO$_2$ composite surface were evaluated by transmission electron microscopy (TEM). TEM investigations were carried out using a Philips CM-120. The samples for TEM analysis were prepared by crushing the obtained powder in an agate mortar. An ultrasonic bath was used to disperse the suspension of the composite, being it deposited onto a 300 mesh copper grid. Scanning electron microscopy (SEM) analyses were carried out using a Philips XL-30 microscope coupled to a field emission gun and an EDX analytical setup. These analyses aim to identify morphological aspects of particles and macro-aggregate composites. The energy-dispersive X-ray (EDX) microanalysis was used to estimate the distribution of ZnPc on the P25 surface. The samples were placed on a conductive carbon support by adhesion and gold metallisation was employed. All characterizations were performed for both catalysts.

### 2.3 Photocatalytic Oxidation of Methanol

The samples containing the TiO$_2$ suspensions (100.0 mg/L) were prepared in a $4.0 \times 10^{-4}$ mol/L aqueous solution of methanol. To investigate the effect of light excitation on semiconductor samples, two irradiation systems were used. In the first irradiation system (called system A) a Xe lamp was employed as a light source. In this system, light delivered by the Xe lamp was collimated into a monochromator, used to select the proper excitation wavelength. The setting of the desired excitation wavelength was done through the use of a portable Ocean Optics spectrophotometer, where 375.0 nm was chosen as the peak of excitation wavelength for TiO$_2$ samples. After pass by the monochromator, the light was focused into the cylindrical quartz flux reactor containing the sample. The incident photonic flux was measured by radiometric assay using a power meter near to the reactor surface. In the experiments employing broad-band visible light, the monochromator was replaced by a band pass filter (Newport-M3M7790) to cut the UV radiation emitted by the Xe lamp. In the second irradiation system, named B, a 400 W high pressure mercury vapour lamp without the protection bulb (HPLN, Osram) was used as radiation font. This lamp was used coupled to a borosilicate glass reactor. The photonic flux of the HPLN lamp was measured according to procedure described in reference (Machado et al., 2008). The pH of the suspensions was adjusted to 3.0 before the photocatalytic experiments.

### 2.4 Solar Photocatalysis

The experiments mediated by solar radiation were done in the city of Catalão, Goiás, Brazil. In this city, during the month of August the typical UVA irradiance shows a maximum fluence near 50 W/m$^2$. The experiments were performed using a CPC-type photoreactor (Machado et al., 2008). During the reaction, around 700.0 KJ of UVA and 5000.0 KJ of visible radiation were accumulated.

The TiO$_2$ suspensions (100.0 mg/L) were also prepared in methanol/water at pH 3.0. The circulation of this suspension was continuously pumped across the glass tube of the reactor with a rate of 660.0 L/h.

### 2.5 Formaldehyde Estimation

The quantum yield of the production of hydroxyl radicals ($\Phi_{HO\bullet}$) in water/methanol suspensions containing TiO$_2$ was estimated using a procedure proposed by Sun and Bolton (Sun & Bolton, 1996), based on Nash's colorimetric method (Nash, 1953).

Such procedure consists in the quantification of the formaldehyde concentration formed during the oxidation of methanol due to the photocatalytic process mediated by TiO$_2$. Along the controlled photoreaction process, small amounts of the suspension were taken at different times, filtered and an aliquot was used to estimate the amount of hydroxyl radicals. The concentration of the formed adduct is twice higher than that of the produced radical. The formation of the adduct was monitored by colorimetric analyses carried out in a Shimadzu UV-1650 spectrophotometer at 412.0 nm ($\varepsilon = 8,000.0$ mol$^{-1}$cm$^{-1}$) (Nash, 1953).

## 3. Results and Discussion

### 3.1 Light Absorption

The diffuse reflectance spectra for the composite, ZnPc and P25 are shown in Figure 1. The presence of ZnPc coating the P25 particles changes the typical light absorption spectrum of TiO$_2$ establishing new absorption bands near 1.5 eV (Machado et al., 2008). The broad absorption band observed at visible region of the spectrum (Figures 1b and 1c) has been attributed to ZnPc molecules (Machado et al., 2008; Mangialardo et al., 2008). From Figure 1 we see that, compared with pure ZnPc, a red-shift in the maximum position of the band assigned to ZnPc is observed when the molecules are adsorbed onto P25 surface. The low structuration of the visible absorption band and the observed red shift of such band can be attributed to the strong intermolecular interactions due to the aggregation of ZnPc molecules, forming ZnPc Frenkel´s J-aggregates (Machado et al.,

2008), since it is known that such kind of π stacked structure can be formed between metal-phthalocyanines (Mangialardo et al., 2008).

Additionally, the electronic absorption near the band edge of pure P25 also suffered a red-shift (compare Figures 1b and 1d), changing the band-gap, probably due to the coupling between electronic states from P25 and ZnPc.



Figure 1. Diffuse reflectance spectrum for: (a) Zinc Phthalocyanine (red solid line). (b) $TiO_2$/ZnPc (green solid line). (c) $TiO_2$/ZnPc using $TiO_2$ as reference (black solid line). (d) P25 (blue solid line). For a, b and d barium sulphate was used as a reference material

As said previously, the displacement and new absorption band, assigned to ZnPc with P25, can be related to the ZnPc molecule aggregations as a consequence of P25 particles recovery (Deng et al., 1998; Kc et al., 2013). As suggested in previous studies (Dozzi & Selli, 2013; Machado et al., 2008) this tends to extend the generation of electron-hole pairs throughout the visible spectral region, improving the solar energy absorption of P25. However, a possible drawback related to the composite is that beyond the mechanism of electron transfer present in P25 nanoparticles, in the composite, additional recombination paths due to the formation of ZnPc Frenkel's aggregates, arises (Machado et al., 2008).

*3.2 Specific Surface Area (SSA)*

The recovery of P25 particles by ZnPc furnishes a material with specific surface area of 40.5 m²/g, 20% smaller than pure P25 (Linsebigler et al., 1995). Although a relation of the 1.6% (m/m) of ZnPc in the composite implies in a coating of around 40% of the P25 particles surface by ZnPc molecules, assuming a particle average size of 25 nm, if the difference between the size of nitrogen molecules and zinc phthalocyanine (the surface area of a ZnPc molecule, estimated by semiempyrical calculation, is around 1.2 nm²) is considered, the increase of aggregation turns out to be more favourable. Even so, a 20% SSA decrease in $TiO_2$/ZnPc is coherent with the formation of a ZnPc pellicle on the surface of $TiO_2$ and with the self-aggregation of ZnPc molecules, possibly forming ladder J type aggregates (Kumaran et al., 2010; Senthilarasu et al., 2003). Theoretical studies based on the use of the meta-hybrid GGA M06 DFT functional (Machado et al., 2012), have confirmed this possibility.

Furthermore, covered areas on the $TiO_2$ surface and ZnPc domains can be responsible for generating suitable conditions for adsorption of different organic matter, favouring the electron injection through the creation of domains with different electronic potentials (Nelson et al., 2000; Nowacka et al., 2013).

Through the analysis of the adsorption and desorption isotherms, it is noted that for the same values of relative pressure (P/P0), the adsorption of gas is 20% higher in the composite than in P25, see Figure 2. This can lead to differences in the photocatalytic activity of both compounds (Oliveira et al., 2012), and therefore to difference in the reactions induced by such photocatalysts (Janczyk et al., 2006; Oliveira et al., 2012; Nowacka et al., 2013).

Figure 2. The open and solid circles are related to the gas adsorption and desorption on P25, respectively, while open and solid train gle stands for the gas adsorption and desorption on P25/ZnPc composite

### 3.3 Zeta Potential–Estimation of the Isoelectric Point

The association between ZnPc and P25 leads to the formation of a new material that, differently of the raw materials, presents new surface characteristics. These characteristics and the domain of the $TiO_2$/ZnPc interface can be sensed by the changes of charge distribution over the particle. For this purpose, the electrophoretic mobility of these particles at different pHs was investigated aiming to estimate changes in the value of isoelectric point (IEP) after coating of P25. In Figure 3, the electrodynamic behaviour of $TiO_2$ P25 and its composite, at different pHs, is shown. The P25 IEP was estimated at pH 7.3, about one unit of pH higher than the value reported by Hoffmann and co-workers (Hoffmann et al., 1995). For the composite material our data show that IEP occurs at pH 5.5, suggesting that the presence of ZnPc alters the charge distribution over the surface of the catalyst, resulting in the formation of a more electropositive surface.

Furthermore, as the stability of photoactive suspensions is closely related to the pH, other factors such as the concentration of ions in solution also can have an effect on the load distribution and therefore change the adsorption of organic matter on the surface of the particles (Bogdanova et al., 2004; Nelson, et al., 2000). Somehow, the formation of a double layer under this condition favours a better adsorption of anionic substances, which can ampliate the reaction performance due to an increased local concentration of organic matter on the sites of production of oxidant radicals (Du et al., 2013; Oliveira et al., 2012; Suttiponparnit et al., 2013). Moreover, the distribution of $TiO_2$ polymorphs also has an influence on the characteristics and photoactivity of the surface, where the presence of oxygen vacancy and other defects contribute significantly (Carp et al., 2004).

The formation of the composite, induced by a non-spontaneous adsorption of ZnPc, generates a new active surface with different electrodynamic and electrostatic behaviours. The behaviour exhibited by the composite can be associated to the effect of encapsulation of $TiO_2$ particles, the formation of ZnPc aggregates, and also to the clusters of particles of ZnPc and $TiO_2$ present in the material.

Finally, we verify that at pH 3.0 we have the largest array of positive charges on the surface of $TiO_2$ and composite. This pH value should favour the photoactivity of both photocatalysts.

Figure 3. ZPC estimation in ZnPc/P25 (open circles) and P25 suspensions (black squares). The solid lines a just guide to the eyes

### 3.4 TEM and SEM Analysis

The analysis of Figure 4a suggests that the particles are aggregated with different morphologies and without a regular geometric pattern. The analysed material consists of a dispersion of particles with sizes ranging between 10.0 and 40.0 nm. From this figure two types of particles, identified by their degree of colour density in the image, can be noticed, presenting the $TiO_2$ particles a higher electronic density than ZnPc. Two distinct regions, delimited by the squares S and T, show a interesting self-assembled structure, which can be associated with the ordering and orientation of $TiO_2$ (dark streams) and ZnPc (clear streams).

The pattern of association of ZnPc aggregates can be seen in greater detail in Figure 4b. In this case, there is an isolated aggregate of approximately 200.0 nm, consisting of $TiO_2$ particles and also particles of ZnPc coated as a film. The presence of this type of structure corroborates the assumption that ZnPc molecules are responsible for the adhesion between the aggregates, as shown in Figure 4c, and reinforces the existence of ordered J aggregate structures, as provided by the DRS measurements. Also in Figure 4c the image obtained by SEM, the composite shows aggregated particles that allow the formation of clusters. This morphological structure based on a spheroid pattern can be observed, following particles with 40.0 nm size. There is no a wide dispersion in the size of aggregates or any spatial pattern. The link between aggregate particles is maintained by material with plastic characteristic.

Figure 4. (a) TEM image of the composite. Areas S and T in the figure represent the ordering patterns observed by electro-density differences. Figure 4(b) represents a ZnPc aggregate and P25 particle recovery. In 4(c) it is shown the $TiO_2$ particles associated with ZnPc in composite materials

### 3.5 Quantum Yield of Hydroxyl Radical Formation

Due to the increasing interest in new materials based on $TiO_2$ able to mediate efficiently photocatalytic processes, the investigation of variables influencing their photoactivity is imperative. A well-established way to assess the photoactivity of $TiO_2$ based materials is through the estimation of the quantum yield of hydroxyl radical ($HO^{\bullet}$) production ($\Phi_{HO^{\bullet}}$) during photocatalytic processes. Here, the estimation of this parameter was done exploring different variables, such as: pH, oxidizable substrate and its concentration, load of $TiO_2$ or composite material, light fluence and wavelength of the incident radiation, and method of catalyst preparation. It is worth to mention that the influence of preparation method on hydroxyl radical generation has been previously investigated (Chu & Anastasio, 2005; Gao et al., 2002; Loddo et al., 2006). These studies look for a way to link the inner mechanism of formation of electron-hole pairs and the action of the photocatalyst over an oxidizable substrate (Gao et al., 2002; Chu & Anastasio, 2005; Loddo et al., 2006; Tryba et al., 2007; Hoertz et al., 2013; Shieh et al., 2013; Zhang & Nosaka, 2013).

This part of our effort was focused on estimate the generation of hydroxyl radical from P25 and P25/ZnPc composite employing different photon energies and excitation sources. The estimation of $\Phi_{HO^{\bullet}}$ was based on the methanol oxidation in formaldehyde. The assessment of the concentration of formaldehyde was done indirectly by a colorimetric method following Nash's procedure (Nash, 1953). The radiation sources employed in these experiments and the respective energy dose are expressed in Table 1. The interaction among the incident radiation, the photocatalyst and the substrates triggers a sequence of elementary photochemical reactions

(Linsebigler et al., 1995; Machado et al., 2008). Consequently, the yield of formaldehyde formation can be related to the oxidation of methanol induced by hydroxyl radicals. The photocatalytic conditions employed in this reaction were assigned to the first oxidation product of methanol (Naldoni et al., 2013; Sun & Bolton, 1996).

Table 1. Radiation fluence employed to illuminate the raw P25 and composite, for different sources

|  | SOLAR [†] | 375nm | HPLN [‡] | visible |
|---|---|---|---|---|
| Total Fluence (MJ/m$^2$) | 15 | 0,1 | 100 | 3,2 |

[†] peak value, [‡] nominal lamp value. It is a new one.

In Figure 5, we represent the energy distribution profile delivered by different light sources employed in this study, aiming the photolysis of methanol. Since the enhancement in HO$^\bullet$ radical generation depends on the electron transfer between the adsorbed dye and activated catalyst, the radiative emission of each radiation source can be tuned to match with the light absorption by the photocatalyst in order to optimize the electron-hole pair generation. In the case of dye/TiO$_2$ composites, studies have suggested that an important route for this interaction is through the direct injection of excited electrons of the electronically excited dye in the conduction band of TiO$_2$ (Giannakas et al., 2013; Ino et al., 2005; Machado et al., 2008).



Figure 5. Source (**1**) is the HPLN emission filtered through the borosilicate reactor wall. Here the UV portion of the spectrum (above 2.5 eV) was multiplied by a factor 10 in order to obtain better visualization (**2**) is Xe visible emission lamp with UV filter. (**3**) Emission of Xe lamp tuning to 375 nm peak. (**4** and **5**) Normalized solar spectra obtained at 11h and 12h respectively. (**A**) Optical absorption of TiO$_2$ P25. (**B**) Optical absorption composite TiO2 P25/Zinc Phthalocyanine TiO$_2$/ZnPc

The efficiency of hydroxyl radical formation was investigated with different fluences. It is important to mention that fluence can be considered as the main variable to analyse the performance of a photocatalyst since this parameter is capable to furnish the density of photons used in the process. The capability of the photocatalysts under study to perform, in solution, the oxidation of methanol when evaluated with respect to the use of different sources of light energy, and under the same conditions of heterogeneous photocatalysis (HP), is shown in Figure 6. We see that for all radiation sources used the formation of radicals increases almost linearly as the fluence (F) of the incident light increases.

Figure 6. Estimation of hydroxyl radical formation for P25 and P25/ZnPc exciting the samples with different luminous sources. (a) HPLN: (1) P25 and (2) P25/ZnPc; (b) Solar light: (3) P25 and (4) P25/ZnPc; (c) Radiation centered at 375 nm: (5) P25 and (6) P25/ZnPc; and (d) Visible radiation: (7) P25 and (8) P25/ZnPc

We can compare the efficiency of the composite, which seems to depend preponderantly on the electron transfer between the adsorbed dye and $TiO_2$, with respect to the P25-$TiO_2$ in the generation of hydroxyl radicals. The release of electrons by the excited ZnPc will depend on its electronic absorption, resulting in differentiated transfer rates according to the distribution of energy or, rather, the wavelengths that compose the incident radiation.

The best rate of hydroxyl radical formation was obtained by raw P25 when illuminated by radiation centred at 375.0 nm. This wavelength lies in a higher energy than that required to produce a direct electronic excitation in this semiconductor. In the composite, one must consider some important and concurrent events (Machado, et al., 2008): the photophysical processes triggered by the electronic excitation of $TiO_2$ that culminates in the formation of hydroxyl radicals; the processes due to interface effects induced by the electronically excited pair $[(ZnPc)_n/TiO_2]^*$, including the electron injection from $ZnPc_{agg}$ excitons to the conduction band of the catalyst, exciton-exciton annihilation due to the excessive coating of the $TiO_2$ surface, and other processes mediated by $ZnPc_{agg}$ excitons, able to establish other chemical processes. The concurrence between these processes should be pointed as the reason by which $\Phi_{HO\bullet}$ by pure $TiO_2$ is usually higher (Figure 6 and Table 2). On the other hand, when a high pressure mercury vapour lamp (HPLN) was employed as radiation source, the composite presented a higher $\Phi_{HO\bullet}$ (Table 2).

Table 2. Correlation between the different luminous sources and generation of hydroxyl radical

|  | Solar | 375.0 nm | HPLN | Visible |
|---|---|---|---|---|
| Ø OH$^*$- P25 | 14.0 ± 0.3 | 25.5 ± 0.3 | 2.5 ± 0.2 | 0.50 ± 0.05 |
| Ø OH$^*$- P25/ZnPc | 4.0 ± 0.2 | 1.5 ± 0.1 | 4.5 ± 0.2 | 0.18 ± 0.03 |

The kinetic constants of zero order from the photocatalyst are expressed in $\mu M.m^2/MJ$

Despite these results, we have observed a photocatalytic activity for this composite higher than the measured for the action of $TiO_2$-P25, in the mineralization and degradation of different organic substrates (Machado et al., 2008). An example is the mineralization of Ponceau 4R (Acid red 18): although $\Phi_{HO\cdot}$ estimated for the composite is three times smaller than the verified for pure $TiO_2$-P25, the photocatalytic activity of the composite, in the mineralization of such compound, was almost three times higher than the verified with the use of $TiO_2$ P25 (Oliveira et al., 2012). Photoelectrons injected from $ZnPc_{agg}$ excitons into the $TiO_2$ conduction band should be the reason for this behavior. These photoelectrons should amplify the importance of processes mediated by electron-rich reactive species generated from the $TiO_2$ conduction band that begin to compete with hydroxyl radicals in the reactions that can lead to mineralization of the substrate.

Still, on the generation of oxidizing radicals in the different experiments of heterogeneous photocatalysis performed in this study, the comparison of performances between $ZnPc/TiO_2$ and the pure $TiO_2$ P25 suggests that the processes of de-excitation of ZnPc aggregates occur sharply, since the production rates (HO•) were lowered in almost all experiments, especially when solar and UV radiation were employed in the excitation. Following this approach, the de-excitation should greatly compete with the efficiency of the overall radical production. Analysing only the contribution of the fraction of the visible spectrum, it is clear that its contribution has a low significance in the generation of hydroxyl radicals in comparison to other sources. On the other hand, using the font that provides expressive amounts of visible radiation, combined with a small amount of UV (HPLN lamp), this characteristic is reversed (see Table 2). Such finding explains why the efficiency of the composite when illuminated by solar radiation is higher than when the composite is illuminated just by UV or just by visible radiation. Both, HPLN and solar light presents the radiation profile composed by visible associated with small amounts of near UV radiation.

These results suggest that they depend strongly on the interaction of species produced by zinc phthalocyanine and the $TiO_2$, and point to a scenario in which a mechanism capable to be triggered in the presence of small fractions of UV radiation, together with a large range of visible radiation, is the most favourable to the performance of the composite material.

Finally, the association between ZnPc and $TiO_2$ leads to the possibility of exploitation of composite in conducting other chemical reactions, considering the electrostatic behaviour of the reactive surface, capable to enhance the photocatalytic activity.

## 4. Conclusions

The association between zinc phthalocyanine and $TiO_2$ P25 results in a photoactive material. This new material showed an optical absorption which appears different from the sum of the optical absorption of the materials separately. The association of zinc phthalocyanine material occurs with the formation of structures probably neatly arranged in the form of stacked J-type aggregate, which was measured by electron microscopy transmission images and corroborated by the observed bathochromic displacement associated to the Q band of ZnPc.

In this new material, new surface properties were obtained from the formation of two types of established interfaces. In the first interface type, a favourable electron transfer occurs from the excited zinc phthalocyanine to the conduction band of $TiO_2$. In the second interface type, the distribution of electrical charges at pH 3, as suggest the measure of isoelectric point at the surface of the material, favours the degradation of anionic substances.

The composite showed a great heterogeneity in its composition, as revealed through microscopic measurements, which showed three types of these distinct regions, namely, a region composed of clusters of $TiO_2$-P25, another composed of clusters of ZnPc and P25 and another ZnPc was expected to consist of $TiO_2$ P25 particles encapsulated by layers of zinc phthalocyanine. The composite material exhibited a 20% reduction of its specific surface area, as consequence of the creation of phthalocyanine aggregates domains and their associations with oxide surface.

However, this decrease in the area provided a positive material with photocatalytic properties extended to the visible region. The effects related to the production of hydroxyl radical in the composite and $TiO_2$-P25 show to be sensitive to different light sources used in the tests, pre-setting the composite the best efficiency when illuminated by radiation composed by visible and UV.

Moreover, the performance of this new material when judged on the use in solar radiation was highly efficient. Present rates of hydroxyl radical formation are competitive with those developed in the process of excitation by an artificial source of radiation of high radiative power (mercury vapour lamp). This is a quite interesting result

since the use of solar radiation is highly desirable due to its great abundance and viability. These results show the feasibility of the application of composite, with extended absorption to visible region, in AOP´s, as well as for applications related to DSSC.

Finally, the results suggest that more refined studies should be developed in order to assess the effects related to electron transfer from the excited phthalocyanine to the conduction band of $TiO_2$, since considerable differences in the photoactivity were observed from the use of sources that were able to excite the material both in the visible region and in the region of the ultra-violet spectrum.

**Acknowledgements**

**References**

Ahmad, M., Ahmed, E., Zhang, Y. W., Khalid, N. R., Xu, J. F., Ullah, M., & Hong, Z. L. (2013). Preparation of highly efficient Al-doped ZnO photocatalyst by combustion synthesis. *Current Applied Physics, 13*(4), 697-704. http://dx.doi.org/10.1016/j.cap.2012.11.008

Anpo, M., & Takeuchi, M. (2003). The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation. *Journal of Catalysis, 216*(1-2), 505-516. http://dx.doi.org/10.1016/S0021-9517(02)00104-5

Bogdanova, N. F., Shved, Y. A., Klebanov, A. V., Zheldakov, I. L., Ermakova, L. E., Sidorova, M. P., & Savina, I. A. (2004). Tin- and titanium-oxygen nanostructures on the various hydr(oxides) surfaces. *Colloid Journal, 66*(4), 418-425. http://dx.doi.org/10.1023/B:Coll.0000037446.32004.67

Carp, O., Huisman, C. L., & Reller, A. (2004). Photoinduced reactivity of titanium dioxide. *Progress in Solid State Chemistry, 32*(1-2), 33-177. http://dx.doi.org/10.1016%2fS1010-6030(97)00118-4

Chen, B., & Lu, K. (2013). Selective focused-ion-beam sculpting of $TiO_2$ nanotubes and mechanism understanding. *Physical Chemistry Chemical Physics, 15*(6), 1854-1862. http://dx.doi.org/10.1039/C2cp43354k

Chu, L., & Anastasio, C. (2005). Formation of hydroxyl radical from the photolysis of frozen hydrogen peroxide. *Journal of Physical Chemistry A, 109*(28), 6264-6271. http://dx.doi.org/10.1021/Jp051415f

Deng, H., Lu, Z., Shen, Y., Mao, H., & Xu, H. (1998). Improvement in photoelectric conversion of a phthalocyanine-sensitized $TiO_2$ electrode by doping with porphyrin. *Chemical Physics, 231*, 95-103. http://dx.doi.org/10.1016/S0301-0104(98)00066-4

Diebold, U. (2003). The surface science of titanium dioxide. *Surface Science Reports, 48*(5-8), 53-229. http://dx.doi.org/10.1016/S0167-5729(02)00100-0

Dozzi, M. V., & Selli, E. (2013). Doping $TiO_2$ with p-block elements: Effects on photocatalytic activity. *Journal of Photochemistry and Photobiology C-Photochemistry Reviews, 14*, 13-28. http://dx.doi.org/10.1016/j.jphotochemrev.2012.09.002

Du, H. B., De Sarkar, A., Li, H. S., Sun, Q., Jia, Y., & Zhang, R. Q. (2013). Size dependent catalytic effect of $TiO_2$ clusters in water dissociation. *Journal of Molecular Catalysis a-Chemical, 366*, 163-170. http://dx.doi.org/10.1016/j.molcata.2012.09.019

Fox, M. A., & Dulay, M. T. (1993). Heterogeneous Photocatalysis. *Chemical Reviews, 93*(1), 341-357. http://dx.doi.org/10.1021/Cr00017a016

Fujishima, A., & Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature, 238*, 37 - 38.

Gao, R. M., Stark, J., Bahnemann, D. W., & Rabani, J. (2002). Quantum yields of hydroxyl radicals in illuminated $TiO_2$ nanocrystallite layers. *Journal of Photochemistry and Photobiology a-Chemistry, 148*(1-3), 387-391. http://dx.doi.org/10.1016/S1010-6030(02)00066-7

Garcia-Segura, S., Dosta, S., Guilemany, J. M., & Brillas, E. (2013). Solar photoelectrocatalytic degradation of Acid Orange 7 azo dye using a highly stable $TiO_2$ photoanode synthesized by atmospheric plasma spray. *Applied Catalysis B-Environmental, 132*, 142-150. http://dx.doi.org/10.1016/j.apcatb.2012.11.037

Giannakas, A. E., Seristatidou, E., Deligiannakis, Y., & Konstantinou, I. (2013). Photocatalytic activity of N-doped and N-F co-doped $TiO_2$ and reduction of chromium(VI) in aqueous solution: An EPR study. *Applied Catalysis B-Environmental, 132*, 460-468. http://dx.doi.org/10.1016/j.apcatb.2012.12.017

Hoertz, P. G., Magnus-Aryitey, D., Gupta, V., Norton, C., Doorn, S., & Ennis, T. (2013). Photocatalytic and radiocatalytic nanomaterials for the degradation of organic species. *Radiation Physics and Chemistry, 84*, 51-58. http://dx.doi.org/10.1016/j.radphyschem.2012.06.045

Hoffmann, M. R., Martin, S. T., Choi, W., & Bahnemann, D. W. (1995). Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews, 95*, 69-96. http://dx.doi.org/10.1021/cr00033a004

Ino, D., Watanabe, K., Takagi, N., & Matsumoto, Y. (2005). Electron Transfer Dynamics from Organic Adsorbate to a Semiconductor Surface: Zinc Phthalocyanine on $TiO_2$ (110). *Journal of Physical Chemistry: B, 109*, 18018 - 18024. http://dx.doi.org/10.1021/Jp052078d

Janczyk, A., Krakowska, E., Stochel, G., & Macyk, W. (2006). Singlet oxygen photogeneration at surface modified titanium dioxide. *Journal of the American Chemical Society, 128*(49), 15574-15575. http://dx.doi.org/10.1021/Ja065970m

Joshi, P. H., Korfiatis, D. P., Potamianou, S. F., & Thoma, K. A. T. (2013). Optimum oxide thickness for dye-sensitized solar cells-effect of porosity and porous size. A numerical approach. *Ionics, 19*(3), 571-576. http://dx.doi.org/10.1007/s11581-012-0755-3

Kc, C. B., Stranius, K., D'Souza, P., Subbaiyan, N. K., Lemmetyinen, H., Tkachenko, N. V., & D'Souza, F. (2013). Sequential Photoinduced Energy and Electron Transfer Directed Improved Performance of the Supramolecular Solar Cell of a Zinc Porphyrin-Zinc Phthalocyanine Conjugate Modified $TiO_2$ Surface. *Journal of Physical Chemistry C, 117*(2), 763-773. http://dx.doi.org/10.1021/Jp308923e

Khalid, N. R., Ahmed, E., Hong, Z. L., Sana, L., & Ahmed, M. (2013). Enhanced photocatalytic activity of graphene-$TiO_2$ composite under visible light irradiation. *Current Applied Physics, 13*(4), 659-663. http://dx.doi.org/10.1016/j.cap.2012.11.003

Khalid, N. R., Ahmed, E., Ikram, M., Ahmad, M., Phoenix, D. A., Elhissi, A., & Jackson, M. J. (2013). Effects of Calcination on Structural, Photocatalytic Properties of $TiO_2$ Nanopowders Via TiCl4 Hydrolysis. *Journal of Materials Engineering and Performance, 22*(2), 371-375. http://dx.doi.org/10.1007/s11665-012-0272-6

Kim, K. P., Lee, S. J., Kim, D. H., Hwang, D. K., & Heo, Y. W. (2013). Dye-sensitized solar cells based on trench structured $TiO_2$ nanotubes in Ti substrate. *Current Applied Physics, 13*(4), 795-798. http://dx.doi.org/10.1016/j.cap.2012.12.010

Kumaran, N., Veneman, P. A., Minch, B. A., Mudalige, A., Pemberton, J. E., O'Brien, D. F., & Armstrong, N. R. (2010). Self-Organized Thin Films of Hydrogen-Bonded Phthalocyanines: Characterization of Structure and Electrical Properties on Nanometer Length Scales. *Chemistry of Materials, 22*(8), 2491-2501. http://dx.doi.org/10.1021/Cm903127w

Linsebigler, A. L., Lu, G. Q., & Yates, J. T. (1995). Photocatalysis on $TiO_2$ Surfaces-Principles, Mechanisms, and Selected Results. *Chemical Reviews, 95*(3), 735-758. http://dx.doi.org/10.1021/Cr00035a013

Liu, X. J., Pan, L. K., Lv, T., & Sun, Z. (2013). Investigation of photocatalytic activities over ZnO-$TiO_2$-reduced graphene oxide composites synthesized via microwave-assisted reaction. *Journal of Colloid and Interface Science, 394*, 441-444. http://dx.doi.org/10.1016/j.jcis.2012.11.047

Loddo, V., Addamo, M., Augugliaro, V., Palmisano, L., Schiavello, A., & Garrone, E. (2006). Optical properties and quantum yield determination in photocatalytic suspensions. *Aiche Journal, 52*(7), 2565-2574. http://dx.doi.org/10.1002/Aic.10883

Machado, A. E. H., França, M. D., Velani V., Magnino, G. A., Velani, H. M. M., Freitas, F. S., … Schmücker, M. (2008). Characterization and evaluation of the efficiency of $TiO_2$/Zinc phthalocyanine nanocomposites as photocatalysts for wastewater treatment using solar irradiation. *International Journal of Photoenergy, 2008*(482373), 482-373. http://dx.doi.org/10.1155/2008/482373

Machado, A. E. H., dos Santos, L. M., Borges, K. A., Batista, P. S., Borges de Paiva, V. A., Müller Jr, P. S., ... França, M. D. (2012). Potential Applications for Solar Photocatalysis: From Environmental Remediation to Energy Conversion. In E. B. Babatunde (Ed.), *Solar Radiation* (Chapter 19, pp. 339-378). Rijeka, Croatia: Intech.

Malato, S., Blanco, J., Vidal, A., Alarcón, D., Maldonado, M. I., Cáceres, J., & Gernjak, W. (2003). Applied studies in solar photocatalytic detoxification: an overview. *Solar Energy, 75*, 329-336. http://dx.doi.org/10.1016/j.solener.2003.07.017

Mangialardo, S., Larciprete, M. C., Belardini, A., Sibilia, C., & Bertolotti, M. (2008). Determination of the Aggregation Degree of Zinc-Phthalocyanines Derivatives into Polymeric Films via the Characterization of the Linear-Optical Absorption. *Laser Physics, 18*(12), 1371-1377. http://dx.doi.org/10.1134/S1054660x08120013

Mills, A., & Le Hunte, S. (1997). An overview of semiconductor photocatalysis. *Journal Photochemistry and Photobiology A, 108*, 1-35. http://dx.doi.org/10.1016/S1010-6030(97)00118-4

Nash, T. (1953). The colorimetric estimation of formaldehyde by means of the Hantzsch reaction. *Biochemistry, 55*, 416-421.

Nelson, B. P., Candal, R., Corn, R. M., & Anderson, M. A. (2000). Control of surface and zeta potentials on nanoporous $TiO_2$ films by potential-determining and specifically adsorbed ions. *Langmuir, 16*(15), 6094-6101. http://dx.doi.org/10.1021/La9911584

Niu, Y. X., Xing, M. Y., Zhang, J. L., & Tian, B. Z. (2013). Visible light activated sulfur and iron co-doped $TiO_2$ photocatalyst for the photocatalytic degradation of phenol. *Catalysis Today, 201*, 159-166. http://dx.doi.org/10.1016/j.cattod.2012.04.035

Nowacka, M., Siwinska-Stefanska, K., & Jesionowski, T. (2013). Structural characterisation of titania or silane-grafted $TiO_2$-$SiO_2$ oxide composite and influence of ionic strength or electrolyte type on their electrokinetic properties. *Colloid and Polymer Science, 291*(3), 603-612. http://dx.doi.org/10.1007/s00396-012-2762-3

Ohno, T., Tokieda, K., Higashida, S., & Matsumura, M. (2003). Synergism between rutile and anatase $TiO_2$ particles in photocatalytic oxidation of naphthalene. *Applied Catalysis a-General, 244*(2), 383-391. http://dx.doi.org/10.1016/S0926-860x(02)00610-5

Oliveira, D. F. M., Batista, P. S., S., M. J. P., Velani, V., França, M. D., Souza, D. R., & Machado, A. E. H. (2012). Evaluating the effectiveness of photocatalysts based on titanium dioxide in the degradation of the dye Ponceau 4R. *Dyes and Pigments, 92*, 563-572. http://dx.doi.org/10.1016/j.dyepig.2011.06.007

Qi, J. H., Li, Y., Duong, T. T., Choi, H. J., & Yoon, S. G. (2013). Dye-sensitized solar cell based on AZO/Ag/AZO multilayer transparent conductive oxide film. *Journal of Alloys and Compounds, 556*, 121-126. http://dx.doi.org/10.1016/j.jallcom.2012.12.127

Senthilarasu, S., Velumani, S., Sathyamoorthy, R., Subbarayan, A., Ascencio, J. A., Canizal, G., & Perez, R. (2003). Characterization of zinc phthalocyanine (ZnPc) for photovoltaic applications. *Applied Physics a-Materials Science & Processing, 77*(3-4), 383-389. http://dx.doi.org/10.1007/s00339-003-2184-7

Shieh, D. L., Huang, S. J., Lin, Y. C., Lin, Y. S., Lin, J. L., Yeh, T. F., & Teng, H. S. (2013). $TiO_2$ derived from TiC reaction in $HNO_3$: Investigating the origin of textural change and enhanced visible-light absorption and applications in catalysis. *Microporous and Mesoporous Materials, 167*, 237-244. http://dx.doi.org/10.1016/j.micromeso.2012.08.032

Sun, L., & Bolton, J. (1996). Determination of the quantum yield for the photochemical generation of hydroxyl radicals in $TiO_2$ suspensions. *Journal Physical Chemistry,* (100), 4127-4134. http://dx.doi.org/10.1021/jp9505800

Suttiponparnit, K., Tiwari, V., Sahu, M., Biswas, P., Suvachittanont, S., & Charinpanitkul, T. (2013). Effect of Pt or Pd doping on stability of $TiO_2$ nanoparticle suspension in water. *Journal of Industrial and Engineering Chemistry, 19*(1), 150-156. http://dx.doi.org/10.1016/j.jiec.2012.07.017

Tryba, B., Toyoda, M., Morawski, A. W., Nonaka, R., & Inagaki, M. (2007). Photocatalytic activity and OH radical formation on $TiO_2$ in the relation to crystallinity. *Applied Catalysis B-Environmental, 71*(3-4), 163-168. http://dx.doi.org/10.1016/j.apcatb.2005.12.036

Vyacheslav, N. K., & Serprone, N. (2006). Visible light absorption by various titanium dioxide specimens. *Journal of Physical Chemistry B, 110*(50), 25203 - 25209. http://dx.doi.org/10.1021/jp064253b

Wold, A. (1993). Photocatalytic Properties of $TiO_2$. *Chemistry of Materials, 5*(3), 280-283. http://dx.doi.org/10.1021/Cm00027a008

Zhang, J., & Nosaka, Y. (2013). Quantitative Detection of OH Radicals for Investigating the Reaction Mechanism of Various Visible-Light TiO$_2$ Photocatalysts in Aqueous Suspension. *Journal of Physical Chemistry C, 117*(3), 1383-1391. http://dx.doi.org/10.1021/Jp3105166

Zhong, M., Shi, J. Y., Xiong, F. Q., Zhang, W. H., & Li, C. (2012). Enhancement of photoelectrochemical activity of nanocrystalline CdS photoanode by surface modification with TiO$_2$ for hydrogen production and electricity generation. *Solar Energy, 86*(2), 756-763. http://dx.doi.org/10.1016/j.solener.2011.12.006

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