

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 $\Phi_{HO\bullet}$ 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.

Keywords: HPLC, PDA, stability indication method, drug.

1. INTRODUCTION:

Titanium dioxide (TiO₂) 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ composite, e.g. generation of hydroxyl radicals, is a keystone study. In the present work, the commercial TiO₂ (P25) and a composite material constituted by TiO₂ P25 and zinc phthalocyanine (TiO₂/ZnPc), were studied using different forms of characterization and the role of the radiation wavelength on the efficiency of hydroxyl radical formation induced by TiO₂ P25 and the composite TiO₂/ZnPc is evaluated.

2. MATERIALS ARE USED:

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 TiO₂ was kindly provided by Ph.D. Christian Sattler (Institute of Technical Thermodynamics, Solar Research, DLR, Köln, Germany), and the composite TiO₂ P25/Zinc Phthalocyanine (P25/ZnPc) was prepared in our laboratory by dissolution of ZnPc in dimethyl sulfoxide, impregnation of the TiO₂ 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 TiO₂ 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 TiO₂ 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.

3. PROPOSED METHODOLOGY:

The samples containing the TiO₂ suspensions (100.0 mg/L) were prepared in a 4.0x10⁻⁴ 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 TiO₂ 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.

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 TiO₂ 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., 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.

5. CONCLUSION:

The association between zinc phthalocyanine and TiO₂ 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 TiO₂. 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 TiO₂-P25, another composed of clusters of ZnPc and P25 and another ZnPc was expected to consist of TiO₂ 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.

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