

Research Article

Synergetic Enhancement of the Photocatalytic Activity of TiO₂ with Visible Light by Sensitization Using a Novel Push-Pull Zinc Phthalocyanine

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A new one-pot synthesis of a novel A₃B-type asymmetric zinc phthalocyanine (AZnPc) was developed. The phthalocyanine complex was characterized unambiguously and used to prepare a TiO₂ hybrid photocatalyst to enhance its photocatalytic activity in the visible range. Different compositions of the phthalocyanine dye were tested in order to find the optimum amount of sensitizer to get the highest activity during the photocatalytic tests. The hybrid photocatalyst was characterized by UV-Vis diffuse reflectance (DRS) and Fourier transform infrared spectroscopy (FT-IR) and its photocatalytic activity was compared with that of the individual components considering the effects of sensitization on their efficiency to degrade Rhodamine B as a model reaction. A synergic improvement of the photocatalytic activity for the hybrid system was explained in terms of an improved electron injection from the photo-activated phthalocyanine to the TiO₂. Considering the structural features of the phthalocyanine sensitizer and their effect on aggregation, some mechanistic aspects of its binding to TiO₂ are suggested to account for the photocatalytic activity enhancement. Finally, the inhibitory effect on the sprouting of chia seeds (*Salvia hispanica*) was evaluated in order to test the toxicity of the water effluent obtained after the photodegradation process. According to our growth inhibition assays, it was found that the Rh-B degradation by-products do not lead to an acute toxicity.

1. Introduction

Since the discovery of the photocatalysis process [1], several research areas have been developed to get an insight into its operation with the ultimate aim of implementing a practical application, particularly in the fields of energy conversion and water depuration which have been identified as the biggest problems facing humanity over the next decades. For the latter, photocatalysis has received lately a lot of attention and the endeavors have been aimed at three different research fronts: improving the efficiency of the charge transfer processes, widening the absorption spectrum to the visible range, and ensuring catalyst recovery. In addition,

photocatalysis research has been focused on the depuration of water contaminated mainly with three kinds of recalcitrant organic compounds: dyes, pesticides, and pharmaceuticals, and in this field TiO₂ has established itself as the benchmark material [2]. However, the fact that it can only be activated with ultraviolet radiation due to its wide bandgap constitutes a drawback. Because of this, more recently, the scientific effort has been directed to broaden the visible light response band of TiO₂ using different approaches such as metal and nonmetal doping, coupling with other narrower bandgap semiconductors, and dye sensitization [3].

Dye sensitization is an inexpensive approach to extend the wavelength range of the incident radiation required to

activate TiO₂ and several methods can be used. However, due to its simplicity, impregnation of TiO₂ has been employed predominantly [4]. For the latter, the solubility of the dye must be considered in order to assure that only single molecules are adsorbed onto the TiO₂ instead of having clusters that eventually will quench the photo-activated species during the degradation process.

Due to the advantageous physical properties of phthalocyanines, in this work, a hybrid photocatalytic TiO₂/phthalocyanine system was conceived in which a novel asymmetric phthalocyanine dye was used as sensitizer. This idea was reinforced by the fact that some phthalocyanine based materials are known to exhibit photocatalytic activity by themselves [5]. In their work, Zhang et al. reported that the hierarchical tetranitrocopper phthalocyanine (TNCuPc) hollow spheres exhibited, simultaneously, high adsorption capacity and an excellent visible-light-driven photocatalytic degradation performance for Rhodamine B under visible light. However, taking into account that a myriad of phthalocyanine complexes exist, in the context of photocatalysis, the fact that only diamagnetic Pc-derivatives may act as efficient photosensitizers in the conversion of triplet oxygen (³O₂, ground state) into singlet oxygen (¹O₂, excited state) had to be considered [6].

Another important aspect to take into consideration, in order to increase the photocatalytic activity of the hybrid photocatalytic system, is the molecular structure of the phthalocyanine sensitizer. In this regard, Sharma et al. suggested [7] that the incorporation of push-pull phthalocyanines shows great potential to improve the electron injection into the semiconductor and at the same time to avoid the back electron transfer (recombination).

Accordingly, in the present work, we aimed to prepare a novel A₃B type asymmetric phthalocyanine complex with a structural design that incorporates both a diamagnetic central metal and a push-pull electronic functionality for the sensitization of a commercial TiO₂ material. In addition, we compared the photocatalytic activity of the hybrid photocatalyst considering the effects of sensitization on its efficiency to degrade the fluorescent dye Rhodamine B with visible light. Different compositions of the phthalocyanine dye were tested in order to find the optimum amount of sensitizer to get the highest activity during the photocatalytic tests. Finally, the inhibitory effect on the sprouting of chia seeds (*Salvia hispanica*) was evaluated in order to test the toxicity of the water effluent obtained after the photodegradation process.

2. Materials and Methods

2.1. Reagents and Materials. Dimethyl sulfoxide -DMSO- (99.9%, J.T. Baker), ethanol (99.6% J.T. Baker), pyridine (99.93%, J.T. Baker), ethyl acetate (99.9%, J.T. Baker), TiO₂ Evonik P25 -DP25- and Rhodamine B (95%, Aldrich), phthalonitrile (98%, Fluka), urea (99.5%, Merck), trimethyl borate (99%, Aldrich), chlorobenzene (J.T. Baker, 99%), 4,5-dichlorophthalonitrile (98%, TCI), zinc chloride (99.8%, Merck), H₂SO₄ (98%, Omnicem), and NaHCO₃ (99.99%, J.T. Baker) were used as received without further purification.

Silica gel for column chromatography, 60 (Fluka), was used as adsorbent for the purification of the asymmetric phthalocyanine.

2.2. Synthesis of the A₃B Type Asymmetrical Zinc Phthalocyanine (AZnPc). The synthesis of the AZnPc was carried out using a different synthetic approach developed by our group. In this one-pot synthesis, a boron subphthalocyanine was first prepared “in situ” using the phthalonitrile A precursor and then the second phthalonitrile B precursor was incorporated in the same flask to obtain the A₃B-type asymmetric phthalocyanine. The general procedure is described as follows. In a 100 mL two-necked round-bottom flask, 2 g of phthalonitrile, 315 mg of urea, and 2 mL of trimethyl borate were mixed together in 20 mL of chlorobenzene under N₂ atmosphere. The reaction was let to proceed at 130–135°C for 120 min under reflux conditions. Later on, the mixture was let to cool to room temperature and, then, 960 mg of 4,5-dichlorofthalonitrile and 680 mg of zinc chloride were added under N₂ flow and heating was restarted to complete the second step of the reaction at 130°C for 50 min. The final crude product was isolated after precipitation of a saturated H₂SO₄ solution into deionized water, neutralization with NaHCO₃, and filtration.

The purification of the AZnPc material was accomplished by repeated chromatographic separation taking advantage of the chelation effect of pyridinic compounds with zinc phthalocyanines (see Results and Discussion). For that, a 500 mg of crude AZnPc product was completely dissolved in dry pyridine and loaded into a chromatographic column packed with silica gel. Then, the column was eluted with ethyl acetate and several fractions were collected. In order to elute the pure AZnPc product completely, more pyridine was used to redissolve the phthalocyanine material stuck at the top of the column and then more ethyl acetate was used for the elution until no more product was separated. The pure material was recovered (18% yield) by evaporation of solvent and then it was analyzed by FT-IR, UV-Vis spectroscopies, and FAB mass spectrometry.

2.3. Sensitization of TiO₂ with AZnPc. In order to find out the optimum amount of phthalocyanine dye required to sensitize effectively the TiO₂ material, a series of tests varying the volume (0.5, 1.0, 2.5, 5.0, 7.5, and 10 mL) of dye solution in DMSO (6 μM) were carried out using the asymmetric phthalocyanine complex. The latter was chosen because it proved to be the most effective sensitizer compared to the other zinc phthalocyanine materials.

The sensitization of the TiO₂ materials was carried out as follows: in a 50 mL round-bottom flask, 15 mL of DMSO and 200 mg of TiO₂ (DP25) were mixed together and then the corresponding volume in mL (0.5, 1.0, 2.5, 5.0, 7.5, and 10.0) of a 6 μM AZnPc solution in DMSO was added. DMSO was chosen in both cases because, in the first place, it favors the dispersion of the TiO₂ material [8]; on the other hand, DMSO is the best solvent for the AZnPc material. The mixture was dispersed using an ultrasonic bath and, then, heating with the microwave oven was provided for 5 min. Then, after

cooling, magnetic stirring was provided for 10 min and then the photocatalyst was recovered by filtration after rinsing it with deionized water and ethanol and drying it at 100°C for 30 min.

The degradation tests were carried out using a hermetically closed chamber equipped with a 10 W LED visible light source (400–800 nm). The glass reactor was jacketed and the water inside was kept at $23 \pm 3^\circ\text{C}$ and air was bubbled into the system. For each degradation test, 15 mg of the photocatalyst were dispersed in 75 mL of a 7 mM water solution of Rhodamine B and stirred in the dark for 30 min to establish an adsorption-desorption equilibrium. The degradation process during irradiation was monitored by UV-Vis spectroscopy taking aliquots every 20 min during a 180 min period.

2.4. Characterization. XRD analysis was performed using a Bruker D8 Discover diffractometer on a parallel beam geometry using monochromatic $\text{CuK}\alpha 1$ radiation. System alignment was verified using a silicon single crystal. Data were collected for a 2θ range of $20\text{--}60^\circ$ with 0.02° steps.

UV-Vis absorbance and diffuse reflectance spectra for both the photocatalyst and phthalocyanine samples were obtained at room temperature using a Varian Cary 400 spectrophotometer equipped with a Harrick RD accessory. The FT-IR characterization was performed using a Perkin Elmer Spectrum One spectrophotometer with an ATR accessory. For the novel asymmetric phthalocyanine complex, the characterization was completed by mass analysis using the FAB ionization technique with a JMS-700 MStation Mass Spectrometer.

3. Results and Discussion

3.1. Experimental Aspects for the New One-Pot Synthesis of an Asymmetrical Phthalocyanine by In Situ Generation of a Boron Subphthalocyanine. Up to now, the most effective synthetic method to prepare a boron subphthalocyanine has been reported by Claessens et al. [9]. However, in spite of the higher reproducibility and yields obtained following their method, the authors still make use of BCl_3 (in xylene solution) and this brings to attention the disadvantages of using an air sensitive reagent. In addition, the chemical incompatibility of the BCl_3 y BBr_3 boron sources that, under the reaction conditions, can react as halogenating reagents of the benzenic ring in the phthalonitrile precursors has to be taken into account if a better synthetic protocol is going to be developed.

Due to this incompatibility, it has not been possible to obtain SubBPcs from substituted phthalonitriles that have strong electron-donor groups such as OH, F, and -OR and not even from weak electron-donor substituents like the alkyl -R groups so far. In the last case, the presence of benzylic positions that can be easily halogenated using BCl_3 has prevented the synthesis of hexa-alkyl substituted boron subphthalocyanines even under favorable reaction conditions that include the use of DBU and DBN as promoters and higher temperatures [10].

After several synthetic attempts using trimethyl borate as the boron source, the appropriate reaction conditions were determined. However, for the isolation step of the pure product, some difficulties were encountered, particularly, the conspicuous degradation of the SubBPc product, which has been documented in the literature [11], during the chromatographic purification using silica gel as adsorbent. Because of this, we conceived the idea of obtaining the final asymmetric push-pull phthalocyanine product by preparing “in situ” a SubBPc using first the phthalonitrile precursor A and, then, without isolating the SubBPc product, adding the second phthalonitrile precursor B and the metal salt to obtain the A_3B asymmetric phthalocyanine. Several high boiling point solvents were tested and chlorobenzene was probed to be the best solvent for the whole one-pot reaction (two steps) which was carried out using urea as NH_3 source to favor the formation of the SubBPc.

Due to the well documented intractable nature of most phthalocyanine materials, the isolation step for the complete characterization of the asymmetric Pc-product posed a challenge. In this respect, the lack of solubility, the possibility of oligomerization of the phthalocyanine units, and the aggregation phenomenon are the most prominent features encountered during the isolation step and during the chemical analysis of such compounds [12].

In our case, the purification of the push-pull asymmetric phthalocyanine material was accomplished by chromatographic separation taking advantage of the chelation effect of pyridinic compounds with zinc phthalocyanines [13]. For this, some pyridine was used repeatedly to chelate the AZnPc crude product at the top of the chromatographic column and, then, ethyl acetate was used as eluent. The identification of the main phthalocyanine product eluted first during the chromatographic purification was determined by the UV-Vis spectrum, FT-IR, and FAB mass spectrometry analysis and the spectra are shown in Figure 1.

3.2. DRX Analysis. The X-ray diffraction patterns of the commercial TiO_2 -DP25 and of the DP25-Pc composite are compared in Figure 2. The peaks observed for the TiO_2 -DP25 material match well with those from the JCPDF 21-1272 data base corresponding to the anatase phase ($2\theta = 25.4^\circ$) with additional peaks that correspond to the presence of the rutile phase as expected. The incorporation of the AZnPc dye does not modify the crystal structure of the TiO_2 -DP25 material, as can be seen by comparing the diffractograms in Figure 2, and this can be rationalized in terms of the very low quantity of phthalocyanine dye in the DP25-Pc composite.

3.3. UV-Vis and FT-IR Analysis. In Figure 3, the evidence from the UV-Vis and FT-IR spectroscopic analysis for the TiO_2 sensitization with the AZnPc complex is shown. The Soret band (300–400 nm) as well as the Q band (500–800 nm) in the visible spectrum are the typical absorption bands of phthalocyanines and for the phthalocyanine compound are very apparent. However, for the DP25-Pc photocatalyst, the presence of the dye is hardly appreciated in the spectrum and its effect in the bandgap energy is not very conspicuous either

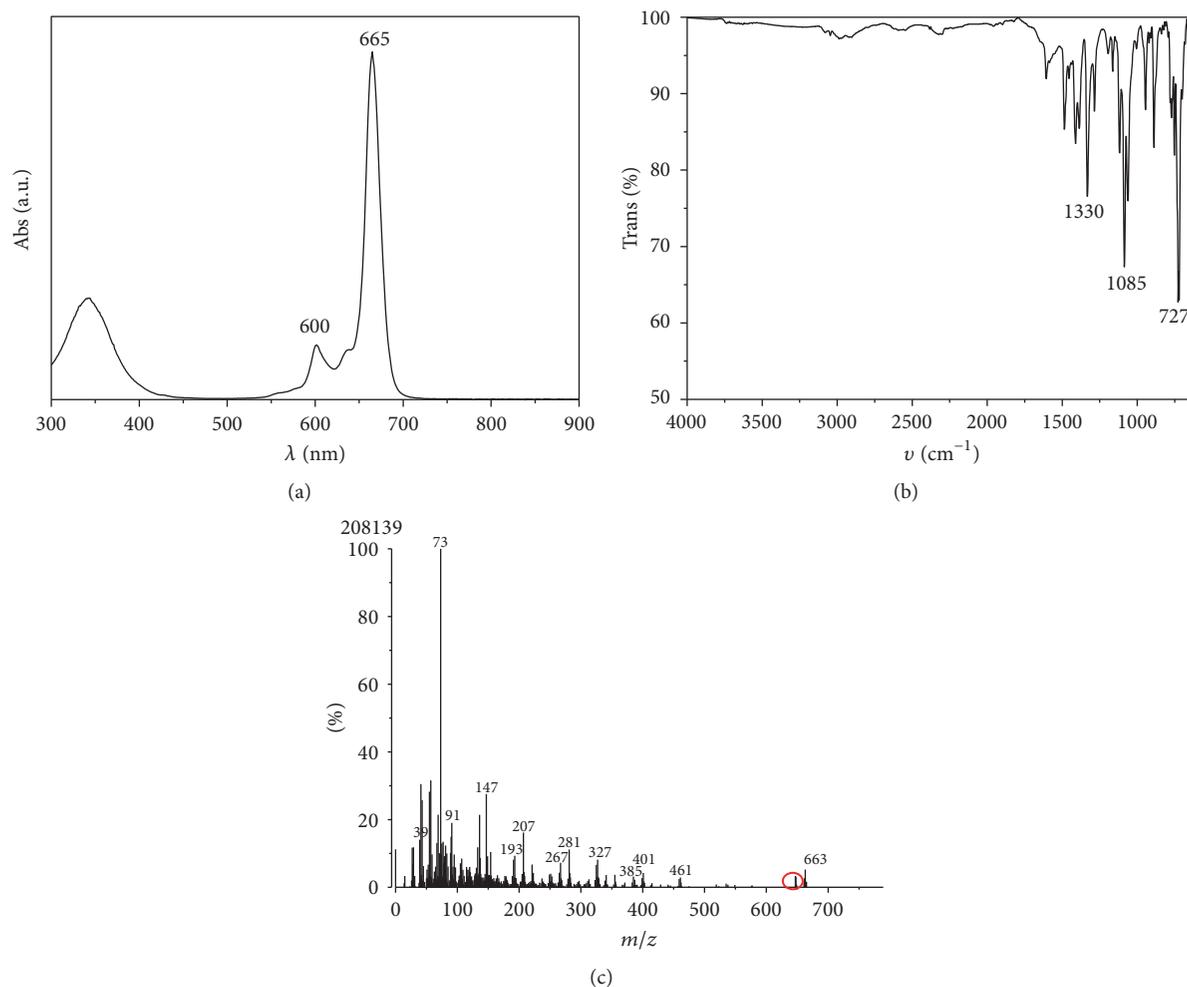


FIGURE 1: (a) UV-Vis spectrum in ethyl acetate, (b) FT-IR spectrum, and (c) FAB mass spectroscopy analysis for the AZnPc complex.

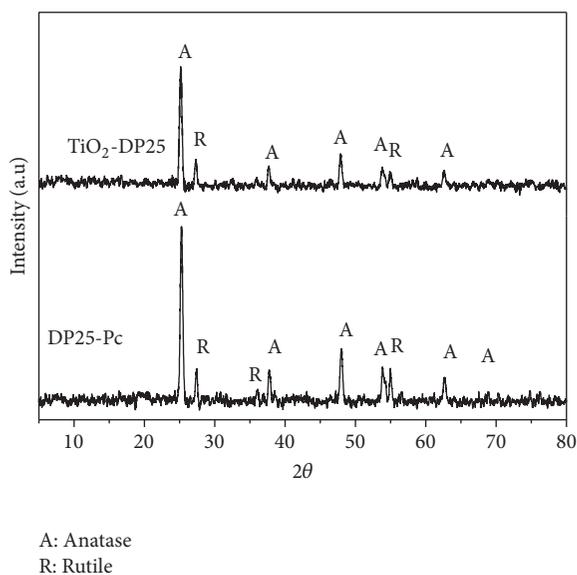


FIGURE 2: XRD patterns for commercial $\text{TiO}_2\text{-DP25}$ and dye-sensitized DP25-Pc photocatalyst.

due to the very low concentration of phthalocyanine used for sensitization. The bandgap energy of the materials was determined from the Kubelka-Munk equation [14] by using raw data of Figure 3(a) and is 3.10 eV and 3.09 eV for the $\text{TiO}_2\text{-DP25}$ and DP25-Pc , respectively.

The FT-IR spectrum of phthalocyanine compounds in the fingerprint region has characteristic vibration peaks that can be used to unambiguously identify the incorporation of these macrocycles onto the dye-sensitized photocatalysts. However, in our case again, due to the very low quantity of AZnPc used for the sensitization, only a few slight changes in the appearance of the FT-IR spectrum are observed (Figure 3(b)).

The incorporation of AZnPc to the commercial $\text{TiO}_2\text{-DP25}$ can be corroborated by the presence of a peak around 1332 cm^{-1} assigned to the stretching of the C-C of the isoindole group. Another feature that gives evidence of the presence of the phthalocyanine sensitizer is the intensity increase around 1087 cm^{-1} assigned to the $\beta(\text{C-H})$ vibration and, finally, the 727 cm^{-1} assigned to the $\gamma(\text{C-H})$ out of plane deformation of the phthalocyanine unit [15] in the FT-IR

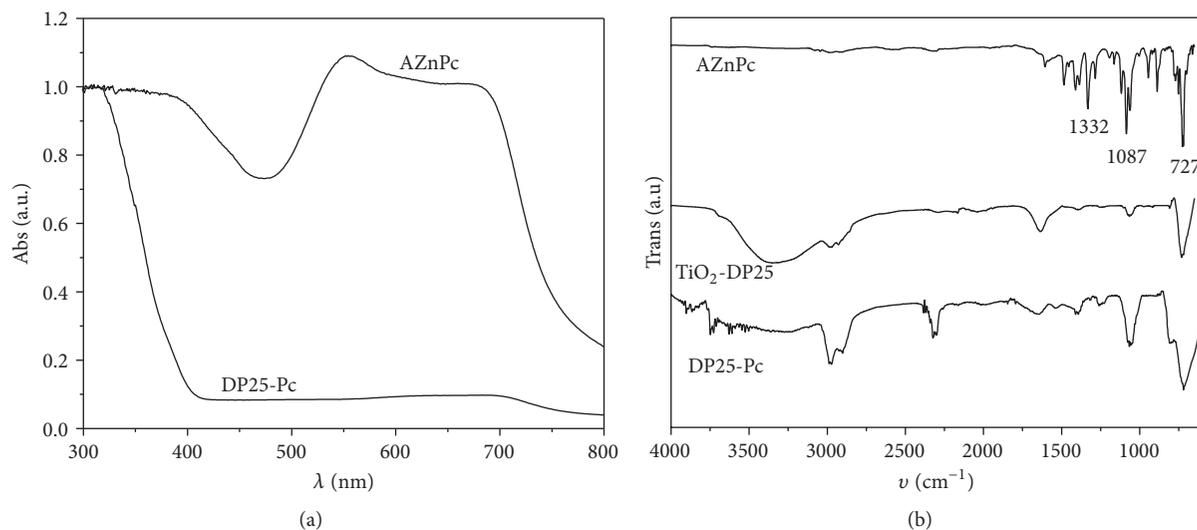


FIGURE 3: (a) UV-Vis spectra for AZnPc and dye-sensitized DP25-Pc. (b) FT-IR spectra for AZnPc, TiO₂-DP25, and dye-sensitized DP25-Pc.

spectrum. The peak around 2300 cm⁻¹ in DP25-Pc is due to carbon dioxide adsorbed from the atmosphere on the photocatalyst surface [16].

3.4. Screening Tests to Find the Best Photocatalytic System. Rhodamine B was selected as a model compound to evaluate the photocatalytic performance of both components of the hybrid system (TiO₂ and AZnPc) and that of the TiO₂/Pc composite.

In order to improve the activity of TiO₂-DP25 in the visible range, sensitization with a functional phthalocyanine dye was considered and a series of preliminary tests using four different ZnPcs was carried out. The complexes, which were prepared in our laboratory, included a nonsubstituted ZnPc (used in a previous work [17]), F₁₆ZnPc, tetracarboxy-ZnPc, and AZnPc. The aim was to find the best dye to be used as sensitizer taking into account the well-known fact that peripheral substitution of the phthalocyanine macrocycle allows the tuning of its electronic, optical, and photophysical properties and certain control over its aggregation and binding behavior.

From all the above phthalocyanine complexes used as sensitizers, AZnPc was the one that gave the highest activity for the degradation of Rhodamine B and this can be rationalized in terms of the effect that the nonsymmetrical structure of the dye has on the aggregation and binding behavior which, in turn, have a noticeable effect on the interface and surface charge transfer processes involved during the photocatalytic process.

With respect to aggregation, the AZnPc complex, having an asymmetric macrocycle, exhibited the highest solubility and this was confirmed experimentally in our laboratory using the methodology proposed by Ghani et al. [18]. Less aggregation has a positive effect in the charge transfer processes since the formation of clusters of the planar complexes is avoided and in this way the electron

transfer from the photo-activated phthalocyanine unit occurs toward the semiconductor TiO₂ instead of being quenched by the presence of other phthalocyanine units from the cluster [19].

On the other hand, the binding behavior of the sensitizer is known to have an important effect on the electron injection and recombination dynamics [20]. The binding of the dye to the TiO₂ surface can occur by physical adsorption, covalent bonding, or electrostatic interaction. These binding types have an effect on the charge transfer from the photo-excited chromophores to the conduction band of TiO₂ [21].

The preferential binding mode depends on the surface properties of TiO₂ which are also modulated by the environmental conditions. In this respect, it has been proposed that water molecules adsorbed onto the so-called bridging OH groups from the crystal lattice of TiO₂ polarizes its surface when the hydronium H₃O⁺ and the bridging O⁻ species are formed due to a hydrogen bonding interaction between them [22].

In our case, the A₃B type asymmetric AZnPc, where two chlorine atoms were substituted for two hydrogens in one of the four quadrants of the macrocycle, must be a polarized molecule due to the higher electronegativity of chlorine. Therefore, the electronic density is more concentrated on the asymmetric quadrant leaving the other benzenic rings positively charged and concomitantly creating a push-pull effect that favors the charge transfer processes in the photocatalytic system. We confirmed this by doing DFT theoretical calculations using the B3LYP hybrid functional to obtain the potential energy surface shown in Figure 4(a).

From all the above, it is very plausible that the AZnPc is anchored onto the TiO₂ surface through physical adsorption between its more positive side and the bridging O⁻ site from the TiO₂ crystal lattice (see Figure 4(b)). All the above accounts for the improved and faster electron transfer of the AZnPc dye which determines its better photocatalytic

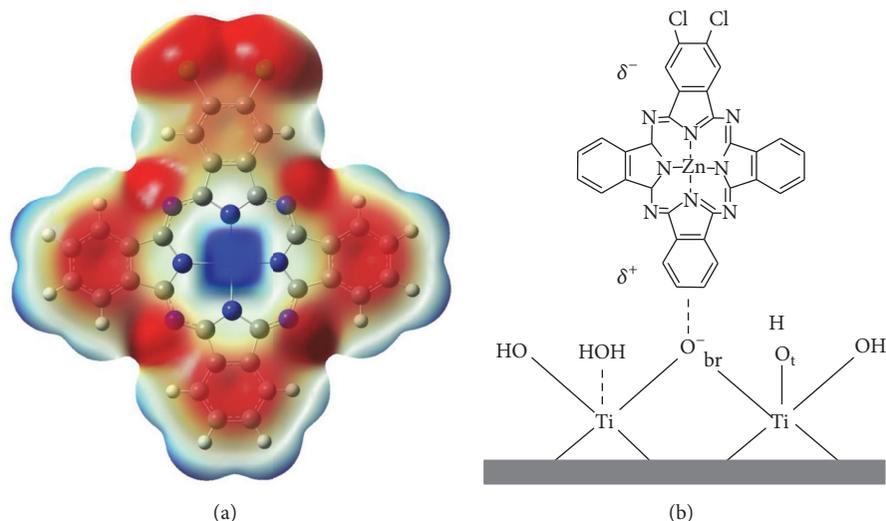


FIGURE 4: (a) B3LYP potential energy surface (PES) using Pople 6-311++G(d,p) as a basis set for the C-H-O-N-Cl atoms and the pseudopotential LANL2DZ for the Zn atom. (b) Preferential binding mode of AZnPc onto the TiO_2 surface.

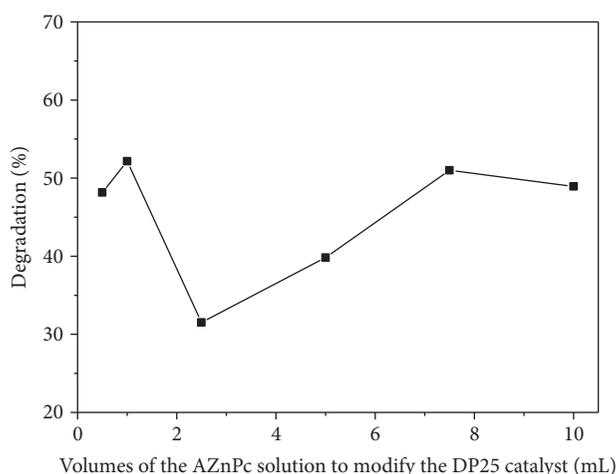


FIGURE 5: Rhodamine B degradation percentage for the TiO_2 -based photocatalysts sensitized with different volumes of the AZnPc solution, after 60 minutes of irradiation with visible light.

performance compared to the other ZnPc materials used as sensitizers in the preliminary tests.

The optimum amount of sensitizer was tested using 0.5 mL, 1.0 mL, 2.5 mL, 5.0 mL, 7.5 mL, and 10.0 mL of a 6 μM AZnPc dye solution in DMSO to modify the TiO_2 -DP25 catalyst (see Figure 5). From these results, a 1.0 mL of dye sensitizer was used thereafter for all the sensitized photocatalysts prepared.

3.5. Photocatalytic Degradation of Rhodamine B. The variation of UV-Vis absorption spectra of the Rhodamine B aqueous solution degraded by itself and in the presence of TiO_2 -DP25, AZnPc, and the composite DP25-Pc shows a gradual shift of absorption maxima from 554 nm for Rhodamine B to 500 nm for the degradation products obtained

after the photocatalytic degradation (Figure 6(a)). This has been already attributed to the formation of N-deethylated Rhodamine B [23] as the first step of degradation. The disappearance of the maximum peak at 554 nm indicates that Rhodamine B has been degraded.

The time-course photolysis and degradation of Rhodamine B with visible light can be observed in Figure 6(b). For the TiO_2 -DP25 alone, which should only be activated by UV light due to his wide bandgap, the original concentration of Rhodamine B is reduced up to a 68% after 180 min of reaction time, and this can be accounted for by considering that Rhodamine B itself is a dye which can sensitize the TiO_2 semiconductor promoting in this way its autodegradation [22].

The synergetic effect of dye sensitization for the photocatalytic degradation can be observed from the concentration plots in Figure 6(b) by comparing the gradual decreases of Rhodamine B concentration for all the single components and for the hybrid system after the 180 minutes process.

Here, it is worth mentioning that, compared to other reports from the literature [24–26] in which they use a similar TiO_2 /phthalocyanine composite to degrade Rhodamine B contained in water, our results show an improvement for both the photocatalyst preparation method and its efficiency during the process. In our case, the sensitization process is simpler and it only takes about an hour compared with other works where at least two and a half hours are required to prepare the photocatalyst [26]. In addition, the efficiency of our photocatalyst during the degradation process is comparable or even higher than those determined for other similar composite systems even though the dye quantity in weight for our sensitized photocatalyst (0.02%) and the power of the lamp we used (10 W) are lower than the ones used in the other reports [25, 26].

In addition, the experimental data for the concentration of Rhodamine B versus time should fit the integrated form

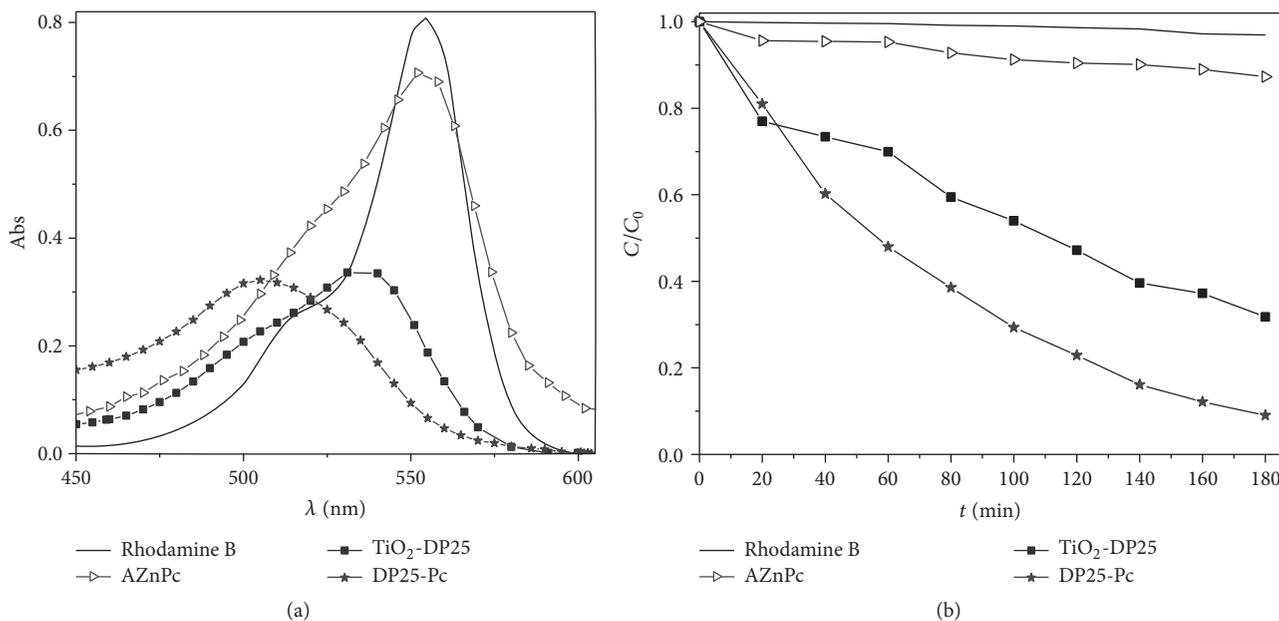


FIGURE 6: (a) UV-Vis final concentration of Rhodamine B with (AZnPc, TiO₂-DP25, and DP25-Pc) and without photocatalysts after 180 min of irradiation with visible light. (b) Time-course monitoring of Rhodamine B concentration with (AZnPc, TiO₂-DP25, and DP25-Pc) and without photocatalysts during 180 min irradiation with visible light.

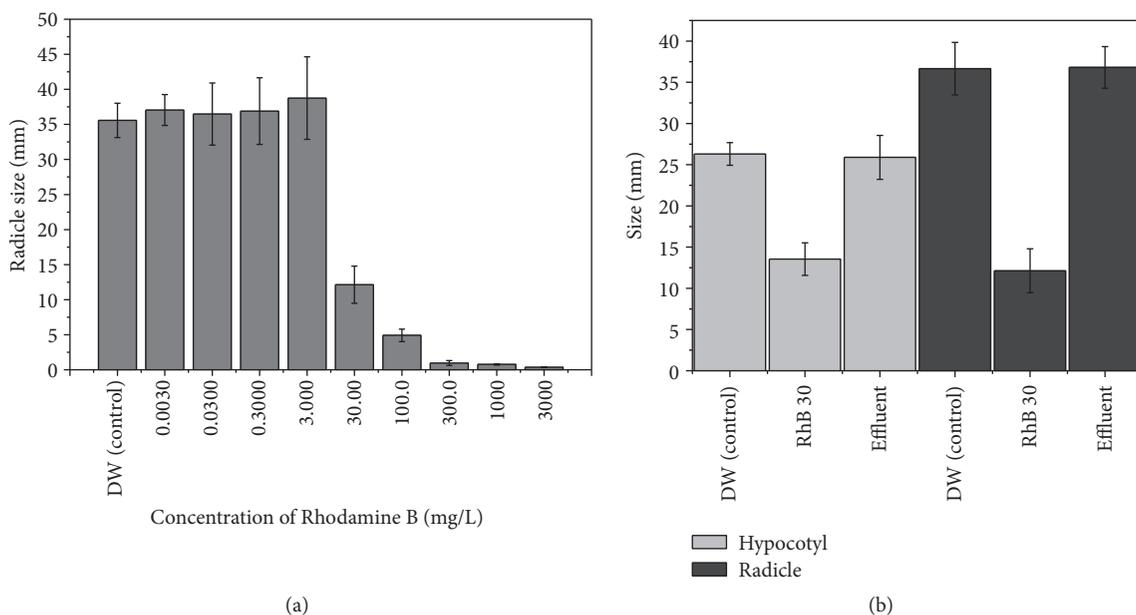


FIGURE 7: Growth inhibition assays for “*Salvia hispanica*” plants. (a) Effect of Rhodamine B concentration of the inhibition of growth for the radicle. (b) Radicle and hypocotyl growth test for the different solutions: deionized water (DW), 30 mg/L of Rhodamine B, (RhB 30) and effluent.

of a first-order rate law [27] (the rate constants are $6.40 \times 10^{-3} \text{ min}^{-1}$ and $12.90 \times 10^{-3} \text{ min}^{-1}$ for the TiO₂-DP25 and DP25-Pc, resp.).

Finally, growth inhibition assays for the radicle and hypocotyl (two parts of the seed embryo) in chia plants (*Salvia hispanica*) were performed to test the acute toxicity of the aqueous effluents obtained after photodegradation. The

quantification was carried out by comparison of the growth inhibition percentage of the seed parts after exposure to the effluents with respect to that of the control test following the methodology of Ramirez-Romero and Mendoza-Cantú [28]. For this, a series of Rhodamine B solutions with ten different concentrations was prepared (including the control) to find out the threshold concentration for growth inhibition

of those seed parts. From the results shown in Figure 7(a), it can be observed that the threshold concentration for the inhibition is 30 mg/L. With this information, all the experiments of Rhodamine B degradation were carried out using this concentration and the resultant effluents obtained were used thereafter for the toxicological tests. The results for the inhibition assays are presented in Figure 7(b) and they clearly show that the effluents do not inhibit the growth of both the radicle and hypocotyl.

4. Conclusions

We developed a new synthetic protocol to obtain an A₃B type asymmetric zinc phthalocyanine AZnPc by generating “in situ” a boron subphthalocyanine precursor. The former was used to sensitize a commercial TiO₂ material to obtain a composite TiO₂/AZnPc photocatalyst which was used to accomplish the photocatalytic degradation of Rh-B under visible light irradiation. The incorporation of the asymmetric zinc phthalocyanine to the semiconductor oxide revealed apparent changes in its optical and structural properties; particularly, a synergetic enhancement of the photocatalytic activity of the dye-sensitized materials was observed compared to the nonsensitized products. It was found that the TiO₂/AZnPc composite has higher photocatalytic activity for the degradation of Rh-B under visible light than pure TiO₂. This outstanding result was rationalized in terms of the orientation of the dye (favored by its asymmetric nature) that improves the electron injection from the photo-activated phthalocyanine to the TiO₂.

Finally, the growth inhibition assays demonstrated that the Rh-B degradation by-products do not lead to an acute toxicity.

Competing Interests

The authors declare that they have no competing interests.

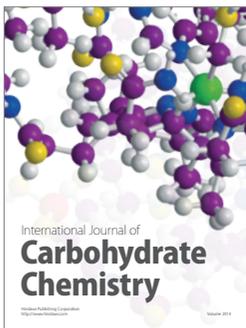
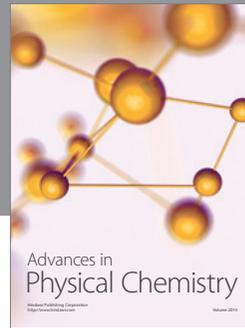
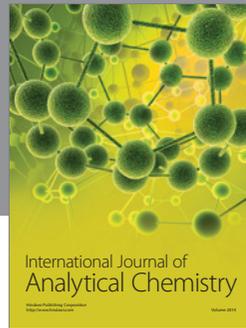
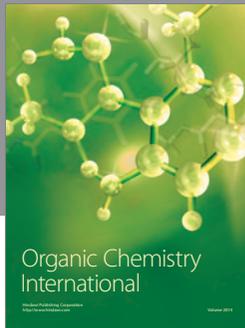
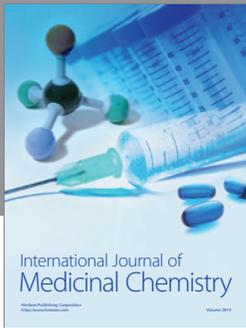
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