

**Review Article**

# Phthalocyanine-TiO<sub>2</sub> Nanocomposites for Photocatalytic Applications: A Review

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**Abstract:** Dye sensitized semiconductor can constitute efficient photochemical systems for the environmental remediation. Using metal free phthalocyanines (H<sub>2</sub>Pc) and metallophthalocyanine (MPc) complexes, has attracted much interest owing to its high stability, visible light photosensitivity and catalytic properties. Phthalocyanine sensitized titaniumdioxide (Pc/TiO<sub>2</sub>) catalyst is able to achieve the degradation of many organic pollutants by visible light as energy and O<sub>2</sub> in the air as the oxidant under ambient conditions. Owing to above mentioned properties, H<sub>2</sub>Pc and MPc immobilized TiO<sub>2</sub> photocatalysts have been tested for photocatalytic removal of organic and inorganic pollutants. In this review, production, characterization and application of Pc/TiO<sub>2</sub> catalysts are described and particularly focused on the studies concerning the photocatalytic applications either in the form of nano dust for suspension applications or thin film. Pollutants were classified into two main groups; namely organic toxic pollutants and dyes.

**Keywords:** Heterogen Photocatalysis, Photocatalytic Remediation, Dye Sensitized TiO<sub>2</sub>, Phthalocyanine Sensitized TiO<sub>2</sub>

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## 1. Introduction

The advanced oxidation technologies (AOTs) are especially attractive for micro pollutants at very low concentration with having high toxicity. As a class of AOTs, photocatalysis widely has been studied by many researchers. Titanium dioxide (TiO<sub>2</sub>) is one of the best known catalyst being employed for photocatalytic applications. Owing to its ecofriendly nature, it is frequently used in various applications. This semiconductor is used in environmental applications (especially in water and air treatment), catalyst in the conversion of large molecules into small mineralization products, electron transfer in electronics and solar cells, production of surface active self-cleaning materials etc. Even several reviews reported photocatalytic applications though this paper presented here also focuses on the same goal [1-12]. Modification of TiO<sub>2</sub> has gained great momentum after discovery of its photoaction by Fujishima [13, 14]. These

modifications and their applications have already been reviewed by several groups.

Some basic criteria should be taken into account in terms of an effective mineralization of specific pollutants. Principally the catalyst itself should be highly effective that degrade or mineralize the target compound in a short exposure period with incident light at low concentration. This criteria should be met first then the other important parameters could be considered such as cost, toxicity, re usability etc. Modification of TiO<sub>2</sub> with dye molecules is one of the preferred options that facilitates the electron transfer of TiO<sub>2</sub>. Chen et al. [11] coined a new definition for dye sensitized TiO<sub>2</sub> "surface-adsorbed antenna molecule (dyes or other color species)". They reviewed the dye sensitized TiO<sub>2</sub> photocatalysis and discussed the unique mechanistic characteristics, the constitution of photo degradation systems and their performances. The aforesaid review also deal with the involved radicalic reactions during the degradation as well as electron transfer

mechanism.

Electron transfer at the interfaces between dye molecule and semiconductor surface is a fundamental process in organic semiconductor devices such as organic light emission diodes and dye-sensitized photochemical cells [15, 16]. In particular, ultrafast charge separation by means of electron injection from electronically excited dye molecules to a conduction band of wide-gap metal oxide is a key step for improving the performance of dye-sensitized solar cells [17].

The main target of dye sensitization is to increase absorption of the photons from the light, especially visible light photons. Therefore, dye sensitization of TiO<sub>2</sub> produces more effective catalyst system by facilitating the electron transfer and shifting the wavelength of the light to the visible region. Basically, special organic or inorganic molecules can transfer the electrons under two circumstances:

1. if they have  $\pi$  electrons
2. if they have substituted Lewis base (such as O, N or S) containing unbounded electrons.

The sensitizer molecule (Dye) can absorb light to become excited (Dye\*) and can inject electrons into the conduction band of the semiconductor, forming conduction band electrons ( $e^-_{cb}$ ) and the oxidized antenna molecules. Mechanistic electron transfer is illustrated in Figure 1.

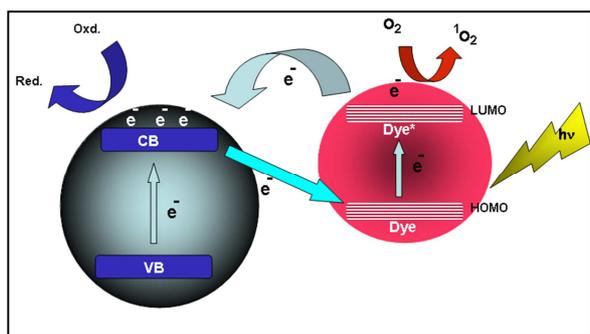
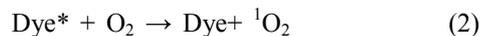


Figure 1. General electron transfer in dye sensitized solar cells.

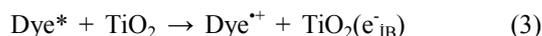
Electron transfer is stimulated via dye molecules. Basic mechanism of which is given below:



These excited molecules transform molecular oxygen to singlet oxygen via electron and energy transfer.



Other possible electron transfer mechanisms involves transfer of electrons from dye molecule to empty conductive band of TiO<sub>2</sub> resulting the formation of dye cationic radical and TiO<sub>2</sub> become conductor.



Dye sensitization is usually considered in solar cell applications and some important reviews are available in the current literature [11, 18, 19, 20]

The use of organometallic dyes, especially metal free phthalocyanines (H<sub>2</sub>Pc) and metallophthalocyanine (MPc)

complexes, has gained much interest owing to its high stability, visible light photosensitivity and catalytic properties. Phthalocyanines (Pc) are planar 18  $\pi$ -electron macroheterocycles and four isoindole subunits being linked together through nitrogen atoms (Figure 2).

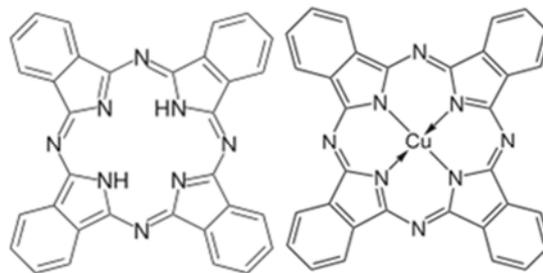


Figure 2. Chemical structure of metal free phthalocyanines (H<sub>2</sub>Pc) and metallophthalocyanine (CuPc) molecule.

Various Pc derivatives have been produced either changing the central metal ion or using different substituents at macrocyclic ring. Typical Pc molecule contains peripheral, nonperipheral and axial positions as given in Figure 3. Substitution generally affects the Soret and Q band of the molecule and this usually lead a significant band shifting of photocatalyst to visible region.

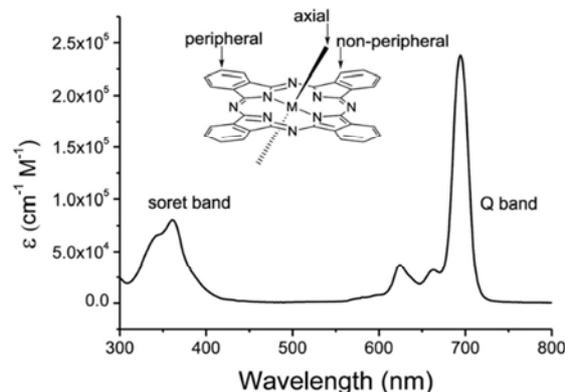


Figure 3. Typical structure of a phthalocyanine showing the non-peripheral, peripheral and axial positions to be functionalized [20].

Photosensitization of TiO<sub>2</sub> employing MPc is a promising method to shift the absorbance spectra of TiO<sub>2</sub> into the visible region, and it has already been reported in the current literature. Recent advances in phthalocyanine-based sensitizers for dye-sensitized solar cells and molecular properties of the phthalocyanines have been discussed by Ragoussi *et al.* [18]. Owing to above mentioned properties H<sub>2</sub>Pc and MPc immobilized TiO<sub>2</sub> photocatalysts have been tested in the photocatalytic removal of organic and inorganic pollutants for water remediation. This review is specifically focused on reported studies concerning phthalocyanine sensitized TiO<sub>2</sub> photocatalyst applications. Chen *et al.* [11] published an excellent review depicting all details of electron transfer in dye sensitization. However, this review did not mention phthalocyanine sensitized applications that have been quite popular in recent years. Therefore, here we summarize photocatalytic degradation/removal studies specifically

employing phthalocyanines as dye sensitizer. Pollutants were classified into two main groups; namely organic/inorganic pollutants and dyes. Phthalocyanines have been immobilized into/onto  $\text{TiO}_2$  either to obtain nano dust for suspension applications or thin film form.

## 2. Photocatalytic Degradation of Toxic Organic Pollutants

Various organic pollutants have been degraded or mineralized to the smaller molecules using phthalocyanine sensitized  $\text{TiO}_2$ . These are summarized in Table 1. One of the first application of Pc sensitized  $\text{TiO}_2$  was carried out by Fan and Bard. [21]. They employed  $\text{H}_2\text{Pc}$  or magnesium phthalocyanine ( $\text{MgPc}$ ) coated  $\text{TiO}_2$  particles, which was immobilized on an electrode surface, for the oxidative degradation of hydroquinone. They reported the photooxidation of hydroquinone took place on phthalocyanine sites and the reduction of oxygen on  $\text{TiO}_2$  sites simultaneously on the same particle. This was postulated from the energy diagram given in Figure 4. The band gap of  $\text{H}_2\text{Pc}$  (-2 eV) is lower than that of  $\text{TiO}_2$ . Therefore, irradiation with the light of energy smaller than the band gap of  $\text{TiO}_2$  but greater than the band gap of  $\text{H}_2\text{Pc}$  causes excitation of an electron to the conduction band of  $\text{H}_2\text{Pc}$  leaving a hole in the valence band. The photo-generated holes are sufficiently energetic (-0.8 V vs. NHE) to oxidize hydroquinone while the photo-generated electrons are injected into the conduction band of  $\text{TiO}_2$  leading to the reduction of oxygen. Other studies were also reported by the same group [22, 23]. Similar to their previous study the sensitized oxidation of several species (such as  $\text{I}^-$ ,  $\text{Fe}(\text{CN})_6^{4-}$ , hydroquinone,  $\text{Fe}(\text{II})\text{-EDTA}$ ) had been observed on electrode surface. Nevertheless overall reduction was not effective and provide only 20 percent degradation of target compound.

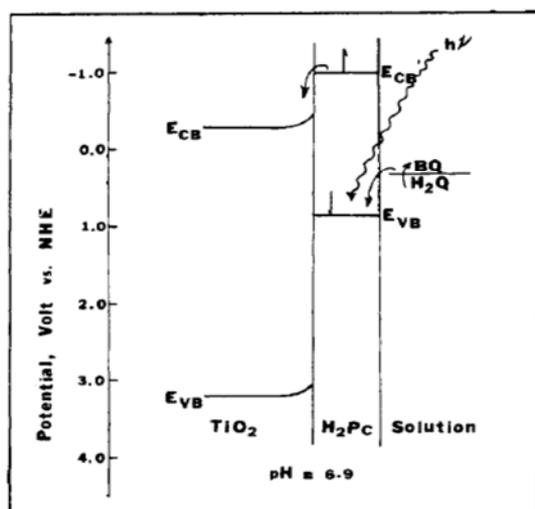


Figure 4. Schematic diagram for the electron transfer at  $\text{H}_2\text{Pc}$  on  $\text{TiO}_2$  [21].

Photocatalytic degradation of various pollutants has been studied by other researchers as given in Table 1, where the reports were chronologically summarized. Model compounds

were chosen from the most resistant pollutants, such as phenol, chlorophenols and nitrophenols. Various  $\text{H}_2\text{Pc}$  or  $\text{MPC}$  derivatives were employed as catalyst using either UV or visible light.

Hodak et al. [24] reported the preparation, characterization and stability of hydroxy aluminium tri carboxy monoamide phthalocyanine ( $\text{AITCPC}/\text{TiO}_2$ ) catalyst being prepared via wet deposition method. Photocatalytic activity of the modified semiconductor for the transformation of EDTA, oxalic acid, benzoquinone, KI, phenol, thiophenol, 4-chlorophenol, hydroquinone and salicylic acid under a visible range W lamp were investigated. The catalyst was ineffective in case of EDTA, oxalic acid and benzoquinone but the others. Degradation/transformation mechanism of each model compound was discussed and reaction mechanisms were evaluated.

Successful removal rates were reported by Ranjit et al. [25] employing  $\text{Fe}(\text{III})\text{Pc}/\text{TiO}_2$  catalyst, being prepared by sol-gel method. Structural characterizations were achieved by XRD, BET, TEM, EPR analyses and quite high degradation percentages were reported at 2.0-2.5 g/L catalyst mass in a batch reactor. Presence of  $\text{H}_2\text{O}_2$  in reaction medium significantly increased the degradation of p-aminobenzoic acid, being the most resistant species amongst all studied model compounds.

In another study, Iliev et al. [26] reported photocatalytic degradation of phenol and p-benzoquinone (0.64 mmol) with metal free phthalocyanine immobilized catalyst  $\text{H}_2\text{Pc}/\text{TiO}_2$ , being prepared by a wet deposition method. The anchoring of the Pc on  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  was carried out by their impregnation with a solution of the Pc in concentrated sulfuric acid. An amount of 1 g of the support was impregnated with 1.4 ml concentrated  $\text{H}_2\text{SO}_4$ , containing 10 mg of the Pc. Effectiveness of the catalyst was expressed as  $\text{O}_2$  consumption (mol  $\text{O}_2/\text{min}$ ). As conclusion  $\text{H}_2\text{Pc}/\text{TiO}_2$  was more effective than neat titania. Degradation was monitored and compared with other catalysts.

4-Nitrophenol had been used as a model pollutant for some research groups to test  $\text{Pc}/\text{TiO}_2$  catalysts. Same group produced  $\text{H}_2\text{Pc}/\text{TiO}_2$  and  $\text{CuPc}/\text{TiO}_2$  [27, 28] and double-decker lanthanum phthalocyanine ( $\text{LaPc}_2/\text{TiO}_2$ ) [29, 30] catalysts by impregnation to polycrystalline  $\text{TiO}_2$ . Structural analyses confirmed the formation of anatase crystal structure and  $\text{CuPc}/\text{TiO}_2$  was more effective than metal free  $\text{H}_2\text{Pc}$  sensitized  $\text{TiO}_2$  [27, 28]. Double-decker LnPc impregnated polycrystalline  $\text{TiO}_2$  ( $\text{LnPc}_2/\text{TiO}_2$ ) catalysts were prepared by employing a group of lanthanide group elements (Ce, Pr, Nd, Sm, Ho, and Gd) [29]. 1.85%  $\text{HoPc}_2/\text{TiO}_2$  and 1.38%  $\text{SmPc}_2/\text{TiO}_2$  were the most effective catalysts for 4-nitrophenol degradation and double-decker LnPc immobilization was effective on delocalization of positive charge. On the other hand, nano and micro sized double-decker  $\text{NdPc}_2/\text{TiO}_2$  catalysts were compared with their photocatalytic ability on 4-nitrophenol at the same concentration. Reaction rate for micro  $\text{NdPc}_2/\text{TiO}_2$  ( $8.2 \times 10^{-3} \text{ min}^{-1}$ ) was higher than nano  $\text{NdPc}_2/\text{TiO}_2$  ( $2.4 \times 10^{-3} \text{ min}^{-1}$ ) implying that micro structure is nearly 4 times higher than

nanostructured catalyst. Main criteria were declined not the crystal size but the interaction between the dye and TiO<sub>2</sub>. Lanthanide (Sm, Gd, Ho) bis-phthalocyanines (LnPc<sub>2</sub>) and TiO<sub>2</sub> composites were also tested for photocatalytic removal of 2-propanol (915 and 3660 mg/L in gas-solid phase and liquid-solid phase) [31]. In this case, 1.85% HoPc<sub>2</sub> immobilized TiO<sub>2</sub> was found to be the most effective catalyst, enabling to degrade almost 83% of initial 915 mg/L 2-propanol in gas-solid system. End products were propanon (70%) and acetaldehyde (5%). Photocatalytic oxidation of 2-propanol was lower at higher initial concentration (3660 g/L) and it was mainly converted to propanon (66%) and acetaldehyde (6%). Produced catalyst was able to 40% removal/conversion of 2-propanol in liquid-solid system. Gas phase photo-conversion seems to be more promising.

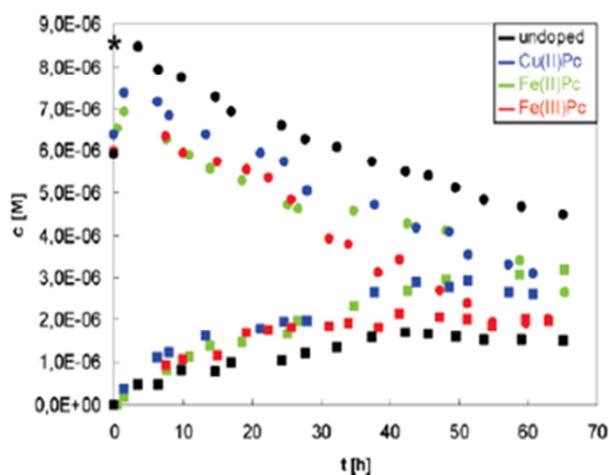
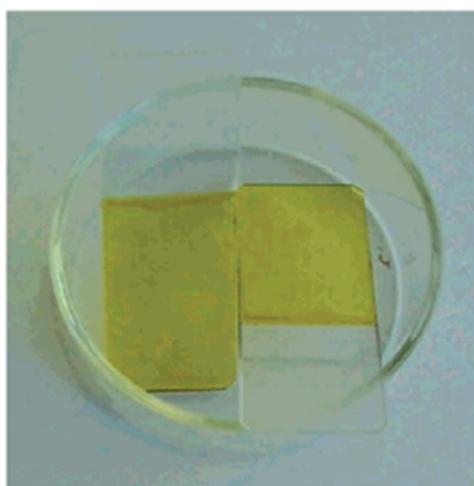
Ogunbayo and Nyokong [32] reported photocatalysts produced from palladium phthalocyanine complexes [PdPc: 2,3,9,16,17,23,24-octakis(R)Pd(II) and 1,4,8,11,15,18,22,25-octakis(R)Pd(II) derivatives] initially immobilized on single wall carbon nanotubes then impregnated on TiO<sub>2</sub>. Carbon nanotube was 0.7-1.2 nm diameter and 2-20 μm in length. 4-Nitrophenol degradation was monitored by spectrophotometric or gas chromatographic methods. PdPc modified catalysts were highly effective but produced degradation products such as fumaric acid, 4-nitro catecol, 1,4-nitro benzokinin.

An interesting study was published by Sun *et al.* [33] A series of metallo phthalocyaninesulfonates in sodium form

[MPcS, where M = Al(III), Sn(II), Zn(II), Cu(II), Fe(III), Co(II), Ni(II), Cr(III), V(V), Pd(II), Ru(II)] were prepared and tested for photo-bleaching these compounds by TiO<sub>2</sub> photocatalyst. The stability of the synthesized compounds were checked against UV (λ>320 nm) or visible light (λ>450 nm). In conclusion bleaching tendency was strongly dependent on the central metal in the complex. UV irradiation was much more effective than visible light in terms of degradation of all complexes, implying that Pc itself might go massive degradation which makes the Pc/TiO<sub>2</sub> catalyst's stability susceptible. However, the same study proved the presence of a sacrificing agent such as 4-chlorophenol, which was the main pollutant in many cases, prevented the degradation of Pc.

In a previous study, CuPc/TiO<sub>2</sub> catalyst was used in the photocatalytic removal of furfural (20 mg/L) [34]. A simple wet deposition method was employed and various CuPc concentrations were impregnated into TiO<sub>2</sub> crystal structure. Strong UV light source (500 W, λ=275 nm) was successfully degraded the target pollutant furfural in the presence of 0.1 g/L CuPc/TiO<sub>2</sub> catalyst after 3 hours exposure. 1.5% (w/w) mass fraction CuPc/TiO<sub>2</sub> was found to be the most effective catalysts for furfural degradation and strong aggregation had been observed over this concentration.

2-Propanol degradation was investigated by Palmisano *et al.* [35] MPc/TiO<sub>2</sub>/organosilica (ORMOSIL) catalysts were prepared, where M: Cu(II), Fe(II) or Fe(III) ion, by sol gel hydrolytic condensation.



**Figure 5.** MPc/TiO<sub>2</sub>/Organosilica (ORMOSIL) catalysts coated glass plates (left). Concentration of substrate (★, 2-propanol) and intermediate product (■, acetone) in the photocatalytic degradation mediated by undoped and phthalocyanines-doped ORMOSIL/TiO<sub>2</sub> films under solar light irradiation [35].

Details of preparation of sol-gel system was discussed in details and dip coated glass slides were used in the photocatalytic conversion of 2-propanol in the gas-phase mineralization of 2-propanol (Figure 5). The films exerted pronounced stability with the Fe(III)Pc-doped film showing the best performance in gas-phase mineralization of 2-propanol. Degradation percentage significantly increased with presence of MPc and metal ions in Pc macrocycle exhibited different catalytic ability. While

Cu(II)Pc/TiO<sub>2</sub>/ORMOSIL thin film degraded 63% of 2-propanol, Fe(III)Pc/TiO<sub>2</sub>/ORMOSIL thin film degraded 77% of 2-propanol after 60 hours exposure (Xe lamp, 1500 W, λ=275 nm). Acetone had been determined as intermediate product and CO<sub>2</sub> was reported as only one end product. System seems to be weak for effective degradation and total degradation takes relatively long time (over 60 hours).

4-Chlorophenol was one of the target compounds to be

tested for the Pc/TiO<sub>2</sub> catalysts. Sun and Xu [36] reported the preparation of a group of metallo tetracarboxyphthalocyanine catalyst (TC-Pc, adsorbed on TiO<sub>2</sub>, M: Al(III), Zn(II), Cu(II) and Co(II)) by wet deposition method. Chemical structure of TC-AlPc derivative is given in Figure 6. Three TiO<sub>2</sub> crystal structures were used namely CPT (Degussa P25, anatase phase 84%), CAT (anatase phase 97%) and CRT (anatase phase 92%), respectively. These oxides have different physical parameters such as peak intensity, crystallite size, surface area, pore size and pore volume. As Hodak et al. [24] suggested that using a Pc derivative containing polar groups (such as carboxyl or sulfonate) facilitates the attachment of large Pc molecule on TiO<sub>2</sub> particles which has polar character. If the attachment is strong enough, electron transfer becomes easier with better photocatalytic properties. Details of this mechanism have already been discussed by this group. TC-AlPc/TiO<sub>2</sub> (0.4% immobilized on TiO<sub>2</sub>) was the most effective catalyst (92% degradation) for oxidative degradation of 4-chlorophenol. TC-ZnPc/TiO<sub>2</sub> degraded easily and activation of others as partially slow. CAT crystal phase of TiO<sub>2</sub> is more effective than CPT and CRT. Effect of the bubbling of aqueous suspension with pure O<sub>2</sub>, air or N<sub>2</sub> had been investigated.

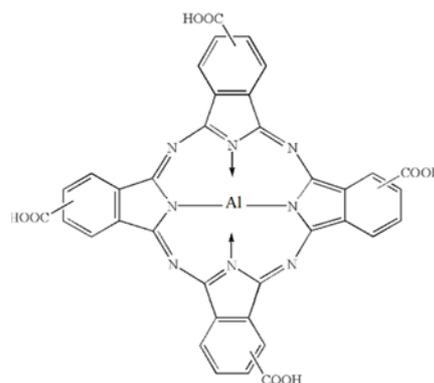


Figure 6. Aluminum 2,9,16,23-tetracarboxyphthalocyanine (TC-AlPc).

Ebrahimian et al. [37] published a paper concerning the removal of 2,4-dichlorophenol (40 mg/L) employing sulphonated cobalt phthalocyanine incorporated TiO<sub>2</sub> (S-CoPc/TiO<sub>2</sub>). S-CoPc was immobilized on TiO<sub>2</sub> by sol-gel method (2.24%). After a proper characterization of the catalyst (XRD, BET, DRS, TEM, TGA and FTIR) aqueous 2,4-dichlorophenol sample was illuminated with a 400 W Kr lamp (producing 90%UV-A and 10% UV-B light) in the presence of 0.2 g/L catalyst. Structural data given in Figure 7 reveal that main catalyst structure is in the anatase form.

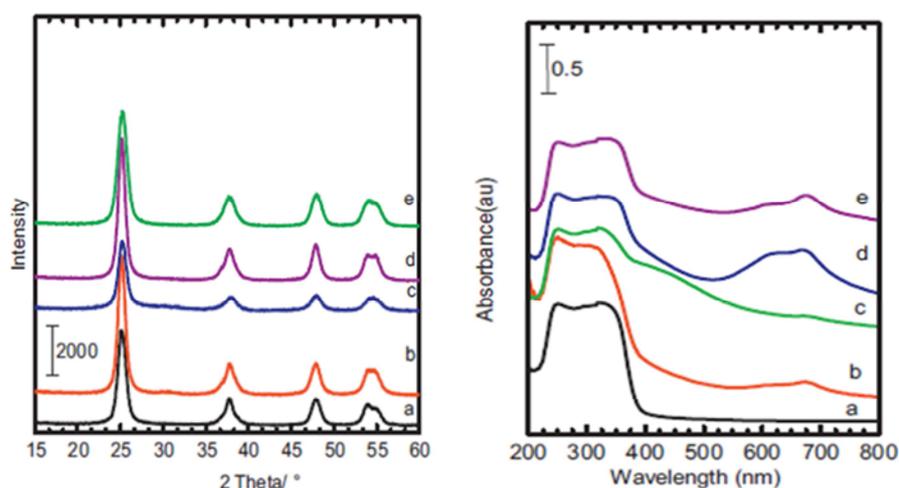


Figure 7. Powder XRD patterns and DRS of a) TiO<sub>2</sub>, b) CoPcS/TiO<sub>2</sub> (0.56), c) CoPcS/TiO<sub>2</sub> (1.12), d) CoPcS/TiO<sub>2</sub> (2.24) and e) CoPcS/TiO<sub>2</sub> (3.36) [37].

Spectrophotometric and GC/MS analysis were performed to monitor the concentration of 2,4-dichlorophenol and intermediate products. It is well known that dichlorinated phenols are highly resistant to the degradation. But catalyst was reported to be quite effective for oxidative degradation of 2,4-dichlorophenol and 96% of the initial concentration had been successfully removed/transformed after 150 minutes exposure. Oxalic acid and maleic acid were determined as major intermediate species.

Zinc phthalocyanine-modified titanium dioxide, ZnPc/TiO<sub>2</sub> was used for degradation of a hydroxytyrosol (Hy) present in olive oil mill wastewater [38]. Photodegradation of Hy was found to be enhanced by the photocatalyst under illumination with solar light. Enhancement is attributed to photocatalyst itself and zinc phthalocyanine sensitization for generation of

more •OH radicals. Intermediate components were also identified by GC/MS.

TiO<sub>2</sub> photocatalyst is effective in the reduction process as much as the oxidation. Phthalocyanine sensitization provokes electron transfer and, as a result, enhancement conductive band of TiO<sub>2</sub> has more electron being capable of the reduction of target compounds. This approach was tested in photocatalytic removal of chromium (VI) ions. One of the previous studies was carried out by Meichtry et al. [39], where hydroxoaluminium tricarboxymonoamide phthalocyanine (TC-AlPc) was adsorbed on TiO<sub>2</sub> by wet deposition. This derivative has been specially chosen as it has three carboxy groups and an amide group attached on Pc ring. These functional groups enhance the absorption of Pc on polar TiO<sub>2</sub> surface as well as facilitating the electron transfer. A Xe lamp

(450 W, cut off filter,  $\lambda > 600$  nm and  $\lambda = 395$  nm) was used for the exposure at pH=2 and catalyst mass was 0.1 g/L. Cr(VI) concentration had been determined by spectrophotometric methods after coloring reaction with diphenylcarbazite. Nevertheless, TC-AlPc/TiO<sub>2</sub> was not effective in terms of Cr(VI) removal (15% removal after 180 min.). Intermediate

product Cr(V) formation was proven by electron paramagnetic resonance experiments (EPR). As reported, presence of 4-chlorophenol as sacrificing agent greatly enhanced reduction of Cr(VI). Mineralization degree was measured by total organic carbon (TOC) analyses.

**Table 1.** Photocatalytic degradation of toxic pollutants using Pc/TiO<sub>2</sub> catalyst.

Catalyst	Method	Experimental Conditions	Target Molecule	Catalyst Characterization	Analysis	Ref. and Explanation
Hydroxoaluminium tricarboxymonoamide phthalocyanine TC-AlPc/TiO <sub>2</sub>	Wet deposition method TiO <sub>2</sub> (1 g in 300 cm <sup>3</sup> water) and 3 mL 5 x 10 <sup>-3</sup> M AITCPC dissolved in DMSO mixed (5x10 <sup>-5</sup> mol AITCPC/g TiO <sub>2</sub> )	Visible range: W lamp (24 V, 250 W) with a 665 nm cutoff filter UV range: High pressure Xe lamp (450 W) with a 645 nm cutoff filter	Thiophenol (2.2x10 <sup>-4</sup> M) KI (2x10 <sup>-2</sup> M) Phenol (1.6x10 <sup>-4</sup> M) Hydroquinone (1.2x10 <sup>-4</sup> M) 4-Chlorophenol (1.3x10 <sup>-4</sup> M) Salicylic acid (1.1x10 <sup>-2</sup> M) Benzoquinone (1.1x10 <sup>-4</sup> M) EDTA (5x10 <sup>-3</sup> M) Oxalic acid (5x10 <sup>-3</sup> M)	SEM, EDX, FTIR, DRS,	UV/Vis., HPLC	[24] Degradation percentages are: Thiophenol: 100% KI: 0.9% Phenol: 47.7% Hydroquinone: 67.1% 4-Chlorophenol: 98% Salicylic acid: 30.8% Benzoquinone: No degradation EDTA: No degradation Oxalic acid: No degradation
Fe(III)Pc/TiO <sub>2</sub>	Sol gel: TIP (7.38 mL) MeOH (10.2 mL) 0.0144 g Fe(III)Pc Hydrolysis: MeOH (10.2 mL) HCl (120 µL) Drying: 100°C (2 h) Calcination: 425°C (14 h)	Xe(Hg) (200 W) 60 min. Catalyst mass: 2.0-2.5 g/L Batch system	p-nitrobenzoic acid (a) p-chlorophenoxy acetic acid (b) p-aminobenzoic acid (c) salicylic acid (d) aniline (e) 9.6x10 <sup>-5</sup> -4.2x10 <sup>-4</sup> M	XRD, BET, TEM, EPR	TOC, GC-MS/FTI UV-Vis. GC-MS	[25] Spectroscopic analyses support by GC-MS Not effective for $\lambda = 455$ nm for (c) H <sub>2</sub> O <sub>2</sub> addition (9.6x10 <sup>-5</sup> M) increases degradation of (c) by 30% H <sub>2</sub> O <sub>2</sub> -Pc is effective for (c) Degradation percentages are: a) 83-32% b) 88% c) 100-50% d) 100% e)>85%
H <sub>2</sub> Pc/TiO <sub>2</sub> H <sub>2</sub> Pc/Al <sub>2</sub> O <sub>3</sub>	Wet deposition TiO <sub>2</sub> (powder, 1 g) H <sub>2</sub> SO <sub>4</sub> (1.4 mL) Pc (10 mg)	Halogen lamp(12V, 50 W) Catalyst mass: 70 mg (containing 1.7 µmol Pc) pH=9 Time: 600 min	Phenol (0.64 mmol) p-Benzoquinone (0.64 mmol)	ET, SEM, X-RAY	Elemental analysis, UV-Vis., IR	[26] Photocatalytic action was evaluated as O <sub>2</sub> consumption (mol O <sub>2</sub> /min) 6.9 mol O <sub>2</sub> /min for Pc/TiO <sub>2</sub> (Phenol) 4.7 mol O <sub>2</sub> /min for Pc/TiO <sub>2</sub> (BQ) 4.2 mol O <sub>2</sub> /min for Pc/Al <sub>2</sub> O <sub>3</sub> (Phenol) 3.9 mol O <sub>2</sub> /min for Pc/Al <sub>2</sub> O <sub>3</sub> (BQ)
H <sub>2</sub> Pc/TiO <sub>2</sub> CuPc/TiO <sub>2</sub>	CuPc impregnated polycrystallin TiO <sub>2</sub>	Hg lamp (125 W) 0.2-1.5% (w/w) CuPc impregnated 1% (w/w) H <sub>2</sub> Pc impregnated 0.5 L photoreactor pH=4 Catalyst mass: 0.8 g/L Time: 5 h	4-Nitrophenol (20 mg/L)	X-RAY, BET, DRS, SEM, H-NMR, MS, UV-Vis., FTIR	UV-Vis., TOC	[27] 1% CuPc/TiO <sub>2</sub> (anatase) is the most effective Presence of Cu(II) increase electron transfer
CuPc/TiO <sub>2</sub> CuPp/TiO <sub>2</sub>	CuPc impregnated polycrystallin TiO <sub>2</sub>	Hg lamp (125 W) 1.0% (w/w) CuPc impregnated 1% (w/w) CuPp impregnated 0.5 L photoreactor pH=4 Catalyst mass: 0.8	4-Nitrophenol (20 mg/L)	X-RAY, BET, DRS	UV-Vis., TOC, Nonpurgable Organic carbon (NPOC)	[28] 1% CuPp/TiO <sub>2</sub> is more effective 1% CuPc/TiO <sub>2</sub> has lower activity due to higher aggregation and dimerization

Catalyst	Method	Experimental Conditions	Target Molecule	Catalyst Characterization	Analysis	Ref. and Explanation
MPc/TiO <sub>2</sub> M: Al(III), Sn(II), Zn(II), Cr(III), Co(II), Ni(II), Fe(III), V(V), Pd(II), Ru(II), Cu(II)		g/L Time: 6 h  Hg lamp (375 W, λ=320 nm) Halogen (500 W, λ=450 nm) 50 mL photoreactor pH=4 Catalyst mass: 1.0 g/L Time: 5 h	Degradation of MPc itself	BET	UV-Vis.-NIR	[33] Central metal ion in Pc molecule is important λ=320 nm is more effective Order of MPc/TiO <sub>2</sub> Ru>V>Sn>Cu>Zn> Fe>Pd>Cr>Co>Ni Bleaching of MPc is prevented in the presence of 4-chlorophenol
Lanthanide-Pc/TiO <sub>2</sub> Ln: Ce, Pr, Nd, Sm, Ho, and Gd	Double-decker LnPc impregnated polycrystallin TiO <sub>2</sub> (LnPc <sub>2</sub> /TiO <sub>2</sub> )	Hg lamp (125 W) LnPc <sub>2</sub> μg/g TiO <sub>2</sub> 0.5 L photoreactor pH=4 Catalyst mass: 0.8 g/L Time: 6 h	4-Nitrophenol (20 mg/L)	X-RAY, BET, DRS	UV-Vis., TOC	[29] 1.85% HoPc <sub>2</sub> /TiO <sub>2</sub> and 1.38% SmPc <sub>2</sub> /TiO <sub>2</sub> are the most effective catalysts for 4-nitrophenol degradation Double decker LnPc immobilization is effective on delocalization of positive charge
CuPc/TiO <sub>2</sub>	0.3 g TiO <sub>2</sub> in 50 mL ethanol and 500 mg/L CuPc in ethanol were mixed	Xe lamp (500 W, λ=275 nm) 200 mL photoreactor pH=9 Catalyst mass: 0.1 g Time: 3 h	Furfural (20 mg/L)	XRD, BET, DRS, UV-Vis.	UV-Vis., TOC	[34] 1.5% CuPc/TiO <sub>2</sub> is the most effective catalysts for furfural degradation Higher CuPc concentration increase aggregation Using ethanol as solvent prevents the aggregation Activity decreases over 1.5% CuPc due to inhibition of light-TiO <sub>2</sub> interaction 90% degradation of furfural measured by UV-Vis. 70% TOC removal
MPc/TiO <sub>2</sub> /Organosilica (ORMOSIL) M: Cu(II), Fe(II), Fe(III)	TiO <sub>2</sub> /ORMOSIL Sol gel hydrolic condensation SOL-1: TEOS and MTMS mixed with HCl (21.2 mM, 670 μL) SOL-2: TiOp and MPc dissolved in 2,4-pentadien SOL-1 and SOL-2 were mixed for 20 min and SOL-3 was obtained. Microscope glasswas dip coated with SOL-3 and dried at 50°C for 3 days	Xe lamp (1500 W, λ=275 nm) 800 mL photoreactor pH=9 Catalyst mass: 0.1 g Time: 6 h	2-Propanol (0.5 μL (8.5x10 <sup>-6</sup> M, gas phase)	SEM, UV-Vis., X-RAY, Contact angle, Elemental analysis	GC	[35] Degradation percentage increased with MPc TiO <sub>2</sub> /ORMOSIL thin film degraded 45% of 2-propanol Cu(II)Pc/TiO <sub>2</sub> /ORMOSIL thin film degraded 63% of 2-propanol Fe(III)Pc/TiO <sub>2</sub> /ORMOSIL thin film degraded 64% of 2-propanol Fe(III)Pc/TiO <sub>2</sub> /ORMOSIL thin film degraded 77% of 2-propanol
Aluminum 2,9,16,23-tetracarboxyphthalocyanine (TC-AlPc/TiO <sub>2</sub> ) Copper 2,9,16,23-Tetracarboxyphthalocyanin (TC-CuPc/TiO <sub>2</sub> ) Cobalt 2,9,16,23-Tetracarboxyphthalocyanin (TC-CoPc/TiO <sub>2</sub> )	Wet deposition Three TiO <sub>2</sub> crystal structure (CAT, CPT and CRT) TiO <sub>2</sub> (1.25 g/L) and AlPc (1% mass fraction of TiO <sub>2</sub> ) mixed overnight and	Halogen lamp (500 W, λ=450 nm) 0.4% AlPcTC immobilized on TiO <sub>2</sub> 50 mL pH=5.5 Catalyst mass: 1 g/L Time: 7 h	4-Chlorophenol (0.23 mM)	XRD, FTIR, BET, DRS, EPR, UV-Vis., Photoluminesans	HPLC, IC	[36] Most effective catalyst is AlPcTC/TiO <sub>2</sub> (92% degradation) ZnPcTC/TiO <sub>2</sub> degraded easily and others were activated slowly CAT form of TiO <sub>2</sub> is more effective than CPT and CRT

Catalyst	Method	Experimental Conditions	Target Molecule	Catalyst Characterization	Analysis	Ref. and Explanation
Lanthanide (Sm, Gd, Ho) bis-phthalocyanines (LnPc <sub>2</sub> ) and TiO <sub>2</sub> composites	Double-decker LnPc impregnated polycrystallin TiO <sub>2</sub> (LnPc <sub>2</sub> /TiO <sub>2</sub> )	dried at 80°C Xe lamp (1500 W) 75 mL photoreactor pH=6.5 Catalyst mass: 1 g/L Time: 5 h	2-Propanol (915 and 3660 mg/L in gase-solid phase and liquid-solid phase )		GC	[31] 1.85-1.38 and 3.30 μmol Sm, Gd and Ho phtalocyanine derivatives were immobilized on TiO <sub>2</sub> . 1.85% HoPc <sub>2</sub> /TiO <sub>2</sub> is the most effective composite. 83% removal for 915 mg/L 2-propanol (producing 70% propanon and 5% acetaldehyde) in gas-solid system. 36% removal for 3660 mg/L 2-propanol (producing 66% propanon and 6% acetaldehyde) in gas-solid system. 40% removal for 915 mg/L 2-propanol in liquid-solid system.
Hydroxoaluminium tricarboxymonoamide phthalocyanin (TC-AIPc)	Wet deposition	Xe lamp (450W, cut off filter, ( λ>600 nm and λ=395 nm ) pH=2 Catalyst mass: 0.1 g/L Time: 3 h	Cr(VI) ions (20 mg/L) 4-Chlorophenol	EPR, ICP-OES, UV-vis., DRS	UV/Vis. TOC	[39] AITCPC/TiO <sub>2</sub> is not effective for Cr(VI) removal (15% removal after 180 min.) Removal rate is increased in the presence of sacrificing reagent 4-chlorophenol.
NdPc <sub>2</sub> /TiO <sub>2</sub> (nano and micro size)	Double-decker NdPc <sub>2</sub> impregnated polycrystallin TiO <sub>2</sub> (NdPc <sub>2</sub> /TiO <sub>2</sub> ) Impregnation to TiO <sub>2</sub>	Hg lamp (125 W) 2.5 L photoreactor pH=3.5 Catalyst mass: 0.4 g/L Time: 2 h	4-Nitrophenol (20 mg/L)	SEM, XRD, DSC/TGA, FTIR	UV/Vis. Chrom. TOC	[30] Reaction rate for micro NdPc <sub>2</sub> /TiO <sub>2</sub> (8.2x10 <sup>-3</sup> min <sup>-1</sup> ) is higher than nano NdPc <sub>2</sub> /TiO <sub>2</sub> (2.4x10 <sup>-3</sup> min <sup>-1</sup> ).
Palladium complexes (PdPc)/SWCNT (SWCNT: 0.7-1.2 nm diameter and 2-20 μm in length)	2,3,9,16,17,23,24 -octokis (R)Pd(II) derivatives 1,4,8,11,15,18,22 ,25-octokis (R)Pd(II) derivatives	Tungsten lamp (100 W, 30 V) Glass reactor 50 mL pH=8.5 Time: 350 min.	4-Nitrophenol (4-10x10 <sup>-5</sup> M)	X-Ray, TEM, Raman Spectroscopy, UV-vis., TOF/MS, MALDI	UV/Vis. GC	[32] Reaction rate for 2,3,9,16,17,23,24-octokis (dodesilthiophthalocyaninato)Pd(II) derivative is the highest. Degradation rate is lower for aryl group containing derivatives. Degradation products are fumaric acid, 4-nitroatecol, 1,4-nitro benzokinon.
ZnPc/TiO <sub>2</sub>		Solar light	Hydroxytyrosol in olive oil mill waste		GC-MS	[38]
Sulphonated cobalt phthalocyanin CoPcS/TiO <sub>2</sub>	Sol-gel 2.24% CoPcS immobilized on TiO <sub>2</sub>	400 W Kr lamp (90%UV-A+ 10% UV-B) pH= Natural Catalyst mass: 0.2 g/L Time: 150 min.	2,4-dichlorophenol (40 mg/L)	XRD, BET, DRS, TEM, TGA, FTIR	UV/Vis. GC/MS	[37] 96% removal of 2,4-dichlorophenol with CoPcS/TiO <sub>2</sub> . Intermediates: Oxalic acid and maleic acid.

### 3. Photocatalytic Degradation of Dyes

Phthalocyanine-TiO<sub>2</sub> nanocomposites were also used in the removal of dye pollutants, and classified as a separate group, all given in Table 2. Similar to the publications given in Table 1, different types of Pc derivatives have been used in the effective removal/degradation of dye pollutants from aqueous medium. Table 2 gives a chronological publication list.

Either H<sub>2</sub>Pc or MPc derivatives were employed in the sensitization of TiO<sub>2</sub>. MPc derivatives were preferred than H<sub>2</sub>Pc ones by many researchers since the metal ion in the

macrocyclic ring provides additional electron transfer properties.

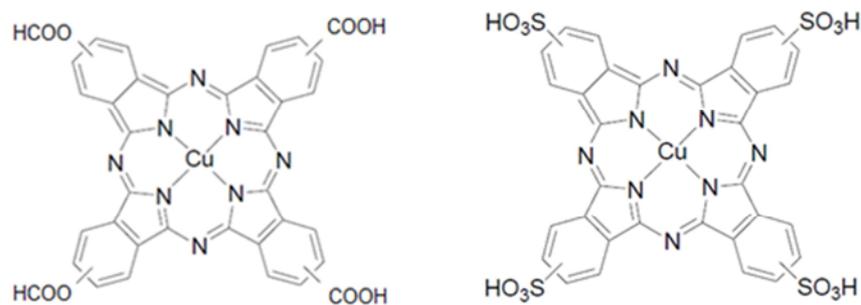
H<sub>2</sub>Pc was used as sensitizer in a number studies. Mesostructured titania particles modified with Pc were prepared by wet deposition method using cetyltrimethylammonium bromide (CTAB) as a template [40]. Formation of hexagonal mesopore structure was confirmed by low-angle XRD and TEM analyses. Pc molecules were immersed in the pores in a monomeric state. H<sub>2</sub>Pc/TiO<sub>2</sub> particles were tested in photocatalytic removal of methyl orange (MO, 9.81 mg/L) using a xenon lamp (>610 nm). Total removal of MO had been achieved with free Pc/TiO<sub>2</sub> (catalyst

mass: 5 g/L) after 96 hours exposure. But the catalyst mass used in this study was quite high and exposure period was longer than usual applications.

Two more studies employing free phthalocyanine for sensitization were also published by the same group. H<sub>2</sub>Pc have been modified on previously Fe-doped TiO<sub>2</sub> nanocrystals (H<sub>2</sub>Pc/Fe-TiO<sub>2</sub>) [41, 42]. In the first work they reported the visible light induced photocatalytic activity of Fe doped TiO<sub>2</sub> (doping was 0, 0.05, 0.5 and 3.0 mol%) as photocatalysts for the degradation of MO. Structural properties of prepared catalysts were confirmed by using XRD, FT-IR, EDX, BET, DRS, UV-Vis, SEM and TEM techniques. Pc/Fe-TiO<sub>2</sub> nanocrystals possessed the anatase phase with crystal sizes of about 10-23 nm and high surface areas of 2.8-37.3 m<sup>2</sup>/g. The doping amount of Fe had remarkably affected the

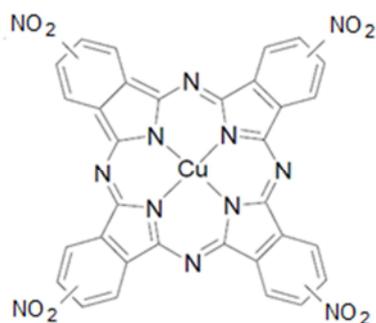
photocatalytic activity of TiO<sub>2</sub> and 0.5 mol% Fe doping had provided the highest dye removal ability. As reported, that both free phthalocyanine and Fe interaction into the structure had resulted a shift in the energy band gap to lower energy region. It was reduced from 3.26 to 2.26 eV in the case of free Pc modified on 3% Fe doped TiO<sub>2</sub> nanocrystals. MO have been degraded at higher ratio using a 500 W halogen lamp using only 0.5 g/L catalyst. But exposure periods were 7-8 hours for a successful removal.

Copper phthalocyanine (CuPc) derivatives were specifically used in many applications [43-52]. Tetracarboxylated CuPc (TC-CuPc) and tetrasulfanated CuPc (TS-CuPc) derivatives (Figure 8) were mostly preferred due to their polar character facilitating the attachment of the Pc itself onto polar TiO<sub>2</sub> surface [43-47, 49, 52].



**Figure 8.** Chemical structure of TC-CuPc and TS-CuPc derivatives.

Apart from these derivatives a tetranitro phthalocyanine CuPc (TN-CuPc) derivative has been used by Zhang et al. [48] (Figure 9).



**Figure 9.** Chemical structure of tetranitro phthalocyanine CuPc derivative.

Unsubstituted CuPc was also employed in the sensitization of TiO<sub>2</sub>. Mekprasart et al. [50] produced a CuPc/TiO<sub>2</sub> catalyst for the degradation of Rhodamine B (RB). Similarly, Liao et al. [51] used CuPc in the production of CuPc/TiO<sub>2</sub> nanotubes by hydrothermal treatment and catalyst was tested for degradation of RB. All available immobilization techniques have been employed for the production of CuPc/TiO<sub>2</sub> catalyst in the literature including sol-gel [43, 47], sonochemical synthesis [44], hydrothermal [45, 49, 51], wet immobilization [46], electrospinning [48] and other methods such as ball-milling [50] and doctor blade [52].

TC-CuPc has been employed in the sensitization of

amorphous TiO<sub>2</sub> [43] and mesoporous TiO<sub>2</sub> [46]. Former study reports the production of amorphous TC-CuPc/TiO<sub>2</sub> catalyst prepared by sol-gel method. Structural characterization was carried out by BET, XRD, DRS and UV-vis. methods. A 100 W halogen lamp that producing radiation higher than 550 nm (visible region) was used in a photo reactor. Degradation of MO (10 mg/L) was investigated and its concentration was monitored by spectrophotometric method. Successfully 80% of initial MO concentration had been removed by amorphous TC-CuPc/TiO<sub>2</sub> catalyst. This catalyst has been reported to be more active than CuPc/SiO<sub>2</sub> and CuPc/TiO<sub>2</sub>. The same researchers reported another study using mesoporous TiO<sub>2</sub>, where a wet immobilization soft template method was used. The catalyst contained 4% TC-CuPc and after appropriate structural characterization it was employed for the degradation of fluorescein. High removal rate has been obtained with this catalyst and it was more effective than the same catalyst prepared with TiO<sub>2</sub>-P25.

Wallejo et al. [52] produced another TcCuPc/TiO<sub>2</sub> catalyst employing simple doctor blade method and the catalyst was tested in the removal of methylene blue (MB). Sensitization significantly improved the degradation rate by 3.6 times.

Wang et al. [44] and Zhiyu et al. [45] reported the removal of MO in the presence of TS-CuPc modified TiO<sub>2</sub> catalyst. Wang et al. [44] prepared the catalyst by sonochemical synthesis using titanium tetrachloride (TiCl<sub>4</sub>), triethanolamine and ethanol as starting compounds. Test solution of MO (20 mg/L) removed by 73.39% after 30 minutes exposure with a halogen lamp (420 W, λ ≥ 450 nm). On the other hand Zhiyu et al. [45] reported

higher removal rate (90% removal) of MO using the same TS-CuPc/TiO<sub>2</sub> catalyst under the similar experimental conditions. In the latter case, they employed a hydrothermal method for production of the catalyst and longer exposure period (3 h). Jing *et al.* [49] produced a TS-CuPc modified TiO<sub>2</sub> catalyst prepared by hydrothermal method for degradation of RhB (50 mg/L). Catalyst mass was lower (0.25 g/L) and exposure period was 2 hours. Dye sensitized catalyst was much more effective than neat TiO<sub>2</sub> for the degradation of RhB.

An interesting study was reported by Hui *et al.* [47] concerning the preparation and characterization of TS-CuPc/TiO<sub>2</sub> thin film. A sol-gel dip coating method was described for the preparation of glass slides and material was used for photocatalytic removal of RhB by visible light. The film had an anatase-brookite-rutile microcrystal structure. Degradation mechanism and formation of intermediate products were also investigated. TS-CuPc had an increase in the photocatalytic action of thin film and it could be reused for 2-3 times.

2,9,14,23-Tetra nitro copper phthalocyanine/TiO<sub>2</sub> catalyst (TN-CuPc/TiO<sub>2</sub>) was prepared by electrospinning technique and solvothermal processing [48]. Catalysts were tested in the degradation of RhB (10 mg/L) in a batch reactor employing a visible light ( $\lambda \geq 450$  nm) source. The mass ratio of TS-CuPc to TiO<sub>2</sub> was 1:50 and 1:20. Catalyst containing higher amount of TN-CuPc was reported to be more effective reaching 87% removal rate of RhB. However, this catalyst was able to remove only 54% of RhB in the presence of ter-butyl alcohol that behaving as radical scavenger.

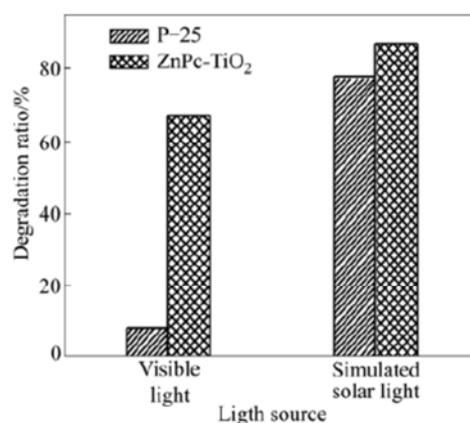
There are two additional reports employed an unsubstituted copper phthalocyanine (CuPc) sensitized TiO<sub>2</sub> [50, 51]. In the first study, CuPc was immobilized to TiO<sub>2</sub> (varying between 0.5-2% mass ratio) by ball-milling assisted process.  $5.9 \times 10^{-6}$  M RhB was degraded by only 20 mg catalyst and UV light (450 W). The amount of catalyst was declared as 20 mg but it was not clear that how much volume of the RhB solution treated with catalyst. Almost 100% removal was achieved with 1% CuPc immobilized TiO<sub>2</sub> after 35 minutes exposure. Presence of CuPc with certain loading amount significantly ameliorated the photocatalytic performance of TiO<sub>2</sub>. At the first sight, this result seems to be quite effective removal of RhB. However, it should be kept in mind that light source was a powerful UV lamp and initial concentration of RhB was quite low (2.62 mg/L). This concentration was so low that dye removal might occur by direct adsorption onto the solid catalyst rather than photocatalytic process.

Liao *et al.* [51] produced TiO<sub>2</sub>-based nanotubes being synthesized by hydrothermal treatment under the alkaline conditions using P25 as the raw material. Copper phthalocyanine was immobilized as a sensitizer to prepare CuPc/TiO<sub>2</sub>NT composite material by the immersion method. Results showed that the unmodified nanotube had large surface area (362.6 m<sup>2</sup>/g) and high pore volume (2.039 cm<sup>3</sup>/g). After modification the composite material still had quite high surface area (244.2 m<sup>2</sup>/g) and pore volume (1.024 cm<sup>3</sup>/g) for 0.2% CuPc containing catalyst. The degradation rate of RhB reached to 59% when compared, it is 3.3 times higher than

pure TiO<sub>2</sub>NT after 180 minutes exposure period.

Apart from CuPc derivatives other metallo phthalocyanines were prepared and tested in the removal of different dyes. Zinc, cobalt, manganese, iron phthalocyanine derivatives were used as sensitizer in various studies [53-61].

ZnPc [56, 59], tetrasulfonated ZnPc (TS-ZnPc) [53] and tetracarboxylated zinc phthalocyanine (TC-ZnPc) derivatives [52] were used as sensitizer and prepared catalysts were tested in dye degradation. RB (10 mg/L) degradation was investigated by in the presence of ZnPc/TiO<sub>2</sub> catalyst (5 g/L) prepared by a hydrothermal method [56]. A 160 W high-pressure mercury lamp with and without a 410 nm cutoff filter was used in the production of visible and solar light. The experimental results indicated that ZnPc extended the photocatalyst's absorption band into the visible region effectively. The sensitized TiO<sub>2</sub> has higher photocatalytic activity than bare TiO<sub>2</sub> (Degussa P25) under the simulated solar light and the visible light. When ZnPc content was lower than 0.20  $\mu\text{mol/g}$  (which was equal to 0.012% mass fraction) the sensitizer itself behaved as electron donor. It was concluded that enhanced transfer of the photo-induced electrons to the conduction band of TiO<sub>2</sub> caused a higher RB removal. However, when ZnPc content was higher than this concentration, ZnPc dimer formed resulting in the decrease of photocatalytic activity. RB concentration was monitored for 30 minutes exposure period. While visible light degradation was 85%, simulated solar light degraded nearly 90% of initial dye. Visible light degradation seems to be slightly lower but it should be taken more seriously since ZnPc sensitization greatly effects the photocatalytic action of TiO<sub>2</sub> (Figure 10).



**Figure 10.** Comparison of photocatalytic activity of P25 and 0.2  $\mu\text{mol/g}$  ZnPc/TiO<sub>2</sub> [56].

Oliveira *et al.* [59] prepared a ZnPc/TiO<sub>2</sub> catalyst by wet deposition method (1.6% ZnPc) along with other TiO<sub>2</sub> based catalysts. After the characterization of the catalyst powder it was used for the photocatalytic degradation of Ponceau 4R (C. I. 16255,  $4 \times 10^{-5}$  M) in a photo reactor. Dye concentration was monitored by spectrophotometric measurement and total organic carbon (TOC) analyses were carried out to evaluate the mineralization of organic structure. Ponceau 4R was successfully removed (100% removal) from aqueous sample with ZnPc/TiO<sub>2</sub> catalyst and UV light. However TOC analyses

revealed that only 50.4% mineralization was achieved even after 120 minutes exposure. This result indicates that Ponceau 4R was transferred to colorless organic structures rather than undergoing total mineralization.

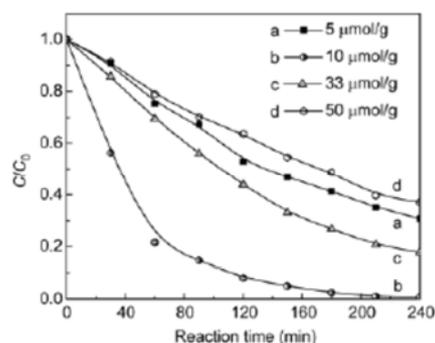
Tetrasulfonated and tetracarboxylated zinc phthalocyanine derivatives were the interests of some groups. TS-ZnPc/TiO<sub>2</sub> catalyst was prepared and used in the RhB degradation by Zhong et al. [53]. In-situ and sol-gel preparation methods were used and materials were characterized by XRD, UV-Vis, FTIR, zeta potential and fluorescence spectroscopic techniques. Vallejo et al. [52] have used a TC-ZnPc derivative for TiO<sub>2</sub> sensitization. Dye was immobilized on TiO<sub>2</sub> using multi step doctor blade method. Catalyst was used for MB removal and it was 2.8 times active than neat TiO<sub>2</sub>.

Cobalt phthalocyanines were another class of sensitizers involving the photocatalytic removal of dye pollutants [54, 55, 57, 61]. Composite photocatalyst TiO<sub>2</sub>/Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> was initially prepared by a sol-gel method [54]. Trinuclear cobalt phthalocyanine ammonium sulfonate (tri-CoSPc) was immobilized onto the surface of composite by simple dipping method. After immobilization the structural analysis was performed. XRD analysis revealed that TiO<sub>2</sub> has an anatase crystal form. As a result of sensitization a significant red-shift was seen and the photo-response range was extended to the visible region. Malachite green degradation was 42.9% after 60 minutes exposure and 90.3% in 6 hours in the presence of catalyst. Another study was published by the same research group [57]. In this case, a composite CoSPc/TiO<sub>2</sub>/K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> was prepared by sol-gel and dipping methods as described above. Different calcination temperatures were applied and their effectiveness were compared. The photocatalytic degradation experiments were performed for Orange II as simulated pollutant under the illumination of visible light. Decolorization rate was 85% in 5 hours.

Cobalt(II) phthalocyanine-sensitized hollow magnetite-silica-titanium dioxide (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub>) hierarchical nanostructures had been prepared by Wu et al. [61]. A combination of solvothermal and dipping process was employed for CoPc sensitization. The material was characterized by sophisticated techniques after immobilization of CoPc on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> the primary nanostructures. The hierarchical nanostructure exhibited excellent photocatalytic efficiency for the degradation of MB under UV-vis and visible light irradiation. Not only being very effective for the MB removal, but the separation of photocatalyst was also reported to be simple applying only an external magnetic field. This property facilitates the separation of solid catalyst and further filtration system is not required.

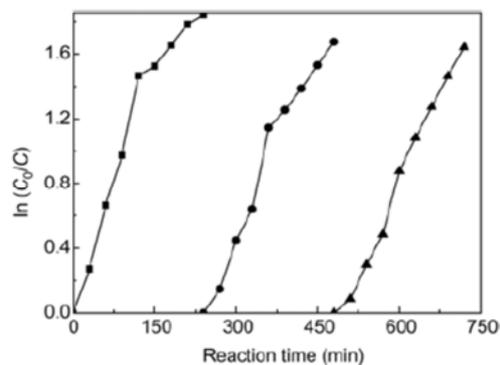
Manganese phthalocyanine tetrasulfonic acid (TS-MnPc) was impregnated onto TiO<sub>2</sub>/SiO<sub>2</sub> by sol-precipitation method using tetrabutyl titanate (TBOS), tetraethyl orthosilicate (TEOS) and n-octylamine as template [58]. TS-MnPc/TiO<sub>2</sub>@SiO<sub>2</sub> was characterized by X-ray diffraction (XRD) and UV-Visible diffuse reflectance spectra (UV-Vis DRS). The photocatalytic degradation of RhB and the catalytic oxidation of o-phenylenediamine (OPDA) under visible light irradiation were used as probe reactions. The mineralization efficiency and

the degradation mechanism were evaluated by using chemical oxygen demand (COD) assay and electron spin resonance (ESR), respectively. RhB was efficiently degraded by TS-MnPc/TiO<sub>2</sub>@SiO<sub>2</sub> under visible light irradiation (Figure 11). Complete decolorization of RhB was achieved after 240 min of irradiation and 64.02% COD removal occurred after 24 h irradiation. ESR results indicated that the oxidation process was dominated by the hydroxyl radical and superoxide radical generated in the system.



**Figure 11.** Degradation of RhB by TS-MnPc/TiO<sub>2</sub>@SiO<sub>2</sub> with different catalyst loadings. ([RhB]=1.10×10<sup>-5</sup> mol/L; catalyst mass=0.20 g/L; pH 6.88) [58].

The dried catalyst samples were used again in the degradation of RhB with identical experimental conditions (Figure 12), and as a result, the catalyst was active for three consecutive cycles and showed good stability.

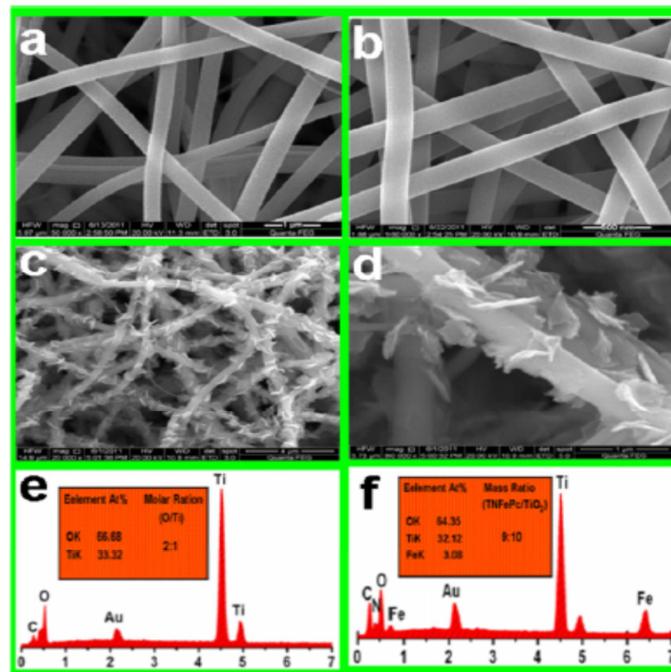


**Figure 12.** Three consecutive cycles of photodegradation with TS-MnPc/TiO<sub>2</sub>@SiO<sub>2</sub> (10 μmol/g). ([RhB]=1.10×10<sup>-5</sup> mol/L, catalyst mass=0.20 g/L and pH 6.88) [58].

Iron containing phthalocyanine immobilized TiO<sub>2</sub> catalyst was carried out by Guo et al. [60]. One-dimensional 2,9,16,23-tetra-nitrophthalocyanine iron(II) derivative was used in the production of TiO<sub>2</sub> nanofiber heterostructures (TN-FePc/TiO<sub>2</sub>). The material was produced by a simple combination of electrospinning technique and solvothermal process. Proper characterization by FE-SEM, EDX, TEM, XRD, XPS, and IR analyses revealed that TNFePc nanosheets were successfully grown on the primary TiO<sub>2</sub> nanofibers. SEM images of nanofibers are given in Figure 13. Photocatalytic tests were carried out in the presence and absence of H<sub>2</sub>O<sub>2</sub>. TN-FePc/TiO<sub>2</sub> nanofiber heterostructures

exhibited much higher degradation rate of methyl orange than the pure TiO<sub>2</sub> and TN-FePc/TiO<sub>2</sub> nanofiber with H<sub>2</sub>O<sub>2</sub> was superior to the others under visible light. The material was

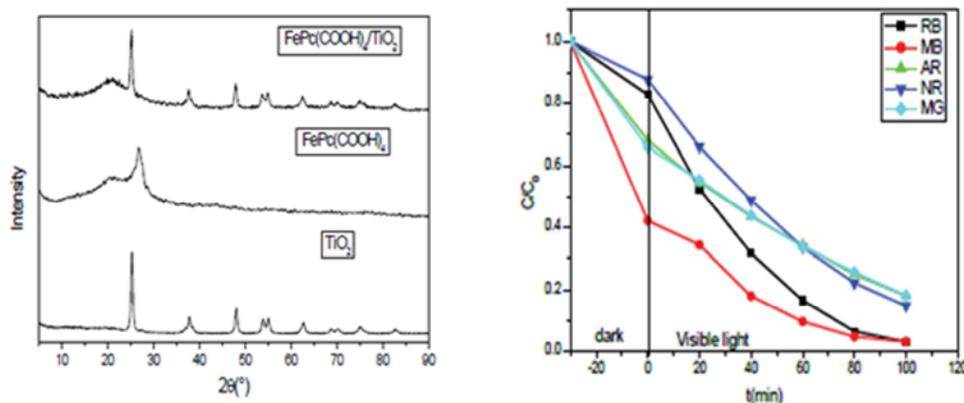
easily recycled and reused without the decrease of the photocatalytic activity due to their one-dimensional nanostructural property of TiO<sub>2</sub> nanofibers.



**Figure 13.** a) and b) SEM images of the TiO<sub>2</sub> nanofiber with different magnifications; c) and d) SEM images of the TN-FePc/TiO<sub>2</sub> nanofiber heterostructures with different magnifications; e) and f) EDX spectra of samples [60].

An interesting study was reported by Yang *et al.* [62], they produced a series of binuclear metal (II) phthalocyanine hexasulphonates, defined as (M-M)Pc, and used these derivatives for the sensitization of nanocrystalline TiO<sub>2</sub> thin films. These derivatives were (Co-Co)Pc, (Co-Zn)Pc, (Co-Mn)Pc, (Zn-Zn)Pc, (Zn-Mn)Pc and (Mn-Mn)Pc. The films were characterized by SEM, XRD and profilometer. The catalytic activity of the film was evaluated by the degradation of MB under visible light irradiation and dark condition. The catalytic activity of hetero Pc sensitized TiO<sub>2</sub> catalysts were more effective than that of homo counterparts.

A tetracarboxylic acid Fe(III) phthalocyanine complex (TC-Fe(III)Pc) was prepared by a solid fusion method, and the product was tested in the photodegradation of MB, RhB, acid red (AR), neutral red (NR), and malachite green (MG) under visible light radiation [63]. The XRD pattern of TC-Fe(III)Pc/TiO<sub>2</sub> was essentially identical to that of anatase structure and all model pollutant dyes were photodegraded by the catalyst within 100 minutes (Figure 14). The photodegradation mechanism was further evaluated by the data obtained using photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS).



**Figure 14.** XRD patterns of TiO<sub>2</sub>, FePc(COOH)<sub>4</sub>, and FePc(COOH)<sub>4</sub>/TiO<sub>2</sub> (left) and photodegradation rates of various dyes by FePc(COOH)<sub>4</sub>/TiO<sub>2</sub> (right) [63].

Kinetic data related to concentration and illumination time were investigated and first-order degradation kinetics

equations were derived. Upon sensitization with Pc, the photoactivity of TiO<sub>2</sub> was extended to the visible light region

and catalyst was evaluated as potential material enabling the use of solar energy for the photodegradation of organic dyes and other pollutants in wastewater.

**Table 2.** Photocatalytic degradation of dyes using Pc/TiO<sub>2</sub> catalyst.

Catalyst	Method	Experimental Conditions	Target Molecule	Catalyst Characterization	Analysis	Ref. and Explanation
2,9,16,23-Tetracarboxyl copper phthalocyanine (TC-CuPc)/ amorphous TiO <sub>2</sub>	Amorphous CuPc/TiO <sub>2</sub> catalyst was prepared using sol-gel method	Halogen lamp (1000 W, $\lambda \geq 550$ nm) 160 mL reactor pH=4 Catalyst mass: 1 g/L Time: 6 h	Methyl Orange (10 mg/L)	BET, XRD, DRS, Uv-vis.	UV/Vis.	[43] 80% removal of MO with amorphous CuPc/TiO <sub>2</sub> is achieved after 3 h exposure. Amorphous CuPc/TiO <sub>2</sub> is better than CuPc/SiO <sub>2</sub> and neat CuPc/P25TiO <sub>2</sub> .
Copper(II) phthalocyanine tetrasulfonate/ TiO <sub>2</sub> (TC-CuPc/TiO <sub>2</sub> )	Sonochemical synthesis using TiCl <sub>4</sub> , trietenolamine and ethanol	Halogen lamp (420W, $\lambda \geq 450$ nm) 50 mL reactor Catalyst mass: 1 g/L Time: 30 min.	Methyl Orange (20 mg/L)	XRD, TEM, DRS	UV/Vis.	[44] 73.39% removal of MO with CuPc/TiO <sub>2</sub> is achieved after 30 minutes.
Copper(II) phthalocyanine tetrasulfonate/ TiO <sub>2</sub> (TC-CuPc/TiO <sub>2</sub> )	Hydrothermal method	Halogen lamp (420 W, $\lambda \geq 450$ nm) 50 mL reactor pH=7 Catalyst mass: 1 g/L Time: 3 h	Methyl Orange (20 mg/L)	XRD, TEM, UV-vis.	UV/Vis.	[45] CuPc was immobilized on ZrO <sub>2</sub> , P25 and TiO <sub>2</sub> . 90% removal of MO with CuPc/TiO <sub>2</sub> is achieved after 3 h exposure. CuPc was photostable for 6 hours illumination.
Cu (II)-tetracarboxyphthalocyanine sensitized mesoporous titania (TC-CuPc/TiO <sub>2</sub> )	Wet immobilization soft template method	Halogen lamp ( W, $\lambda \geq 550$ nm)	Fluorescein	XRD		[46] Higher degradation with 4% CuPc/Tc/TiO <sub>2</sub> catalyst.
Copper(II) phthalocyanine tetrasulfonic acid (TS-CuPc)/TiO <sub>2</sub>	Thin film, sol-gel method dip coating	Vis light	Rhodamine B	XRD, UV-Vis, SEM		[47] TiO <sub>2</sub> film is composed of the anatase-brookite-rutile mischcrystal phase. Rhodamine B first turns into rhodamine via the N-de-ethylation, and the intermediate product are subsequently degraded. CuPcTs/TiO <sub>2</sub> films becomes stable after being used 2-3 times.
Tetrasulfophthalo Cyanineatozinc/titanium dioxide (TS-ZnPc/TiO <sub>2</sub> )	In-situ and sol-gel process	Visible lamp (16 W, $\lambda \geq 390$ nm) Catalyst mass: 1 g/L	Rhodamine B (1x10 <sup>-5</sup> M)	XRD, UV-vis, FTIR, Zeta potential Fluorescence spectroscopic	UV/Vis.	[53] TsZnPc to TiO <sub>2</sub> mol ratio was 1:100
tri-CoSPc/ TiO <sub>2</sub> /Na <sub>2</sub> Ti <sub>3</sub> O <sub>7</sub>			Malachite Green	X-ray DRS		[54] Malachite green decoloration was 42.9% in one hour and 90.3% in 6 hours.
Cobalt sulfophthalocyanine (CoSPc)/TiO <sub>2</sub>	Sol-gel method and fly ash as carrier	Tungsten halogen lamp (300 W) 200 mL reactor Catalyst mass: 0.5 g/L Time: 180 min.	Methylene Blue (7.5 mg/L)	SEM, XRD, FT-IR, DRS	UV/Vis.	[55] CoSPc loading was between 0.02-0.016-0.012-0.008-0.004-0.00 g on TiO <sub>2</sub> . 0.008 CoSPc/TiO <sub>2</sub> provided the highest degradation rate (73.36%).
ZnPc-TiO <sub>2</sub>	Hydrothermal method	High pressure mercury lamp (160 W) Catalyst mass: 5.0 g/L Time: 30 min.	Rhodamine B (10 mg/L)	XRD, DRS, SPS	UV/Vis.	[56]
CoPcS/TiO <sub>2</sub> / K <sub>2</sub> Ti <sub>4</sub> O <sub>9</sub>	Sol-gel method		Orange-II	XRD	UV/Vis.	[57] CoPcS/TiO <sub>2</sub> /K <sub>2</sub> Ti <sub>4</sub> O <sub>9</sub> degraded 85% of Orange-II.

Catalyst	Method	Experimental Conditions	Target Molecule	Catalyst Characterization	Analysis	Ref. and Explanation
2,9,14,23-tetra-nitro phthalocyanine copper (TN-CuPc)/TiO <sub>2</sub>	Electrospinning technique and solvothermal processing	Xenon lamp (150 W, $\lambda \geq 450$ nm) 100 mL reactor Catalyst mass: 1.0 g/L Time: 4 h	Rhodamine B (10 mg/L)	SEM TEM EDX, XRD, XPS, FTIR, DRS, TG-DTA, FESEM	UV/Vis.	[48] PT1 (1:50 mass ratio TN-CuPc/TiO <sub>2</sub> ) degraded 38% and PT2 (1:20 TN-CuPc/TiO <sub>2</sub> ) degraded 87%. Removal percentage with PT2 reduced to 54% in the presence of ter-butyl alcohol as radical scavenger.
H <sub>2</sub> Pc/TiO <sub>2</sub>	Wet deposition on TiOSO <sub>4</sub> in the presence of CTAB	Xenon lamp Catalyst mass: 5 g/L Time: 96 h	Methyl Orange (9.81 mg/L)	XRD, TEM, UV-vis., UV Floresans	UV/Vis.	[40] 100% removal of MO with free Pc/TiO <sub>2</sub> after 96 h. [58]
Manganese phthalocyanine tetrasulfonic acid (TS-MnPc)/ TiO <sub>2</sub> @SiO <sub>2</sub>	Sol-precipitation method using TBOS and n-octylamine as template	Halogen lamp (500 W, $\lambda \geq 554$ nm and 453 nm) pH=6.88 Catalyst mass: 0.2 g/L Time: 4 h	Rhodamine B (5x10 <sup>-4</sup> M) o-Phenylene diamine (OPDA) (3x10 <sup>-3</sup> M)	XRD, UV-Vis DRS	UV/Vis.	5, 10, 33, 50 $\mu$ mol MnPc loaded on TiO <sub>2</sub> @SiO <sub>2</sub> . Highest removal was obtained with 10 $\mu$ mol MnPc loaded on TiO <sub>2</sub> @SiO <sub>2</sub> . 100% removal with MnPcS/TiO <sub>2</sub> @SiO <sub>2</sub> .
ZnPc/TiO <sub>2</sub>	Wet deposition of ZnPc (1.6% ) on TiO <sub>2</sub> (w/w)	High pressure mercury lamp (400 W) 4 L photoreactor pH=3 Catalyst mass: 100 mg Time: 2 h	Ponceau 4R (4x10 <sup>-5</sup> M)	BET, XRD	UV/Vis. TOC	[59] 100% removal of Ponceau 4R with ZnPc/TiO <sub>2</sub> after 80 min. exposure. 50.4% mineralization with ZnPc/TiO <sub>2</sub> after 120 min. exposure.
Binuclear metal (II)phthalocyanine hexasulphonate/ TiO <sub>2</sub> (M-M)Pc: (Co-Co)Pc (Co-Zn)Pc (Co-Mn)Pc (Zn-Zn)Pc (Zn-Mn)Pc (Mn-Mn)Pc	Nanocrystalline TiO <sub>2</sub> thin film		Methylene Blue	SEM, XRD Profilometer		[62] Hetero (M-M)Pc/nano crystalline TiO <sub>2</sub> thin films were more effective than that of homo (M-M)Pc under both visible light irradiation and dark condition.
Copper phthalocyanine tetrasulfonic acid sensitized TiO <sub>2</sub> (TS-CuPc)/ TiO <sub>2</sub>	Hydrothermal method	500 W Xenon lamp pH=7 natural Catalyst mass: 0.25 g/L Time: 2 h	Rhodamine B (50 mg/L)	XRD, UV-Vis, TEM, Floresans	UV/Vis.	[49] Dye-sensitized TiO <sub>2</sub> samples had a wider absorption spectrum range and higher visible-light photocatalytic activity compared to TiO <sub>2</sub> samples. The double dye-sensitized (or co-sensitized) TiO <sub>2</sub> composite with efficient electron collection exhibited higher photocatalytic activity than did the single dye-sensitized TiO <sub>2</sub> composite.
Phthalocyanine-modified Fe-doped TiO <sub>2</sub> nanocrystals (Pc/Fe-TiO <sub>2</sub> )	Sol-gel method: 0-3 mol% fraction of Fe used for TiO <sub>2</sub> Wet deposition of phthalocyanine (1%) on Fe-TiO <sub>2</sub>	Halogen lamp (500 W) pH=7 Catalyst mass: 0.5 g/L Time: 500 min. Air flow 1 mL/sec.	Methyl Orange (10 mg/L)	XRD, TEM, SEM, DRS, BET, EDX, UV-vis.	UV/Vis.	[41] Particle size decreased with Fe <sup>3+</sup> doping. Photocatalytic activity increased with increasing Fe <sup>3+</sup> content. Highest activity obtained with 0.5% Fe <sup>3+</sup> doping. 80% removal of MO with (Pc/Fe-TiO <sub>2</sub> ).
One-dimensional 2,9,16,23-tetra-nitrophthalocyanine iron(II)	Electrospinning technique and solvothermal process	Xenon lamp (150 W, $\lambda \geq 400$ nm) Catalyst mass: 0.5 g/L	Methyl Orange (10 mg/L)	FE-SEM, EDX, TEM, XRD, XPS, IR	UV/Vis.	[60] 48% MO removal with (TNFePc)/TiO <sub>2</sub> nanofiber. 94% MO removal with

Catalyst	Method	Experimental Conditions	Target Molecule	Catalyst Characterization	Analysis	Ref. and Explanation
(TN-FePc)/TiO <sub>2</sub> nanofiber		Time: 3 h H <sub>2</sub> O <sub>2</sub>				(TNFePc)/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> nanofiber.
Phthalocyanine-modified Fe-doped TiO <sub>2</sub> nanocrystals (Pc/Fe-TiO <sub>2</sub> )	Sol-gel method: 0-3 mol% fraction of Fe used for TiO <sub>2</sub> Wet deposition of phthalocyanine (1%) on Fe-TiO <sub>2</sub>	Halogen lamp (500 W) pH=7 Catalyst mass: 0.5 g/L Time: 7.5 h	Methyl Orange (10 mg/L)	TEM, BET, DRS, FTIR, XRD, TG-DTA	UV/Vis.	[42] 87% MO removal with Pc/Fe-TiO <sub>2</sub> after 7.5 h exposure.
CuPc/TiO <sub>2</sub>	0.5-2% CuPc immobilized by ball-milling assisted process	UV lamp (450 W) Catalyst mass: 20 mg/L Time: 35 min.	Rhodamine B (5.9x10 <sup>-6</sup> M)	XRD, XANES, SEM	UV/Vis.	[50] 1% CuPc immobilization on TiO <sub>2</sub> exhibited higher activity. 87.5% RhB removal with CuPc/TiO <sub>2</sub> in 25 min. exposure and 100% RhB removal in 35 min.
Copper phthalocyanine (CuPc) modified TiO <sub>2</sub> nanotubes (CuPc/TiO <sub>2</sub> NT)	Hydrothermal treatment under the alkaline conditions, mole percentage of CuPc was 0.2%		Rhodamine B			[51] 59% RhB removal with CuPc/TiO <sub>2</sub> NT after 180 min. exposure.
Cobalt(II) phthalocyanine-sensitized hollow Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /TiO <sub>2</sub> hierarchical nanostructures	Solvothermal and dipping method 0.2 g Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /TiO <sub>2</sub> particules were dipped into CoPc solution (4.5-13.68x10 <sup>-2</sup> mM)	Halogen lamp (500 W, λ≥420 nm) pH=7 natural Catalyst mass: 75 mg/L Time: 5 h Air flow: 0.5 L/min.	Methylene Blue (10 mg/L)	FE-SEM, TEM, XRD, FTIR, DRS, VSM	UV/Vis.	[61] 60% MB removal with Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /TiO <sub>2</sub> after 5 h exposure. Highest removal was achieved with CoPc/Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /TiO <sub>2</sub> containing 7 μmol CoPc. 86.4% MB removal with CoPc/Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /TiO <sub>2</sub> after 5 h exposure.
Zinc(II) tetracarboxy-phthalocyanine/ TiO <sub>2</sub> Copper(II) tetracarboxy-phthalocyanine/ TiO <sub>2</sub> (TC-ZnPc/TiO <sub>2</sub> ) (TC-CuPc/TiO <sub>2</sub> )	TiO <sub>2</sub> thin films were deposited by doctor blade method		Methylene Blue (25 mg/L)	XRD, IR	UV/Vis.	[52] MB removal was 2.8 and 3.6 times higher with PcTcZn/TiO <sub>2</sub> and PcTcCu/TiO <sub>2</sub> respectively. Photocatalytic process improved in the presence of H <sub>2</sub> O <sub>2</sub> .
Fe (III) 2, 9, 16, 23-phthalocyanine tetracarboxylic acid (TC-FePc/TiO <sub>2</sub> )	Solid fusion method	Halogen lamp (300 W, λ≥400 nm) pH=2-12 Catalyst mass: 1 g/L Time: 100 min.	Methylene Blue Rhodamine B Acid red Neutral red Malachite Green (6.5 mg/L)	XRD, UV-vis., PL, XPS,	UV/Vis.	[63] Dye removal was 96.9%, 96.8%, 82.1%, 85.2%, and 81.9%, respectively. Best degradation efficiency was achieved at pH=6.

## 4. Conclusions and Future Trends

Due to structural properties comprising nitrogen and carbon atoms (eight each) and aromatic conjugated complex, phthalocyanines are the good candidates for dye sensitization. This structural versatility provides the production of countless derivatives. Published studies given in Table 1 and 2 indicate that more studies will appear soon in the literature. Although the applications of unsubstituted phthalocyanines have limitations, sulfonic acid or carboxyl functional group containing derivatives are more promising.

Our group has been working on production of Pc sensitized TiO<sub>2</sub> catalyst and we have evidences that these types of catalyst modification was quite attractive for photocatalytic reduction [64-67]. Novel metal free and copper containing

azomethine-bridged phenolic phthalocyanines (H<sub>2</sub>Pc and CuPc respectively) [64, 65] were synthesized and used for the sensitization of TiO<sub>2</sub>. Prepared catalysts were tested for the reductive removal of toxic Cr(VI) ions in water. It was also compared whether central metal ion has any effect on enhancement of Pc sensitized TiO<sub>2</sub> [66]. Similarly, quaternized zinc(II) phthalocyanine was used in the sensitization and this catalyst was quite effective for Cr(VI) reduction as well as methyl orange [67]. Our experiments indicated that Pc sensitized TiO<sub>2</sub> catalyst was more effective for electron transfer process and facilitated the reduction of target species. This might be a future trend for all researcher working in this field to test those Pc sensitized TiO<sub>2</sub> catalysts for photoreduction process as well as photooxidation.

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