

TiO₂/ORMOSIL Thin Films Doped with Phthalocyanine Dyes: New Photocatalytic Devices Activated by Solar Light

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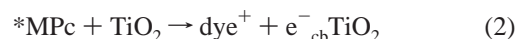
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Hybrid sol–gel TiO₂/organosilica films doped with Cu(II), Fe(II), and Fe(III) phthalocyanines are excellent photocatalysts for the oxidative degradation of organics under visible light irradiation. The films show pronounced stability with the Fe(III)Pc-doped film showing the best performance in the gas-phase mineralization of 2-propanol. The versatile chemistry of both sol–gel materials and phthalocyanines will enable large improvement in terms of performance and technical adaptability of these new photocatalytic devices for future practical application.

TiO₂ thin films are of high practical value since the immobilization of titanium dioxide significantly reduces some of the drawbacks of practical application of heterogeneous photocatalysis in suspension, including the need to separate the powder or the tendency of titania particles to agglomerate in water.¹ ORMOSIL (organically modified silicates) thin films, in their turn, have lately found application in fields as diverse as chemical (bio)sensing, optics, photolithography, catalysis, and OLEDs in electronic devices.² Similar thin functional coatings are attractive to industry since a small amount of hybrid material imparts improved properties at low cost. For instance, homogeneous films of organosilica with thickness up to 1–10 μm can be prepared by the sol–gel method with a single dip-coated layer whereas other techniques such as spin- and spray-coating provide thinner films.

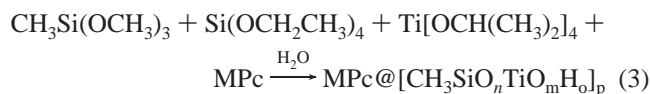
Composite titania/ORMOSIL films are also relevant.³ The presence of TiO₂ enables fine-tuning of the refractive index by varying the preparative conditions, which is of primary relevance in application of the films as optical devices;⁴ increasing the Ti/Si ratio results in enhanced hardness⁵ whereas the organosilica in the matrix improves the film’s flexibility, enabling the preparation of crack-free films with thickness in the range of tens of microns.

The electronic and (photo)catalytic properties of commercial metallophthalocyanine dyes (MPc, Figure 1) have been widely studied.⁶ MPc are potent TiO₂-sensitizers enhancing the activity of titania in photocatalytic reactions under visible light by injecting electrons in the conduction band of titania (eqs 1 and 2).⁷



As widely reported in literature, the electronic transfer can take place through the change of the oxidation state of cations, such as Cu and Fe, that can shift alternatively from +1 to +2, and from +2 to +3, respectively.⁷ Interestingly, MPc dyes have lately been sol–gel entrapped in micro-⁸ and mesoporous⁹ silica showing evidence of monomeric dispersion of the molecules in the sol–gel cages. Such sol–gel molecular encapsulation ensures protection of the dopant molecules against both thermal- and photodegradation, preserving the accessibility of the entrapped dopant to external reagents.¹⁰

On this basis we reasoned that mixed titania/ORMOSIL films doped with phthalocyanines might result in versatile photocatalysts under visible light irradiation. This proved to be the case. We describe herein the first organosilica-titania films doped with Cu(II), Fe(II), and Fe(III) phthalocyanines synthesized by mild sol–gel hydrolytic polycondensation of titanium and silicon alkoxides in equimolar amounts (Si:Ti = 1:1, with MTMS:TEOS = 5.5:1) as in eq 3 (unbalanced):



The film was prepared in the following way. A solution of TEOS (3.78 mmol) and methyltrimethoxysilane (MTMS, 21 mmol) was mixed with 670 μL of aqueous HCl (21.2 mM) and used as film precursor. Fast stirring ensured complete hydrolysis after ca. 5 min. The resulting solution is referred as SOL1. Titanium isopropoxide (24.8 mmol) was added dropwise to a solution of the desired metallophthalocyanine (12.7 μmol) in 49.6 mmol of 2,4-pentadione, that is a bidentate ligand (SOL2). SOL1 was added drop by drop to the SOL2, and the resulting solution (SOL3, Si/Ti ratio of ca. 1/1 on molar base) was left under agitation for 20 min.

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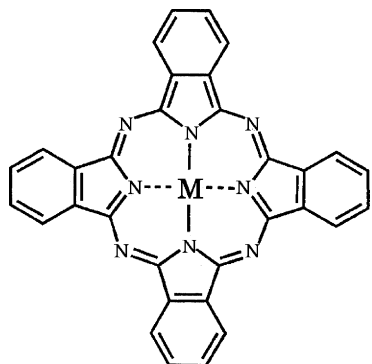


Figure 1. General structure for phthalocyanine metal complexes.

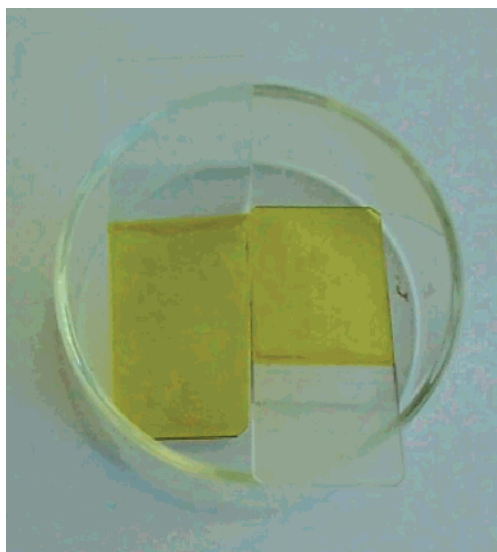


Figure 2. Colored TiO₂-organosilica films doped with Pc dyes (left: Cu(II)Pc; right: Fe(II)Pc).

Dip-coating of SOL3 onto standard glass microscope slides was performed at a controlled rising speed of 15 mm min⁻¹. The films thereby obtained were mildly heated at 50 °C for 3 days to promote polycondensation and solvent evaporation.

The films (Figure 2) were characterized by UV-vis spectroscopy, SEM, and contact angle determinations.

UV-vis absorption measurements were carried out using a Varian Cary 4000 spectrophotometer. Scanning electron microscopy images were recorded with a Zeiss DSM-950 instrument coupled with energy-dispersive analysis of X-rays operating at 80 kV. Contact angle measurements were performed with a First Ten Ångströms Analyzer System (FTA 1000) instrument dropping 50 μL of water at controlled rate in five different areas of the film. The decrease of the contact angle with time was followed until a plateau was reached (time required ca. 5 min). The highest difference among the five recorded values was less than 5%.

Comparison between the UV-vis spectra of pure phthalocyanines (in reflectance, Figure 3) and of the doped films (in transmittance, Figure 4) shows that the sensitizers are retained upon encapsulation with the absorbance peaks typical of the three phthalocyanines between 550 and 750 nm clearly visible in all the spectra. Absorption of the entrapped phthalocyanines in the visible region, however, is considerably higher than that of the undoped film with large absorption in the entire range of visible wavelengths for the Fe(III)Pc-doped film. This clearly points to large changes in the photophysical properties of the metallophthalocyanine confined in the sol-gel cages of the

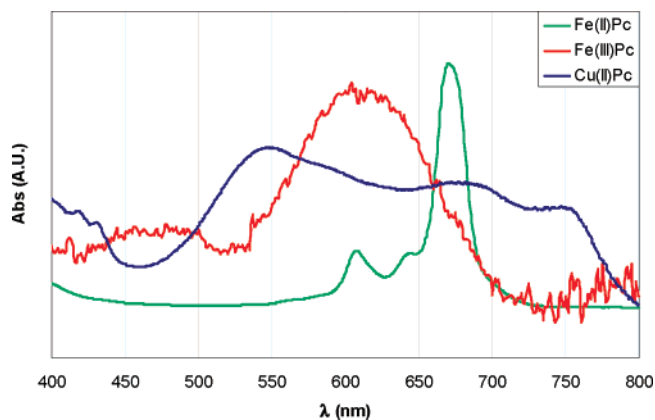


Figure 3. UV-vis diffuse reflectance of pure Cu(II), Fe(II), and Fe(III) phthalocyanines.

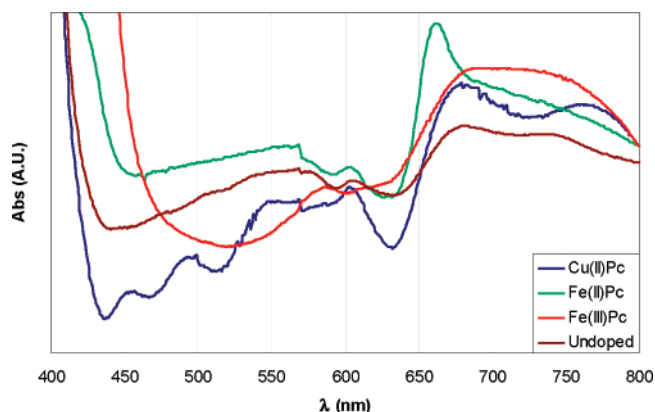


Figure 4. UV-vis absorbance of ORMOSIL/TiO₂ films undoped and doped with Cu(II), Fe(II), and Fe(III) phthalocyanines.

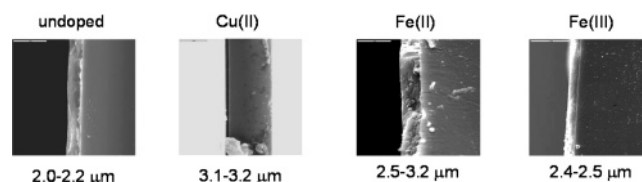


Figure 5. SEM cross-sectional images of ORMOSIL/TiO₂ films undoped and doped with Cu(II), Fe(II), and Fe(III) phthalocyanines.

TiO₂/organosilica films, and it is at the origin of their enhanced photochemistry described in this report. Similar changes were recently observed upon copper phthalocyanine tetrasulfonate entrapment in TiO₂ particles.¹¹

UV-vis spectroscopy also unequivocally shows the pronounced physicochemical stability of the doped films as the spectra of each film prior and after 2 months of aging at room temperature, and before and after photocatalytic runs are unvaried.

SEM images show the film microscopic homogeneity and allow measurement of the film thickness by cross-sectional images (Figure 5).

The thickness of the films is in the 2.0–3.2 μm range and is uniform (the largest variation being ca. 0.2 μm for all samples). Only the film doped with Fe(II) phthalocyanine showed a larger difference in thickness (ca. 0.7 μm) depending on the section analyzed. The activity of photocatalytic films is however due only to their outer part, since light is completely absorbed by films of thickness even lower than 1 μm.

As expected, EDAX elemental analyses show that the molar percentages of Ti and Si are very close for all films (Table 1)

TABLE 1: EDAX Elemental Analysis of ORMOSIL/TiO₂ Films Undoped and Doped with Cu(II), Fe(II) and Fe(III) Phthalocyanines^a

element	undoped	Cu(II)	Fe(II)	Fe(III)
C (mol %)	39.2	38.9	38.6	40.0
O (mol %)	43.8	46.5	46.7	45.5
Si (mol %)	8.2	7.4	7.3	7.4
Ti (mol %)	8.7	7.2	7.4	7.1

^a The table does not provide Cu and Fe amounts, since they were present in concentrations lower than the detectable limit of the instrument.

TABLE 2: Average Contact Angle and Adhesion Energy of ORMOSIL/TiO₂ Films Undoped and Doped with Cu(II), Fe(II) and Fe(III) Phthalocyanines

film	contact angle (deg)	ΔW_{SLG} (mN m ⁻¹)
undoped	69	97.8
Cu(II)	70	96.7
Fe(II)	75	90.7
Fe(III)	72	94.3

pointing to full polycondensation of either silicon and titanium alkoxides in reaction 1.

The X-ray diffractograms (not shown) highlight the absence of any peak due to crystalline TiO₂ (anatase, rutile, and brookite), indicating for all the materials a fully amorphous structure which largely differentiates our materials from quantum dots of crystalline TiO₂ entrapped in organosilica¹² with a molar ratio Ti:Si = 1:10 that, too, are excellent photocatalysts for the degradation of organic pollutants under solar irradiation. Indeed, as mentioned above our materials actually contain equimolar amounts of Si and Ti interconnected through oxo bonds in a composite amorphous structure. Finally, as typical for organosilica gels that undergo only a mild thermal treatment upon the sol-gel synthesis, the relatively large amount of carbon beyond the organic moiety of organosilica precursor is mostly due to the solvent (2,4-pentadione) left entrapped in the film's network.¹

Contact angle measurements gave very similar results (<5% variation) confirming surface uniformity for each film (Table 2). The adhesion energies per unit area of the solid and liquid surfaces are estimated by means of the Young-Dupré equation (eq 4, where γ_{LG} is the water-air surface tension equal to ca. 0.072 mN m⁻¹ at room temperature and θ is the experimental contact angle):¹³

$$\Delta W_{\text{SLG}} = \gamma_{\text{LG}}(1 + \cos \theta) \quad (4)$$

All films are hydrophobic due to the presence of the organic moieties at the surface of the ORMOSIL matrix structure with phthalocyanine dye doping slightly increasing the overall hydrophobicity.

Either doped and undoped TiO₂/ORMOSIL films were used in a batch photoreactor (Figure 6) for the gas-phase degradation of 2-propanol in humid O₂ atmosphere at room-temperature and pressure under concentrated irradiation simulating the spectrum of solar light. The degradation of 2-propanol over TiO₂ catalyst is a model photocatalytic process with different reaction pathways.¹⁴ Photocatalytic runs were performed by using a gas-seal photoreactor (volume ca. 0.8 L). The catalytic film (total surface exposed to irradiation: 30 cm²) was put in contact with wet oxygen by feeding the reactor for 1 h with a flow of water-saturated oxygen. Afterward the inlet and outlet were closed, and 0.5 μL of liquid 2-propanol was inserted through a sampling port by means of a Hamilton microsyringe. After an induction time of 20 min to allow the alcohol evaporation and the



Figure 6. The “Solarbox” reactor employed for carrying out photocatalytic degradation of 2-propanol mediated by doped ORMOSIL/TiO₂ films.

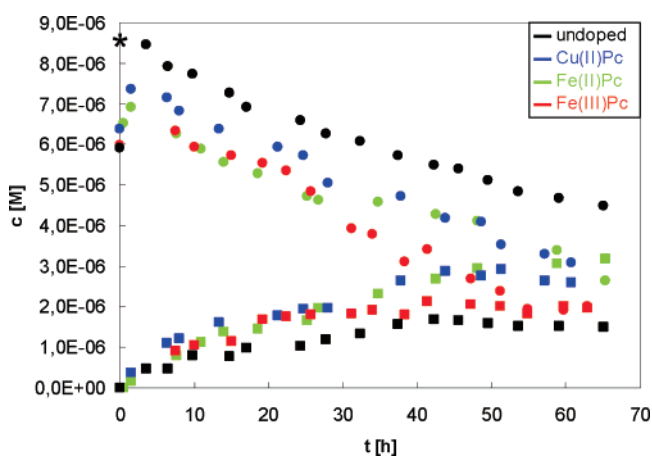


Figure 7. Concentration of substrate (●, 2-propanol) and intermediate product (■, acetone) in the photocatalytic degradation mediated by undoped and phthalocyanines-doped ORMOSIL/TiO₂ films under solar light irradiation (the star indicates the initial 2-propanol concentration in the absence of catalyst).

achievement of steady-state conditions in all the system, the Solarbox irradiation source (Xenon lamp of 1500 W) was switched on. Distilled water was put between the lamp and the reactor to filter the IR radiation and to maintain a constant reactor temperature. Samples of gas (500 μL) were withdrawn during the reaction to determine the gas-phase composition. The 2-propanol and acetone monitoring was carried out by a GC-17A Shimadzu GC equipped with a methyl siloxane (30 m \times 320 μm \times 0.25 μm) HP-1 Hewlett-Packard column and a flame ionization detector. Carbon dioxide was measured by a Hewlett-Packard 6890 GC equipped with a 60/80 Carboxen 1000 Supelco column and a thermal conductivity detector. He was used in both cases as carrier gas. A satisfactory carbon balance was attained for all the runs (sum of the 2-propanol, acetone, and carbon dioxide amounts). The accuracy of GC measurements (maximum error ca. 4%) was verified by multipoint calibration of the three molecules analyzed. For checking the repeatability of the photoreactivity experiments, each run was carried out two times, by achieving a maximum difference in conversion of ca. $\pm 4\%$.

Figure 7 shows the concentration values of 2-propanol and acetone as a function of irradiation time for the four films employed.

No reactivity was observed in the absence of light and/or catalytic film. Bearing in mind that for all the runs the same initial amount of 2-propanol was injected in the reactor (producing a theoretical concentration of ca. 8.5×10^{-6} M by neglecting the molecules adsorbed in the dark), it is worth noting that, at the start of irradiation, an initial photodesorption takes place along with degradation, the photodesorption phenomenon being more relevant in the case of the undoped film (pointing to a lower reaction rate). This phenomenon is often present in photocatalytic reactions: in particular when the oxidizing power of the catalyst is not very high, the surface modifications generated by light can result in a significant desorption of the previously adsorbed molecules, if they do not react with a high rate. During irradiation in the presence of the films, acetone was the only stable intermediate detected and CO₂ the final mineralization product for all films. The transformation of 2-propanol to acetone (eq 5):



is thus followed by subsequent acetone mineralization (eq 6):



The improved activity due to the photoactive films is evident from Figure 7. In all cases, the rates of both substrate degradation and intermediate acetone production are larger for the doped samples compared to the undoped ORMOSIL/TiO₂ film. Recalling that simulated solar light contains only a small fraction of UV-light, the observed rate enhancement can be largely ascribed to the visible part of radiation. The enhanced adsorption properties for organics of the organosilica/titania matrix increase the rate of decomposition of hydrophobic organic pollutants. Moreover, it should be emphasized that the materials preserve their structural and catalytic features after many hours of irradiation.

The calculated conversions after 60 h irradiation are 45, 63, 64, and 77%, for undoped, Cu(II)Pc, Fe(II)Pc, and Fe(III)Pc-doped samples, respectively, by considering that the real initial 2-propanol concentration is equal to ca. 8.5×10^{-6} M. Hence comparison in the photoactivities of the doped films indicates that the films doped with Fe(III)Pc exhibit the highest degradation rate for 2-propanol and the lowest production rate of acetone, i.e., the best performance for substrate mineralization. Interestingly, even after 3 days, mineralization is not complete which points to a slower, more selective photodegradation of 2-propanol under visible light irradiation such as in the case of Fe ion-implanted TiO₂, where Fe ions are implanted through high kinetic energy (150 keV) collision with a high voltage ion accelerator.¹⁵

It is also of relevance to this report that TiO₂ photocatalysts doped with Fe ions by the sol-gel method exhibit very little photocatalytic reactivity under solar light.¹⁵ For comparison, analogous excellent photodegradation of 2-propanol under visible light irradiation was recently reported using nitrogen-substituted TiO₂.¹⁶ The synthesis of this material, however,

required magnetron sputtering deposition method using a N₂/Ar sputtering gas mixture.

In conclusion this paper describes the first example of composite ORMOSIL/TiO₂ thin films doped with metallophthalocyanines as enhanced photocatalysts for both partial oxidation and mineralization of organics under visible light irradiation. The process has been demonstrated for the aliphatic alcohol 2-propanol using copper and iron phthalocyanines and methylsilica as ORMOSIL, but we believe it is of general applicability to a multiplicity of heterogeneous photochemical processes. The materials have an unprecedented high content of titania amorphously structured. In perspective, the versatile chemistry of both sol-gel materials¹⁰ and phthalocyanines will enable large performance improvement for future practical application of these new photocatalytic devices.

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