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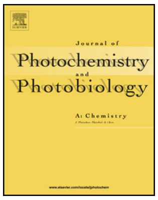

Visible light singlet oxygen production with tetra(4-carboxyphenyl)porphyrin/SiO_2

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ABSTRACT

The production of singlet oxygen with tetra(4-carboxyphenyl)porphyrin adsorbed on SiO_2 irradiated with visible light ($\lambda > 500$ nm) was evidenced by EPR spectra of TEMPO formed by oxidation of 2,2,6,6-tetramethyl-4-piperidone(TEMP) with $^1O_2$. The formation of singlet oxygen was also evidenced by the formation of anthraquinone and oxanthrone as oxidation products of anthracene with $^1O_2$. The absence of the EPR DMPO-$O_2^{\bullet-}$ signal evidenced that superoxide anion was not present. No other oxygen radicals were detected. TCPP and TCPP/SiO_2 were characterized with UV–vis, UV–vis diffuse reflectance and FT-IR spectroscopy.

1. Introduction

Clean oxidation reactions promoted by singlet oxygen ($^1O_2$) are very attractive in environmental remediation processes [1]. In order to study $^1O_2$ oxidation reactions it is necessary to selectively generate this reactive species. However with photochemical methods the superoxide anion ($O_2^{\bullet-}$) may also be produced [2,3] and chemical methods with hydrogen peroxide-sodium molybdate hydroxyl radicals are also generated [4,5].

Recently porphyrins and their analogs have been proposed for environment-friendly singlet oxygen generation. Porphyrins play important biological roles and are not cytotoxic, which is very important in medical applications such as blood sterilization and photodynamic therapy (PDT) [6,7].

Porphyrins may produce either superoxide anion radicals (type I process) or singlet oxygen (type II process). In presence of visible light, porphyrins can efficiently produce singlet oxygen [8–10]. In PDT there is considerable evidence that the type II photooxygenation process predominates in the induction of cell damage due to the interaction between the irradiated photosensitizer and molecular oxygen [11].

Widely used sensitizers such as Rose Bengal (absorption band 500–600 nm) with $^1O_2$ quantum yield $\Phi_\Delta = 0.7$, Methylene blue (absorption band 550–700 nm) with $\Phi_\Delta = 0.5$ in organic solvents [3,12] undergo photodegradation under extensive irradiation [13]. Phenalenone has a very high $^1O_2$ quantum yield $\Phi_\Delta = 1$ but absorbs in the UV region (absorption band 250–425 nm) [14]. Monomeric tetra(4-carboxyphenyl)porphyrin (TCPP) ($\Phi_\Delta = 0.7$–0.9) [15] and many other photosensitizers like the chlorins [16] and phthalocyanines [17] are very suitable and promising for biological applications, produces singlet oxygen with high yield and absorbs in the visible region, which makes it suitable for biological applications.

In solution porphyrins tend to form aggregates without the formation of covalent linkages. Aggregation affects their physicochemical and photophysical properties [18,19], lowers their $^1O_2$ yield [10] and decreases their photodynamic effect. Binding of porphyrin sensitizers to biopolymers and other carriers in order to avoid aggregation has been subject of recent studies [20,21]. There is increasing interest in using SiO_2 as support of photosensitizers. Since SiO_2 can be prepared with large surface area and modulated porosity, it allows the attachment of a large number of photosensitizer molecules to its surface resulting in favorable $^1O_2$ production [22].

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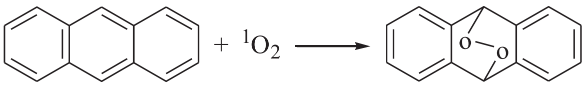


Scheme 1. Reaction singlet oxygen with anthracene.

The interaction of porphyrin molecules with silanol groups (Si—OH) through hydrogen bonds promotes the non-radiative decay of porphyrins. The covalent bond between porphyrin molecules and silica walls probably hinders inter system crossing from the singlet excited state of the porphyrin to the triplet state, which is a crucial step for photochemical activation of dioxygen [23,24].

The singlet oxygen photoproduction by a sensitizer could be evidenced by Electron Paramagnetic Resonance (EPR). Chemical trapping by polycyclic aromatic hydrocarbons is specific for singlet oxygen detection [25]. A very characteristic reaction of singlet oxygen is the [4+2] cycloaddition to conjugated cyclic dienes and polycyclic aromatic hydrocarbons such as anthracene. Anthracene traps reversibly singlet oxygen, see Scheme 1. The formation of radicals in the reaction medium [26,27] can be detected by the formation of 9-hydroxy and 9-ketoanthracene as a product of the reaction between anthracene and oxygen radicals.

Singlet oxygen reacts with 2,2,6,6-tetramethyl-4-piperidone-N (TEMP) to produce 2,2,6,6-tetramethyl-4-piperidone-N-oxyl radical (TEMPO) which can be observed by EPR spectroscopy. Superoxide anion does not react with anthracene. $O_2^{\bullet-}$ may be detected by EPR spin trapping using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) [28].

In the present work, experimental evidences of the formation of singlet oxygen with tetra(4-carboxyphenyl)porphyrin (Fig. 1) adsorbed on SiO_2 under visible light as only photoproducts are provided using chemical trapping and TEMPO EPR spectroscopy [29]. The formation of $^1O_2$ was evidenced by the production of anthraquinone and oxanthrone which are formed by the reaction of anthracene with $^1O_2$. The absence of the EPR DMPO-$O_2^{\bullet-}$ signal evidenced that superoxide anion was not present. No other oxygen radicals were detected.

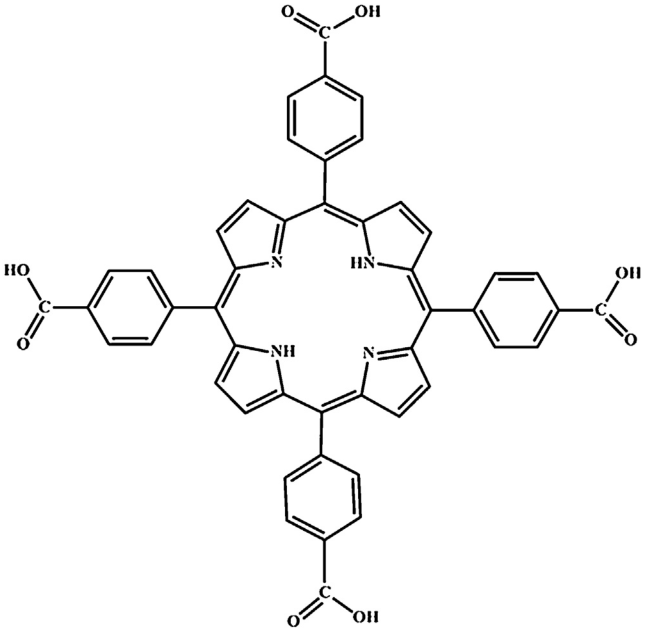


Fig. 1. Representation of porphyrin structure.

2. Materials and methods

2.1. Materials

Solvents were purchased from J.T. Baker. Anthracene and sodium azide were acquired from Merck. 2,2,6,6-tetramethyl-4-piperidone (TEMP) and 5,5-dimethyl-l-pyrroline-N-oxide (DMPO) were manufactured by Sigma–Aldrich. All reactives were of analytical grade.

2.2. Spectroscopic measurements

The UV–vis spectrum of the TCPP in ethanol was measured using a Hewlett-Packard 8453 spectrophotometer. The UV–vis diffuse reflectance absorption spectrum of the solid TCPP/SiO_2 was measured using a Lambda 4 PerkinElmer spectrophotometer equipped with an integrating sphere. FT-IR spectra (KBr) were recorded on a Bruker Tensor 27 spectrometer. Specific surface area (BET) and pore diameter distribution of the catalysts were obtained from N_2 adsorption–desorption isotherms at 77 K using a Quantachrome Nova 1200.

2.3. Synthesis of porphyrin

The carboxyphenylporphyrin (TCPP) was synthesized according to methods described in the literature [30,31]. Pyrrole (30 mmol) was added to a mixture of 4-carboxybenzaldehyde (30 mmol), propionic acid (105 mL) and nitrobenzene (45 mL). The mixture was heated 1 h at 120 °C. After cooling and solvent removal under vacuum, the porphyrin was dissolved in 250 mL of 0.1 M NaOH. The porphyrin was then precipitated with 1 M HCl solution, dissolved in ethanol and recrystallized by solvent evaporation. FT-IR (KBr, cm^{-1}): 1605 s [C=C]; 1110 s, 1006 s, 1307 m, 1311 m, 1531 m, 1485 m [pyrrole ring]; 1699 s [C=O]; 1404 m, 1268 s [C—O] [32].

2.4. Synthesis of SiO_2

SiO_2 was prepared following the reported procedure [33]. 10 mL tetraethoxysilane (TEOS) were refluxed 4 h in 100 mL of a solution of water/absolute ethanol (1/8 M) at pH = 3 (adjusted with HNO_3) at 60 °C with magnetic stirring. Absolute ethanol was added (10 mL), and the temperature was increased to 76 °C the mixture was stirred under reflux for 24 h. The solvent was rotoevaporated and the remaining solid heated in air for 4 h at 450 °C.

2.5. Adsorption of TCPP on SiO_2

8.3 mmol of SiO_2 were suspended in 250 mL of 0.4 mM TCPP solution (pH > 10) during 1 h. The pH was adjusted to 3.0 with 0.1 M H_2SO_4, and the solid was filtered, washed with distilled water and dried at room temperature [34]. The total amount of TCPP adsorbed on SiO_2 was quantified with UV–vis spectroscopy after treating the sample (TCPP/SiO_2) first with NaOH 0.1 M and then with ethanol. We have no evidence of the distribution of TCPP either on the surface or inside the pores.

2.6. EPR experiments

(a) TCPP and TCPP/SiO_2 were characterized by EPR spectroscopy. The solid samples were measured directly in quartz tubes.

(b) EPR-TEMP method to study singlet oxygen formation. Photogenerated singlet oxygen reacts with TEMP leading to the paramagnetic TEMPO, which has a characteristic three-line EPR spectrum [29]. Singlet oxygen was detected in a suspension of 0.12 mmol of the photosensitizer, in a solution of TEMP (10 mM) in toluene. Photoreactions were carried out in an immersion well-type quartz photoreactor system supplied by Ace Glass-7880. The solution was irradiated with visible light (halogen lamp of 100 W) filtered with a potassium dichromate solution (1 M) circulating in the immersion well to remove wavelengths <500 nm. The samples in quartz tubes were measured under normal conditions, with 100 kHz magnetic field modulation, 10 mW microwave power and 5 G modulation amplitude in a JEOL (JES-PE-3X) spectrometer.

(c) Study of radical formation by the EPR-DMPO method. The measurement of the spin trapping EPR by DMPO was used to determine the generation of superoxide anion radical by TCPP/SiO_2. The formation of superoxide anion radical was measured in a suspension of 0.01 g of TCPP/SiO_2 in a solution of DMPO (50 mM) in DMSO. Photoreactions were carried out in an immersion well-type quartz photoreactor system supplied by Ace Glass-7880. The solution was irradiated with visible light (halogen lamp of 100 W) filtered with a potassium dichromate solution (1 M) circulating in the immersion well to remove wavelengths 500 nm. The samples were transferred immediately to 100 μL quartz capillaries and were measured under normal conditions, with 100 kHz magnetic field modulation, 10 mW microwave power and 5 G modulation amplitude in a JEOL (JES-PE-3X) spectrometer. Spectra were simulated using the BRUKER WINEPR SimFonia Version 1.25 software to determine the spin Hamiltonian parameters of DMPO–$O_2^{\bullet-}$.

(d) A MgO:Mn^{2+} (g = 1.981 of the fourth line) reference standard sample (g and intensity marker) was maintained in the EPR cavity of the JEOL spectrometer, the data was recorded simultaneously with the sample.

2.7. Singlet oxygen chemical trapping by anthracene

The experiments were performedin oxygen atmosphere, according to the following procedure: 0.12 mmol of the TCPP or TCPP/SiO_2 was added to 10 mL of a solution of anthracene dissolved in dichloromethane (0.2 mM) in photoreactor system in a batch photo-reactor with a 100 W OSRAM halogen immersion lamp. The light was filtered through a 1 M potassium dichromate solution to remove wavelengths <500 nm. The incident photon flow per unit volume I_o was determined by chemical actinometry [35], using 0.01 M Reinecke salt solution.Irradiation of the suspension was started after 1 h in the dark (with stirring). Sample aliquots of 0.1 mL were taken during irradiation, filtered and measured by UV–vis spectrophotometry at λ_{max} = 375 nm.A sample of the reaction mixture was analyzed by GC–MS in a 5890 Hewlett Packard gas chromatograph, with a 5972 mass selective detector and a HP5-MS (30 m long and 0.25 mm internal diameter) column and with He as the carrier gas (1 mL/min). 1 μL sample aliquots were injected with split (1:30). The following temperature program was applied: heating at 200 °C for 5 min, heating to 300 °C with a rate of 10 °C/min. This temperature was maintained for 15 min. Detector conditions: 70 eV, electronic impact, 35–400 m/z mass range, 200 V EM voltage (A-tune), 20 Hz Sweep Frequency at 230 °C.

3. Results and discussion

3.1. Characterization of TCPP and TCPP/SiO_2

The formation of TCPP was evidenced by the presence of the typical Soret band (419 nm) and four Q bands (514, 548, 588 and 645 nm) in the UV–vis absorption spectra in ethanol (Fig. 2) [36]. The absorption spectrum of TCPP adsorbed on SiO_2 exhibited a red shift with respect to the ethanol solution. This is probably due to the formation of hydrogen bonds between the carboxyl groups of the porphyrin and SiOH on the surface, which affects the electronic structure of the π system of porphyrin, as was found in other previous studies [23,24].

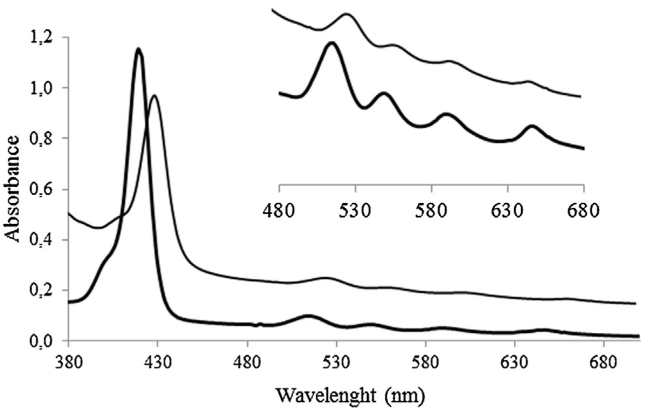


Fig. 2. UV–vis spectra of TCPP in ethanol solution (2.5×10^{-5} M, thick line) and TCPP adsorbed on SiO_2 (0.1 g, thin line).

An average pore diameter of 19.9 Å and a specific surface area of 567 $m^2 g^{-1}$ of SiO_2 were obtained from N_2 adsorption-desorption isotherms at 77 K (BET method). The hysteresis of the

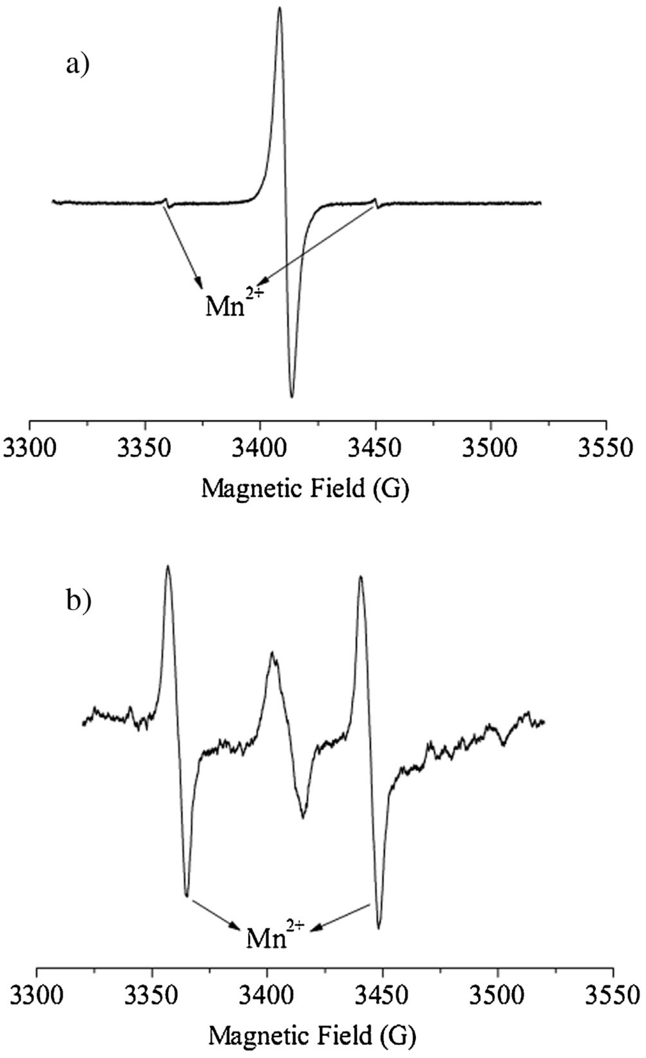


Fig. 3. EPR spectra at room temperature of free TCPP (a); and TCPP adsorbed on SiO_2 (b). MgO:Mn^{2+} was used as g marker and intensity standard. The spectroscopic g factor of TCPP is 2.003 (free) and 2.005 (adsorbed).

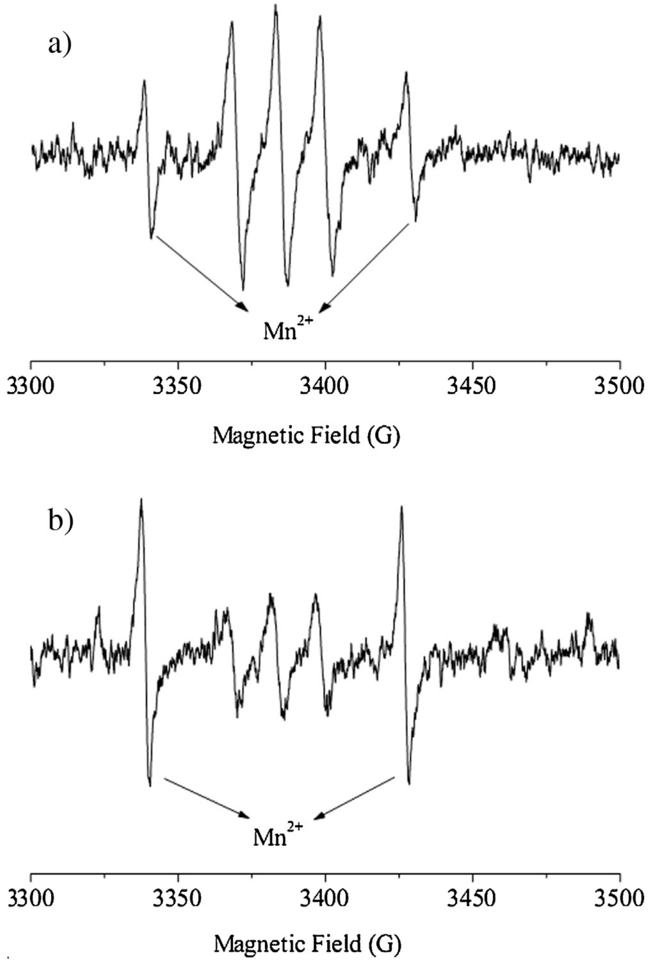


Fig. 4. EPR spectra at room temperature of TEMPO after 2 min of irradiation: (a) TCPP; (b) TCPP/SiO$_2$. MgO:Mn^{2+} was used as *g* marker and intensity standard.

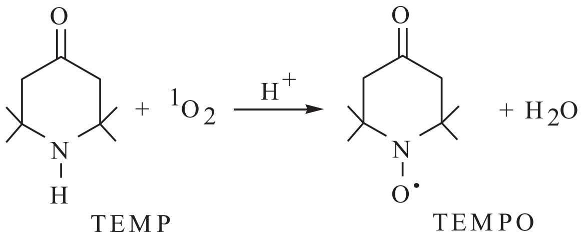
adsorption-desorption isotherms of SiO$_2$ is of Langmuir Type I, which is characteristic for microporous solids [37]. The amount of TCPP adsorbed on SiO$_2$ is 0.254 mmol TCPP/g SiO$_2$.

The EPR spectra of TCPP and TCPP/SiO$_2$ exhibited only one line (Fig. 3a). The EPR signals of porphyrins are generated by the interaction of the delocalized π electrons of the porphyrin with the magnetic field [38]. The free radicals formed are stable and were detected by EPR directly at room temperature. The EPR signal intensity of the TCPP/SiO$_2$ was lower than that of TCPP (Fig. 3b), due to the smaller amount of TCPP in the TCPP/SiO$_2$ sample.

3.2. EPR-TEMP detection of singlet oxygen

The EPR spin trapping technique with TEMP as spin trapper was used to determine the singlet oxygen photo-generationat room temperature from TCPP and TCPP/SiO$_2$. The characteristic EPR spectrum of TEMPO consists of three equally intense lines [29] (Fig. 4). TEMPO is formed by oxidation of TEMP with singlet oxygen (Scheme 2). The TEMPO signal was reduced ($\sim$50%) for TCPP/SiO$_2$ compared to free TCPP in liquid phase, probably due to lower oxygen diffusion in the silica matrix. Similar results were obtained by Wang et al. [39].

The intensity of the EPR signal of TEMPO with TCPP/SiO$_2$ increases with irradiation time (Fig. 5). No signal was observed in the dark. Equilibrium is reached above 100 s.



Scheme 2. Oxidation of TEMP by singlet oxygen.

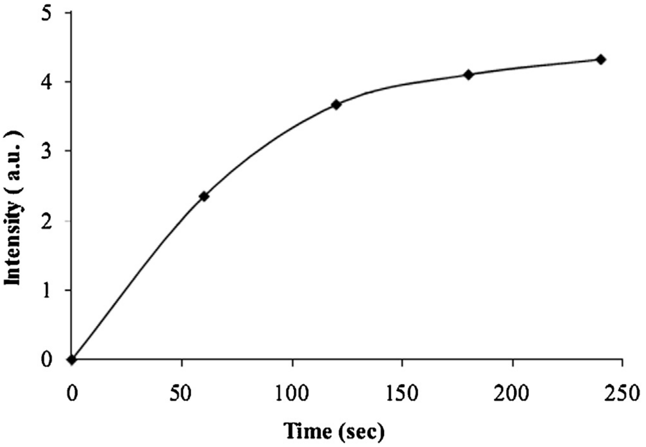


Fig. 5. TEMPO's adduct generation as function of irradiation time.

Fig. 6 shows the TEMPO adduct EPR experimental (continuous line) and simulated (dotted line) spectra. The spin Hamiltonian parameters of TEMPO were determined using the BRUKER WINEPR SimFonia Version 1.25 software as a_N = 15.5 Gauss (hyperfine coupling constant) and g = 2.006 (spectroscopic factor). The g factor and the hyperfine coupling constant of the EPR signal are in very good agreement with the experimental values of TEMPO [40].

When the TCPP/SiO$_2$ system was irradiated with visible light in the presence of DMPO no DMPO-O$_2^{\bullet-}$ adduct was detected. This can be interpreted as follows:

(1) The electron transfer from the TCPP in its photo-excited state (first singlet or triplet excited state) to the SiO$_2$ or TiO$_2$ conduction band (CB) (type I photodynamic reaction) depends on its energy difference. Fig. 7 shows the relative energy levels of SiO$_2$, TiO$_2$ and the adsorbed TCPP. The relative position of the energy levels suggests that the electron transfer process from the excited state of the porphyrin to the TiO$_2$ CB is favorable

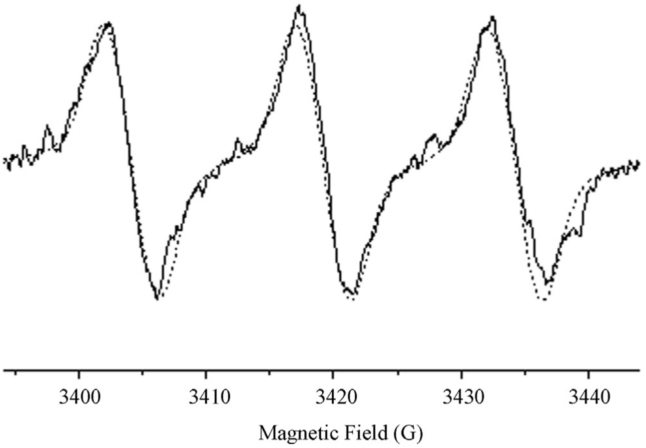


Fig. 6. Experimental EPR spectrum (continuous line) and its simulation (dotted line).

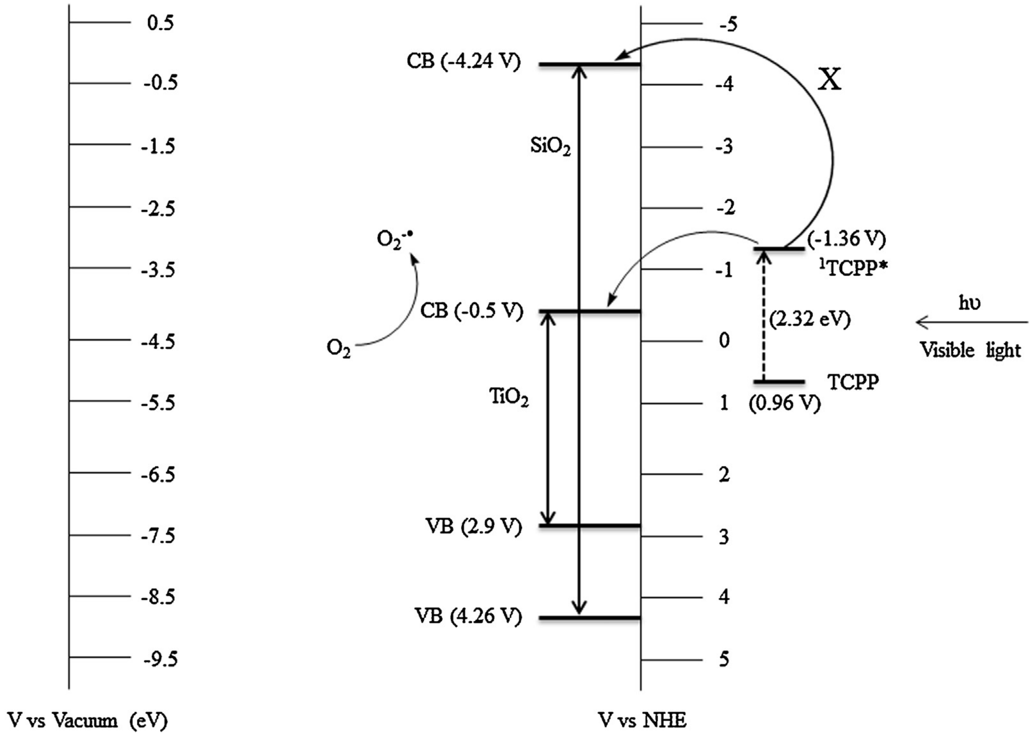


Fig. 7. Diagram illustrating the energetic of sensitation of TiO_2 and SiO_2 particles by TCPP.

[41–43], whereas it is not favorable to the SiO_2 CB consequently in presence of SiO_2, superoxide anion is not formed.

(2) Superoxide anion may be formed via electron transfer from the TCPP excited state to O_2, but the absence of signals from DMPO-$O_2^{\bullet-}$ adducts in the EPR spectra indicates that the presence of superoxide anion generation could be discarded.

3.3. Singlet oxygen chemical trapping by anthracene

Singlet oxygen generation by tetra(4-carboxyphenyl)porphyrin adsorbed on SiO_2 is evidenced by chemical trapping of $^1O_2$ with anthracene. Fig. 8 shows the reduction of the anthracene absorbance at 375 nm due to the formation of the endoperoxide by a [4 + 2] cycloaddition of anthracene with singlet oxygen according to Scheme 3. Addition of azide (0.2 mM) (a strong singlet oxygen quencher [44]) inhibited the oxidation of anthracene with singlet oxygen during the irradiation procedure, and no reactions were further observed in the dark.

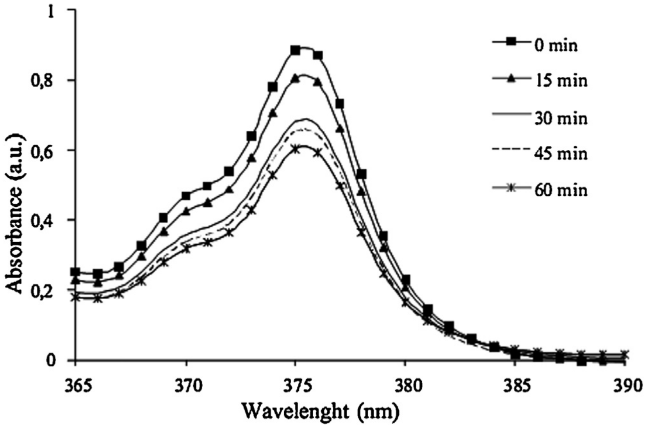
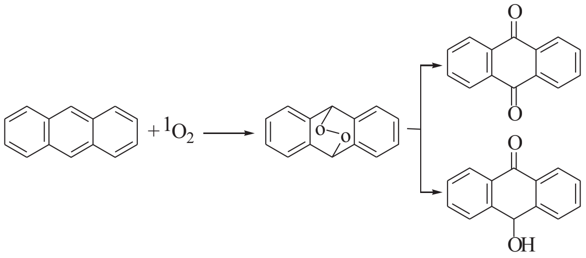


Fig. 8. UV–vis spectra of anthracene as a function of irradiation time with TCPP as photosensitizer.



Scheme 3. Decomposition of the endoperoxide intermediary.

Anthraquinone and oxanthrone produced by the decomposition of the endoperoxide intermediary were identified as the only oxidation products of anthracene (Scheme 3). The absence of the DMPO-$O_2^{\bullet-}$ and DMPO-OH adducts (not detected by EPR) suggest the absence of radicals.

UV–vis spectroscopy does not show presence of TCPP in the solution indicating that the porphyrin has not leached into the solution under the reaction conditions. The GC–MS indicates the presence of anthracene (reagent) and anthraquinone (oxidation product).

4. Conclusions

In the present work, experimental evidences of the formation of singlet oxygen with TCPP/SiO_2 under visible light as only photoproduct are provided using chemical trapping and TEMPO EPR spectroscopy. The formation of $^1O_2$ was evidenced by the production of anthraquinone and oxanthrone which are formed by the reaction of anthracene with $^1O_2$. The absence of the EPR DMPO-$O_2^{\bullet-}$ signal shows that superoxide anion was not present. No other oxygen radicals were detected.

Inorganic semiconductors, such as silicon dioxide, with bound photosensitizers are becoming increasingly important for applications in photocatalysis, dye sensitized solar cells, and many other areas. This paper reports a system where tetrakis(4-carboxyphenyl)porphyin (TCPP) is absorbed onto porous silica particles. Upon photolysis in the presence of oxygen strong evidence is provided that the only detectable photosensitization process involves formation of singlet oxygen. There is no competing superoxide formation. This is demonstrated by reaction of reactive oxygen species with spin probes and also by identification of the chemical products from reaction with anthracene. Although there have been other studies on TCCP bound to silica particles, our results are new and provide information on photosensitization pathways in the presence of oxygen, which will be useful for people working in the area of photocatalysis.

Tetra(4-carboxypenyl)porphyrin adsorbed on SiO_2 with visible light generates singlet oxygen and no other oxygen species, as was evidenced by TEMPO EPR measurements and chemical trapping with anthracene. It can be used as a pure single oxygen generation system for biological applications.

Acknowledgments

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References

[1] M.C. De Rosa, R.J. Crutchley, Photosensitized singlet oxygen and its applications, Coordination Chemistry Reviews 351 (2002) 233–234.
[2] C.R. Lambert, I.E. Kochevar, Does rose Bengal triplet generate superoxide anion? Journal of the American Chemical Society 118 (1996) 3297–3298.
[3] J.P. Tardivo, A. Del Giglio, C. Santos de Oliveira, D. Santesso-Gabrielli, H. Couto-Junqueira, D. Batista-Tada, D. Severino, R. Turchiello, M.S. Baptista, Methylene blue in photodynamic therapy: from basic mechanisms to clinical applications, Photodiagnosis and Photodynamic Therapy 2 (2005) 175–191.
[4] J.M. Aubry, Search for singlet oxygen in the decomposition of hydrogen peroxide by mineral compounds in aqueous solutions, Journal of the American Chemical Society 107 (1985) 5844.
[5] C.E. Diaz-Uribe, F. León, M.C. Daza, F. Martínez, Oxidación de antraceno con oxígeno singulete generado químicamente por el sistema molibdato de sodio/peróxido de hidrógeno, Revista Colombiana de Química 37 (2008) 45–53.
[6] G. Rossi, R. Fedele, C. Comuzzi, D. Goi, Bactericidal activity characterization of an expanded porphyrin on Gram-positive bacteria, Journal of Biotechnology 150 (2010) 438.
[7] F. Schmitt, N. Barry, L. Juillerat-Jeanneret, B. Therrien, Efficient photodynamic therapy of cancer using chemotherapeutic porphyrin–ruthenium metalla-cubes, Bioorganic and Medicinal Chemistry Letters 22 (2012) 178–180.
[8] C. Tanielian, D. Wolff, Porphyrin-sensitized generation of singlet molecular oxygen: comparison of steady-state and time-resolved methods, Journal of Physical Chemistry 99 (1995) 9825–9830.
[9] R. Redmond, J. Gamlin, A compilation of singlet oxygen yields from biologically relevant molecules, Photochemistry and Photobiology 70 (1999) 391–475.
[10] F. Ricchelli, Photophysical properties of porphyrins in biological membranes, Journal of Photochemistry and Photobiology B: Biology 29 (1995) 109–118.
[11] R. Bonnett, Photosensitizers of the porphyrin and phthalocyanine series for photodynamic therapy, Chemical Society Reviews 24 (1995) 19–33.
[12] J. Paczkowskit, D.C. Neckers, Polymer-based sensitizers for the formation of singlet oxygen. New studies of polymeric derivatives of rose Bengal, Macromolecules 18 (1985) 1245–1253.
[13] T.J. Dougherty, Photosensitizers: therapy and detection of malignant tumors, Photochemistry and Photobiology 45 (1987) 879–889.
[14] C. Flors, S. Nonell, Light and singlet oxygen in plant defense against pathogens: phototoxic phenalenone phytoalexins, Accounts of Chemical Research 39 (2006) 293–300.
[15] C.R. Lambert, E. Reddi, J.D. Spikes, M.A. Rodgers, G. Jori, The effects of porphyrin structure and aggregation state on photosensitized processes in aqueous and micellar media, Photochemistry and Photobiology 44 (1986) 595–601.
[16] M. Pineiro, M. Pereira, A.M. Rocha-Gonsalves, L. Arnaut, S. Formosinho, Singlet oxygen quantum yields from halogenated chlorins: potential new photodynamic therapy agents, Journal of Photochemistry and Photobiology A: Chemistry 138 (2001) 147–157.
[17] K. Ishii, Functional singlet oxygen generators based on phthalocyanines, Coordination Chemistry Reviews 256 (2012) 1556–1568.
[18] W. Xu, H. Guo, D.L. Akins, Aggregation of tetrakis(p-sulfonatophenyl) porphyrin within modified mesoporous MCM-41, Journal of Physical Chemistry B 105 (2001) 1543–1546.
[19] R. Giovannetti, L. Alibabaei, L. Petetta, Aggregation behaviour of a tetracarboxylic porphyrin in aqueous solution, Journal of Photochemistry and Photobiology A: Chemistry 211 (2010) 108–114.
[20] K. Lang, J. Mosinger, D.M. Wagnerová, Photophysical properties of porphyrinoid sensitizers non-covalently bound to host molecules; models for photodynamic therapy, Coordination Chemistry Reviews 248 (2004) 321–350.
[21] J. Mosinger, M. Deumié, K. Lang, P. Kubát, D.M. Wagnerová, Supramolecular sensitizer: complexation of meso-tetrakis(4-sulfonatophenyl)porphyrin with 2-hydroxypropyl-cyclodextrins, Journal of Photochemistry and Photobiology A: Chemistry 130 (2000) 13–20.
[22] D. Bechet, P. Couleaud, C. Frochot, M.L. Viriot, F. Guillemin, M. Barberi-Heyob, Nanoparticles as vehicles for delivery of photodynamic therapy agents, Trends in Biotechnology 26 (2008) 612–621.
[23] M. Trytek, M. Majdan, A. Lipke, J. Fiedurek, Sol–gel immobilization of octaethylporphine and hematoporphyrin for biomimetic photooxidation of α-pinene, Journal of Catalysis 286 (2012) 193–205.
[24] W. Kim, J. Park, H.J. Jo, H. Kim, W. Choi, Visible light photocatalysts based on homogeneous and heterogenized tin porphyrins, Journal of Physical Chemistry C 112 (2008) 491–499.
[25] J.M. Aubry, C. Pierlot, J. Rigaudy, R. Schmidt, Reversible binding of oxygen to aromatic compounds, Accounts of Chemical Research 36 (2003) 668–675.
[26] D. Madhavan, K. Pitchumani, Photoreactions in clay media: singlet oxygen oxidation of electron-rich substrates mediated by clay-bound dyes, Journal of Photochemistry and Photobiology A: Chemistry 153 (2002) 205–208.
[27] F. Goulay, C. Rebrion-Rowe, J.L. Le Garrec, S.D. Le Picard, A. Casona, B.R. Rowe, The reaction of anthracene with OH radicals: an experimental study of the kinetics between 58 and 470 K, Journal of Physical Chemistry 122 (2005) 104308(1)–104308(7).
[28] J.R. Harbour, V. Chow, J.R. Bolton, An electron spin resonance study of the spin adducts of OH and HO_2 radicals with nitrone in ultraviolet photolysis of aqueous hydrogen peroxide solutions, Canadian Journal of Chemistry 52 (1974) 3549–3553.
[29] Y. Lion, M. Delmelle, A. Van de Vorst, New method of detecting singlet oxygen production, Nature 263 (1976) 442–443.
[30] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, A simplified synthesis for meso-tetraphenylporphyrin, Journal of Organic Chemistry 32 (1967) 476.
[31] M.A. Schiavon, L.S. Iwamoto, A.G. Ferreira, Y. Iamamoto, M.V.B. Zanoni, M.D. Assis, Synthesis and characterization of a novel series of meso(nitrophenyl) and meso(carboxyphenyl) substituted porphyrins, Journal of the Brazilian Chemical Society 11 (2000) 458–466.
[32] Q. Wang, W.M. Campbell, E.E. Bonfantani, K.W. Jolley, D.L. Officer, P.J. Walsh, K. Gordon, R. Humphry-Baker, M.K. Nazeeruddin, M. Grätzel, Efficient light harvesting by using green Zn-porphyrin-sensitized nanocrystalline TiO_2 films, Journal of Physical Chemistry B 109 (2005) 15397–15409.
[33] T. López, A. López-Gaona, R. Gómez, Synthesis, characterization and activity of Ru/SiO_2 catalysts prepared by the sol–gel method, Journal of Non-Crystalline Solids 110 (1989) 170–174.
[34] Y. Cho, W. Choi, C.H. Lee, T. Hyeon, H.I. Lee, Visible light-induced degradation of carbontetrachloride on dye-sensitized TiO_2, Environmental Science and Technology 35 (2001) 966–970.
[35] J.F. Cornet, A. Marty, J.B. Gros, Revised technique for the determination of mean incident light fluxes on photobioreactor, Biotechnology Progress 13 (1997) 408–415.
[36] M. Gouterman, G.H. Wagnière, L.C. Snyder, Spectra of porphyrins: Part II. Four orbital model, Journal of Molecular Spectroscopy 11 (1963) 108–127.
[37] X. Li, Z. Li, Q. Xia, H. Xi, Effects of pore sizes of porous silica gels on desorption activation energy of water vapour, Applied Thermal Engineering 27 (2007) 869–876.
[38] W. Zheng, N. Shan, L. Yu, X. Wang, UV–visible, fluorescence and EPR properties of porphyrins and metalloporphyrins, Dyes and Pigments 77 (2008) 153–157.
[39] C. Wang, J. Li, G. Mele, G.M. Yang, F.-X. Zhang, L. Palmisano, G. Vasapollo, Efficient degradation of 4-nitrophenol by using functionalized porphyrin-TiO_2 photocatalysts under visible irradiation, Applied Catalysis B: Environmental 76 (2007) 218–226.
[40] C. Hadjur, A. Jeunet, P. Jardon, Photosensitization by hypericin: electron spin resonance (ESR) evidence for the formation of singlet oxygen and superoxide anion radicals in an in vitro model, Journal of Photochemistry and Photobiology B: Biology 26 (1994) 67–74.
[41] C. Diaz-Uribe, M.C. Daza, F. Martínez, E. Páez-Mozo, C. Guedes, E. Di Mauro, Visible light superoxide radical anion generation by tetra(4-carboxyphenyl)porphyrin/TiO_2: EPR characterization, Journal of Photochemistry and Photobiology A: Chemistry 215 (2010) 172–178.
[42] R. Renganathan, A. Kathiravan, Effect of anchoring group on the photosensitization of colloidal TiO_2 nanoparticles with porphyrins, Journal of Colloid and Interface Science 331 (2009) 401–407.
[43] J. He, J. Zhao, H. Hidaka, N. Serpone, EPR characteristics of a dye/colloidal TiO_2 system under visible light irradiation, Journal of the Chemical Society, Faraday Transactions 94 (1998) 2375–2378.
[44] C. Schweitzer, R. Schmidt, Physical mechanisms of generation and deactivation of singlet oxygen, Chemical Reviews 103 (2003) 1685–1757.