

Preparation of Iron(III) Tetrasulfophthalocyanine and Catalysis to the oxidation of 2-chlorophenol

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Abstract

Iron(III) tetrasulfophthalocyanine (Fe(III)PcTs) has been used as a biomimetic enzyme to catalyze the oxidation of 2-CP. Fe(III)PcTs has been Prepared and characterized, including FT-IR, SEM, XRD, UV-Vis and element analysis of Fe(III)PcTs. It showed Fe (III) PcTs has high purity. we studied the oxidation of 2-CP catalyzed by Fe(III)PcTs, the intensities of absorption at 510 nm.

Keywords

Iron(III) Tetrasulfophthalocyanine; Catalysis; 2-Chlorophenol.

1. Introduction

Chlorinated phenols such as 2-chlorophenol (2-CP) are pervasive environmental pollutants not only because of their extensive use for the production of several herbicides, pesticides, preservatives and plant growth regulators, but also because they are formed in the environment as a result of the degradation and metabolism of these agricultural and food chemicals [1–4]. They are widespread and difficult to degrade [5,6]. It had been regarded as the toxic organic substance to be specially controlled[7]. Therefore, the detection of 2-CP concentration is of crucial importance to environmental protection and human health.

Metallophthalocyanines (MPc), which have a perfect symmetrical 18-electron aromatic macrocycle, are easily accessible, very stable to degradation and cost effective, and have been developed as an effective replacement for the nature enzymes.

In this work, iron(III) tetrasulfophthalocyanine (Fe(III)PcTs) has been used as a biomimetic enzyme to catalyze the oxidation of 2-CP. Preparation and characterization of Fe(III)PcTs have been done, including FT-IR, SEM, XRD, UV-Vis and element analysis. It showed Fe (III) PcTs has high purity. we studied the oxidation of 2-CP catalyzed by Fe(III)PcTs, the intensities of absorption at 510 nm, which is the characteristic peak of oxidized product of 2-CP, gradually increased along with the gradually decreased intensities of substrates and 4-AAP in the range of 200-300 nm, suggesting the continuous transformation of 2-CP with 4-AAP to dyes in the presence of Fe(III)PcTs.

2. Experimental

2.1 Preparation and characterization of Fe(III)PcTs

Fe (III)PcTs was synthesized and purified according to the literature[8]. The oxygen sensitive membrane was prepared by using Ru (bpy)₃Cl₂•6H₂O as the fluorescence indicator and cellulose acetate as the matrix according to our previously work[9]. All the reagents were of analytical grade and used without further purification.

The IR spectrum were determined using a Fourier Transform 60SXB infrared spectrometer, SEM image were determined using a SX-40 scanning electron microscope, XRD pattern were determined using a D/MAX-RB X-ray diffractometer, absorption spectra were determined using a UV-2450 spectrophotometer (Shimadzu, Japan), element analysis were determined using a Elementar Vario ELIII elemental analyzer.

2.2 Catalytic oxidation experiment

For the detection of 2-CP concentration, measurements were performed with the set up shown schematically in Fig.5. The reaction of 2-CP assisted with 4-AAP using Fe(III)PcTs as catalyst was performed as follows: A 40 mL of deionized water, 5 mL of 4-AAP aqueous solution (1.0×10^{-3} mol/L) and different concentration of 2-CP (1.0×10^{-3} mol/L stock solution) were added into a 80 mL glass beaker with magnetic continuous stirring. The catalytic reaction was initiated by addition of 31.0 mg of Fe (III)PcTs powder followed by the ultrasonic treatment for 1 min to make it dissolved in the mixture.

3. Results and Discussion

3.1 FT - IR spectrum of Iron(III) Tetrasulfophthalocyanine

The main characteristic absorption peaks of Fe(III)PcTs were shown in figure 1. Infrared spectrum of Fe (III)PcTs mainly included: (1) The absorption peak at 3441cm^{-1} is hydroxyl stretching vibration peak, indicated that metal phthalocyanine contains crystal water; (2) Absorption peak at 1725cm^{-1} showed frame vibration octave band of benzene ring; the absorption peak at 1639cm^{-1} appear absorption peak indicated phthalocyanine ring of C=C stretching vibration, absorption peak at 1417cm^{-1} , indicated that phthalocyanine ring C=N stretching vibration, hence explained the existence of phthalocyanine ring; 1116cm^{-1} and 1192cm^{-1} of absorption peak, showed that substitute benzene ring bending vibration; (3) Absorption peak at 866cm^{-1} is metal-ligand vibration absorption peak formed by central metal Fe and four nitrogen atoms bond on the the luo ring; (4) Absorption peak at 1047cm^{-1} is multiple vibration absorption peak sulfonic group, indicating sulfonic group substituent. These vibrations are consistent with the literature [10], which proved that the preparation of samples has the structure of Fe (III) PcTs.

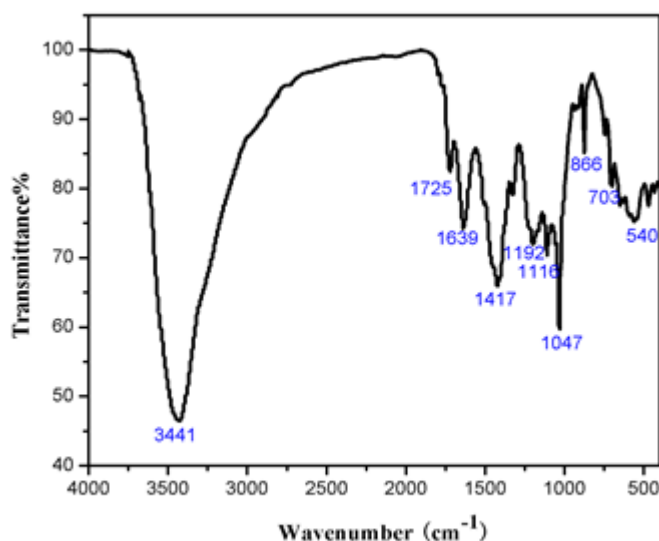


Fig.1 IR spectrum of Fe (III)PcTs

3.2 SEM image of Iron(III) Tetrasulfophthalocyanine

Figure 2 is SEM image of the Fe(III)PcTs. Fe (III) PcTs appeared irregular of columnar crystals, its size is in the range of 1.0~4.0 microns. There are also some irregular aggregate, which constituted by

smaller irregular clubbed and nubby particles. The degree reunion and aggregate size of Fe (III) PcTs are smaller than Fe(II)Pc, this may casused by Fe (III) PcTs is constitute of large amounts of sulfonic acid groups, which produced space steric hindrance to prevent forming aggregates.

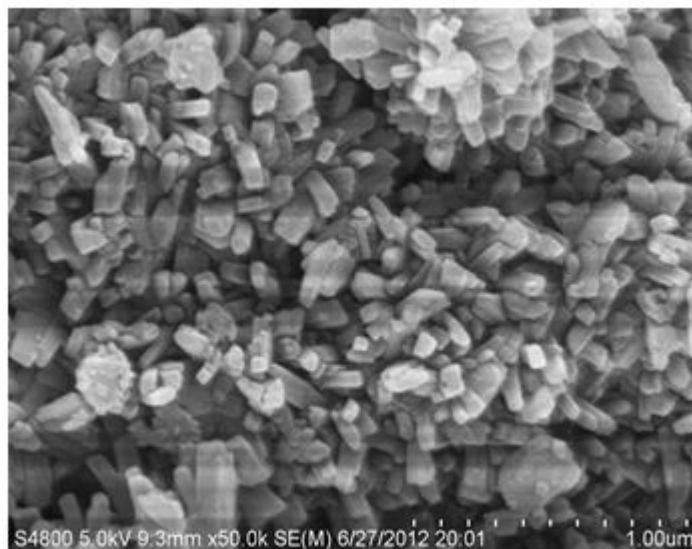


Fig.2 SEM image of Fe(III)PcTs

3.3 XRD pattern of Iron(III) Tetrasulfophthalocyanine

2θ XRD pattern of Fe (III) PcTs in the range from 5° to 30° was shown in Figure 3, which presented the strongest characteristic diffraction peaks corresponding 2θ are 4.97, 9.75, 12.85, 24.26. These 2θ are consistent with corresponding diffraction card (Pdf No. 14-1047) of Fe (II) Pc and literature reported results [11]. In Fe (III) PcTs molecule, center metal ion atom and the N atom have different strength and bond length, make some changes have taken place in the lattice constant of crystal, which result in some changes of the the diffraction peaks and relative position in the XRD spectra of Fe(III)PcTs compared with Fe (II) the Pc, and its main crystal phase is phthalocyanine crystal structure.

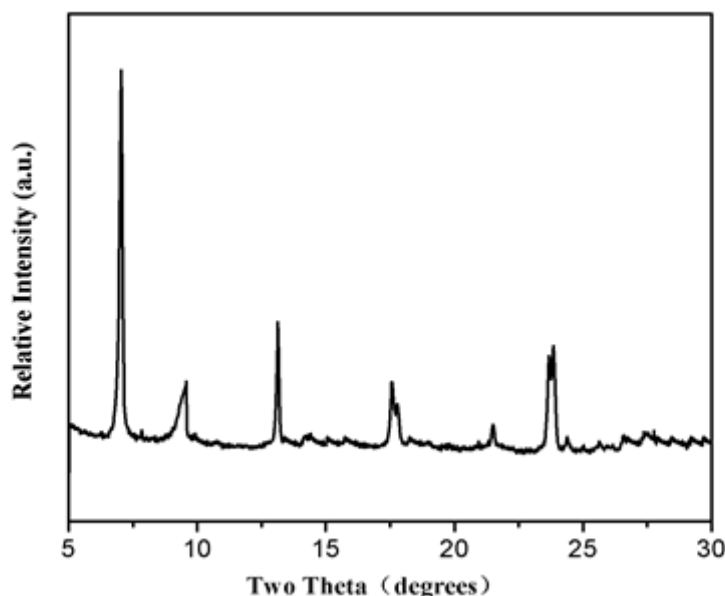


Fig.3 XRD pattern of Fe (III)PcTs

3.4 UV-Vis spectrum of Iron(III) Tetrasulfophthalocyanine

We used the strong polarity dimethyl sulfoxide (DMSO) as solvent in order to prevent Fe (III) PcTs gathered dimer in solution. And similar to UV-Vis absorption spectrum of Fe (II) Pc, a characteristic absorption band (Q) appeared at 638 nm in figure 4, another characteristic absorption band (B) appeared at 321 nm in.

The sulfonic group belongs to electron-withdrawing group, so the maximum absorption wavelength of sulfo phthalocyanine compounds move to the short-wave direction [12]. Q band absorption peak of Fe (III) PcTs at 638 nm is unimodal, slope shape on the right side of the peak existing the aggregate structure of Fe (III) PcTs in solution.

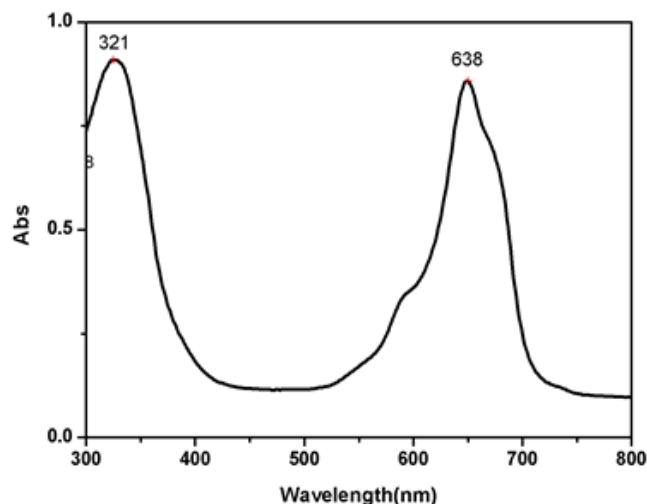


Fig. 4 UV-Vis spectrum of Fe (III)PcTs dissolved in DMSO

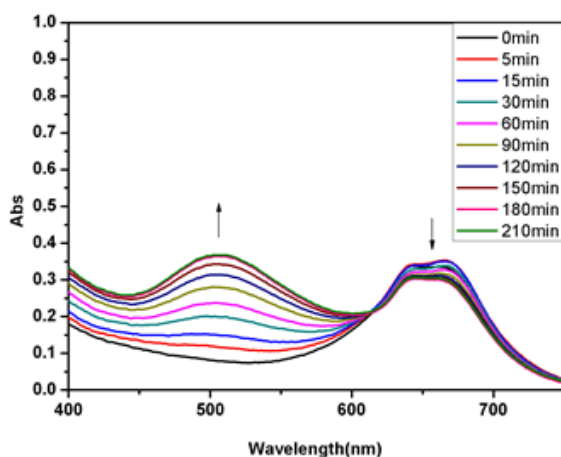


Fig. 5 Typical chromogenic reaction of 2-chlorophenol

3.5 Element analysis of Iron(III) Tetrasulfophthalocyanine

The molecular formula of Fe(III)PcTs is $C_{32}H_{12}FeN_8O_{12}S_4$, the element analysis theoretical value: C, 43.43;H, 1.35;N, 12.67;O, 21.71;S, 14.47, the measured values: C, 43.52;H, 1.47;N, 12.45;O, 21.61;S, 14.38. From this Fe (III) PcTs has high purity.

3.6 Typical chromogenic reaction of 2-chlorophenol

It was documented that oxidation of various phenolic compounds could be catalyzed by phthalocyanine metal complex [13,14]. Fig.5 shows the UV-Vis absorption spectra for chromogenic reaction of 2-CP with 4-AAP in the presence of Fe (III)PcTs at regular intervals, respectively. It can be seen that the intensities of absorption at 510 nm, which is the characteristic peak of oxidized product of

2-CP, gradually increased along with the gradually decreased intensities of substrates and 4-AAP in the range of 200-300 nm, suggesting the continuous transformation of 2-CP with 4-AAP to dyes in the presence of Fe(III)PcTs.

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References

- [1] J. Jantra, H. Zilouei, J. Liu, B. Guieysse, P. Thawarungkul, P. Kanatharana, B. Mat-tiasson, *Analytical Letters* 38 (2005) 1071.
- [2] T. Ruzgas, J. Emnàus, L. Gorton, G. Marko-Varga, *Analytica Chimica Acta*, 1995 311: 245.
- [3] R. Mckinley, J.A. Plant, J.N.B. Bell, N. Vouvouslis, *Environment International*, 2008, 34: 168.
- [4] Z. Mehmood, D.E. Kelly, S.L. Kelley, *Chemosphere*, 1997,34 (11) : 2281.
- [5] Bhattacharya, S.S., Banerjee, R. Laccase mediated biodegradation of 2,4-dichlorophenol using response surface methodology. *Chemosphere*, 2008, 73: 81 ~ 85
- [6] Sahinkaya, E., Dilek, F.B. Biodegradation kinetics of 2,4-dichlorophenol by acclimated mixed cultures. *J. Biotechnol.*, 2007, 127: 716 ~ 726
- [7] Peng, J.F., Liu, J.F., Hu, X.L., Direct determination of chlorophenols in environmental water samples by hollow fiber supported ionic liquid membrane extraction coupled with high-performance liquid chromatography. *J. Chromatogr. A*, 2007, 1139: 165 ~ 170
- [8] Sorokin, A.; Seris, J. L.; Meunler, B. Study on Fiber Optic Gas Sensor Based on Fluorescence Quenching and Its Signal Detecting Method[J]. *Science*. 1995, 268, 1163.
- [9] Sorokin, A.; S. Suzzoni-Dezard, D.; Poullain, D.; Noel, J. P.; Meunier, Application of Lock—in Amplifier in Optical Methane Gas Sensor. B[J]. *J. Am. Chem. Soc.* 1996, 118, 7410.
- [10] Ali H, Langlois R, Wagner J R, et al. Biological activities of phthalocyanines-X syntheses and analyses of sulfonated phthalocyanines[J]. *Photochem. Photobiol.* 1988, 47:713-715.
- [11] Ottaviano L, Lozzi L, Phani A R, et al. Thermally induced phase transition in crystalline lead phthalocyanine films investigated by XRD and atomic force microscopy[J]. *Applied Surface Science*, 1998,136(1-2): 81-86.
- [12] Wencel D, MacCraith B D, McDonagh C. High performance optical ratiometric sol-gel-based pH sensor[J]. *Sensors and Actuators B: Chemical*, 2009, 139(1): 208-213.
- [13] Huang, J.; Fang, H.; Liu, C.; Gu, E. D. and Jiang, D. S. A Novel Fiber Optic Biosensor for the Determination of Adrenaline Based on Immobilized Laccase Catalysis[J]. *Anal. Lett.* 2008, 41, 1430.
- [14] Sorokin, A.; Seris, J. L.; Meunler, B. Study on Fiber Optic Gas Sensor Based on Fluorescence Quenching and Its Signal Detecting Method[J]. *Science*. 1995, 268, 1163.