



# Photocatalytic chromogenic identification of chlorophenol pollutants by manganese phthalocyanine under sunlight irradiation



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## ABSTRACT

A manganese phthalocyanine (MnPc) photocatalytic system for chromogenic identification of several chlorophenol pollutants was reported for the first time. In this system, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol pollutants could be oxidized by dissolved oxygen in the presence of MnPc under sunlight irradiation, and quickly transformed into pink dyes assisted with 4-aminoantipyrene (4-AAP). Control experiments testified that singlet oxygen ( $^1O_2$ ) and superoxide anion radicals ( $O_2^-$ ) were the two key active species for the rapid formation of pink dyes, which were considered to be generated via the combination of well-known metal phthalocyanine mediated Type I and Type II mechanism.

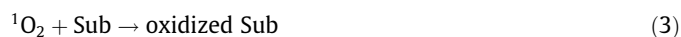
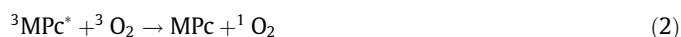
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## 1. Introduction

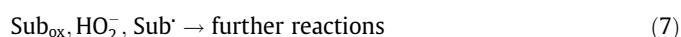
Utilization of solar energy and oxygen in nature to drive chemical reactions has attracted much interest in semiconductor photocatalysis [1]. In the past decades, metal phthalocyanine (MPc), as a representative organic semiconductor material, has been extensively used in photocatalysis for its highly stable  $\pi$ -conjugated macrocyclic structures, nontoxicity, low processing cost, and intensive absorption in visible light region of solar spectra [2–7]. It is well known that the photocatalytic reaction on MPc was initiated by its excitation and the succeeding activation of oxygen [8,9], which mainly involves two kinds of typical processes [10–13]. Firstly, MPc can be excited by light to generate singlet state ( $^1MPc^*$ ) and then usually transforms to the excited triplet state ( $^3MPc^*$ ). Subsequently, the excited  $^3MPc^*$  could activate the ground-state molecular oxygen ( $^3O_2$ ) to produce reactive singlet oxygen ( $^1O_2$ ) for oxidizing or destroying various substrates (such as environmental pollutants and some harmful microorganisms) rapidly, that is the so-called Type II mechanism. Besides, an additional photo-induced electron may also transfer from  $^3MPc^*$

to surface adsorbed  $O_2$  to produce superoxide anion radicals ( $O_2^-$ ), which could contribute to the further oxidation of substrates. These side reactions are defined as Type I mechanism.

The specific Type II and Type I processes can be expressed as follows: Type II mechanism:



Type I mechanism:



Chlorophenol compounds are important industrial raw for manufacture of pesticides, plastics, pharmaceuticals, and other chemicals [14–17]. Due to their high toxicity, non-biodegradation, and cyclic accumulation in aquatic ecosystems, most country's

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environmental protection departments have listed them as the high priority pollutants [18,19]. Therefore, the identification and measurement of chlorophenol pollutants in water have fascinated environmental chemist's interest [20]. Since Emerson and Ettlinger's pioneering work on the  $K_3Fe(CN)_6$ -based chromogenic assay of phenolic compounds [21–23], many investigations have been followed on the improving this standard method or developing novel materials for chromogenic identification of chlorophenol pollutants [18,24]. For example, in 2006 Rajendiran and Santhanalakshmi found that some water-soluble metal tetrasulphthalocyanine complexes could catalyze the chromogenic reaction between phenol and 4-AAP assisted with  $H_2O_2$  [25]. Recently, our group presented that tetranitro iron (II) phthalocyanine (TNFe(II)Pc) could catalyze oxygen oxidation of phenolic compounds and 4-AAP to produce pink quinoneimine dyes in a heterogeneous system [26], which was proved to be a green approach for oxygen was used instead of  $H_2O_2$ . It is noted that the above chromogenic reactions catalyzed by the homogeneous or heterogeneous MPC could proceed successfully without light. In fact, Zhao's group confirmed that the catalytic reaction over MPC could be accelerated significantly under light irradiation compared to that in the dark because of the formation of more active species [27]. Therefore, it is interesting to know whether the chromogenic reaction could be accelerated under light irradiation, which was important for accelerating the chromogenic identification process of chlorophenol pollutants. However, there is still no report on this investigation until now.

In this study, we demonstrate that chromogenic reaction of various chlorophenols with 4-AAP could be obviously accelerated in the manganese phthalocyanine (MnPc) catalytic system under sunlight irradiation. The present catalytic efficiency of 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol on MnPc under sunlight was about 4.01, 4.47, and 5.10 times of that in the dark, respec-

tively. On the basis of the catalytic results, we further studied the detailed process of 2-chlorophenol photo-oxidation catalyzed by MnPc and proposed a cooperative combination of Type I and Type II mechanism governed dyes formation process. To the best of our knowledge, this is the first report on chromogenic reaction of chlorophenols catalyzed by MnPc under sunlight.

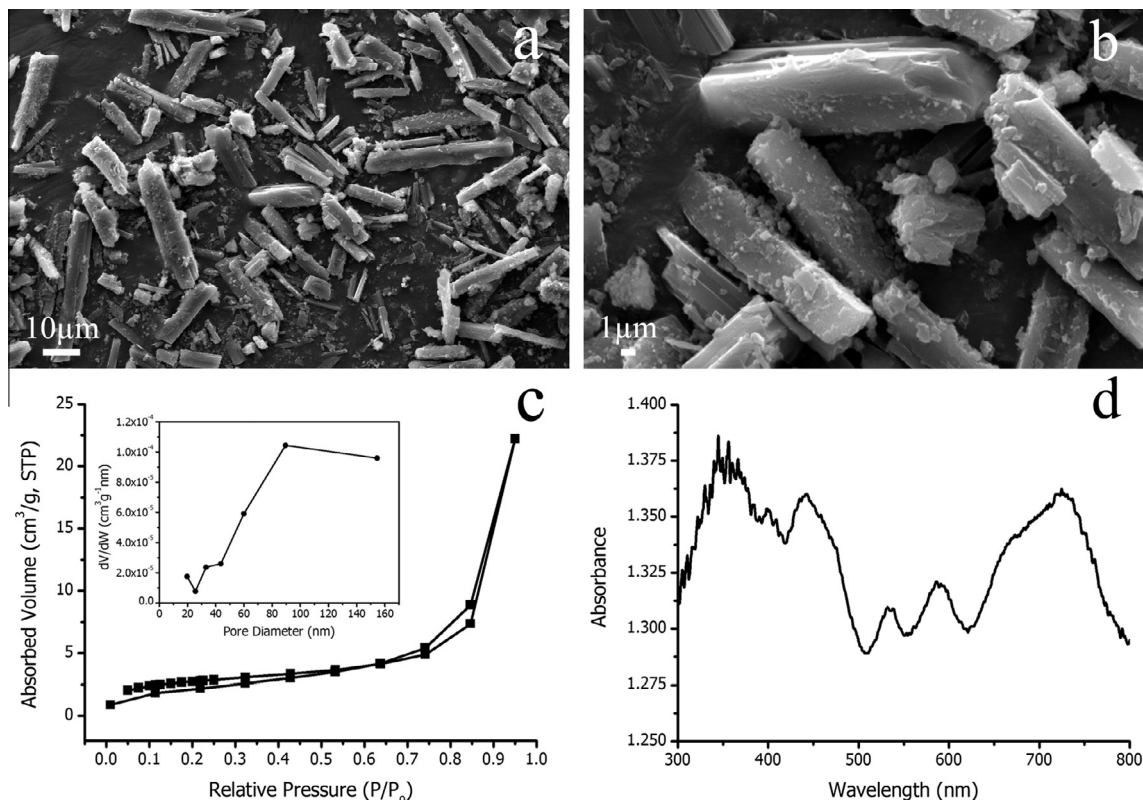
## 2. Experimental

### 2.1. Instrumental

UV-Vis spectroscopy was recorded on a Shimadzu UV-2450 spectrophotometer. IR spectrum was performed on a Thermo Nicolet Nexus FT-IR spectrometer with the standard KBr pellet method. Mass spectrometry (MS) analysis was recorded using Thermo Finnigan LCQ Advantage instrument. Elemental analysis was obtained by using an Elementar Vario ELIII Elemental Analyzer. Fluorescence spectrum (FL) was characterized by a Hitachi F-4500 Fluorescence spectrophotometer. A Zeiss EVO LS-15 Scanning electron microscopy (SEM) was used to investigate the morphology of MnPc. Nitrogen adsorption-desorption isotherm was collected on a Micromeritics Gemini V2380 surface area and porosity analyzer at 77 K after the sample had been degassed in the flow of  $N_2$  at 200 °C.

### 2.2. Materials and reagents

2-Chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 4-aminoantipyrine are AR grade and purchased from Sinopharm Chemical Reagent Co., Ltd. The raw materials for MnPc synthesis are phthalonitrile, manganese (II) acetate tetrahydrate and glycol solvent. All these reagents are from Shanghai D&B Chemicals



**Fig. 1.** (a) SEM morphologies of cube-shaped MnPc crystals; (b) magnified morphologies of MnPc cubes from the central area of (a); (c) nitrogen adsorption-desorption isotherm and pore size distribution curve (inset) of MnPc and (d) UV-Vis diffuse reflectance spectra of MnPc.

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