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Microwave assisted synthesis of ZnPc-COOH and SiO_2/ZnPc-COOH nanopaticles: Singlet oxygen production and photocatalytic property

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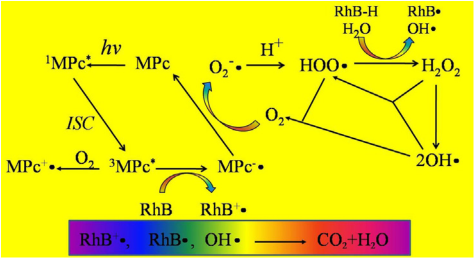
HIGHLIGHTS

- Zinc phthalocyanine was prepared by microwave irradiation method.
- SiO_2/ZnPc-COOH was synthesized with APTES as the coupling agent.
- Singlet oxygen production ability, improved water solubility, good photoactivity.
- Postulated mechanism of the visible-light-induced photodegradation of RhB.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we synthesized α-tetra-(*p*-carboxyphenoxy) phthalocyanine zinc (ZnPc-COOH) by microwave irradiation method, and SiO_2/ZnPc-COOH by using 3-aminopropyltriethoxysilane (APTES) as the coupling agent. Their structural and optical properties were characterized by ^{1}HNMR, MS, IR, SEM, TEM, XRD, TG, etc. The synthesized SiO_2/ZnPc-COOH has a porous structure with a 13 nm film of ZnPc-COOH attached on the surface of SiO_2. Infrared spectroscopy and TG analysis demonstrated that ZnPc-COOH has been covalently bonded to SiO_2 particles. The singlet oxygen quantum yields of ZnPc-COOH and SiO_2/ZnPc-COOH are 0.54 and 0.21, respectively. The photocatalytic studies suggested an enhanced activity of SiO_2/ZnPc-COOH nanoparticles due to its good absorption, better water solubility, enhanced photo stability and accelerated photogeneration of superoxide radicals (O_2^-•) by ZnPc-COOH. The present work shows that SiO_2/ZnPc-COOH has great potential for application in photodynamic cancer therapy as well as in photo-degradation of water pollutes.

1. Introduction

Phthalocyanines have attracted considerable interest for many decades because of their remarkable optical and lasing properties, thermal and chemical stabilities and they have been used as excellent dyes and pigments for many years [1]. Moreover, they have got various applications in modern science and technology, such as photovoltaic materials in solar cells [2,3], systems for fabrication of light emitting diodes (LED) [4], photoconductors in xerography [5], nonlinear optical materials [6,7], sensitizers for photodynamic cancer therapy (PDT) [8–10], dyes at recording layers [11], as well as diverse catalytic systems [12]. Although the singlet oxygen production ability and water solubility are always used to evaluate the synthesized phthalocyanine [13], the production of superoxide radical O_2^-• by irradiation of phthalocyanine also plays a major role for the photo-degradation of some pollutants [14–16].

A drawback for non-substituted phthalocyanines is that they are insoluble in most common solvents, such as water or ethanol, and the aggregation of phthalocyanine species has deleterious effects

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on their desired optical, electrical, and catalytic properties [17]. Thus, for the purpose of heterogeneous catalysts, researches focus on designing and synthesizing phthalocyanine with appropriate substituent groups (e.g.–SO_3H and –COOH) at the periphery of the macrocycle, which can be soluble in the polar solvents mentioned above. Silica nanoparticles have been widely used as a carrier vehicle for drug delivery due to their unique advantages, such as small yet uniform pore size, large specific surface area and pore volume, good water solubility and biocompatibility [18]. In recent years, microwave-assisted organic synthesis (MAOS) has been widely used for efficient synthesis of phthalocyanine [19,20]. Using a microwave oven in MAOS not only reduces chemical reaction times from hours to minutes, but also reduces side reactions, increases the yield, and improves reproducibility [21]. These advantages made MAOS as a forefront technology for rapid reaction optimization, for efficient synthesis of new chemical entities, as well as for discovering and probing new chemical reactivity.

The immobilization of phthalocyanines on a large area of silica (SiO_2) has been widely studied, taking into account its high mechanical, chemical and thermal resistances. Many works focus on finding an effective way of trapping phthalocyanines inside porous silica. Pal [22] prepared phthalocyanine and Silver/Gold nanoparticles incorporated MCM-41with an in situ physical trapping method for the electrocatalytic reductions of O_2 and CO, which can lead to an enhanced electro-catalytic reduction for O_2 reduction. Ribeiro [23] covalently trapped the phthalocyanine into silica network using the sol-gel process, it shows that the composite retained all the optical property and thermal stability as for phthalocyanine. In most studies, the SiO_2 nanoparticles were firstly modified and then they were covalently bonded with phthalocyanine by sol–gel or adsorbing method [24–26]. The reagent of 3-aminopropyltriethoxysilane (APTES) has been most widely used for the immobilization of phthalocyanine in silica network [27,28]. In this study, ZnPc-COOH and SiO_2/ZnPc-COOH nanoparticles were synthesized and their morphology, structure, thermal stability and optical property etc were investigated. The as-synthesized SiO_2/ZnPc-COOH shows the capability to produce singlet oxygen, improved water solubility and photo-catalytic ability for the degradation of Rhodamine B in aqueous solution. We also proposed a mechanism that may explain the enhanced properties of as-synthesized SiO_2/ZnPc-COOH.

2. Experimental section

2.1. Materials

N,N-dimethylformamide (DMF), methanol (MeOH), acetone (C_3H_6O), hydrochloric acid (HCl), potassium carbonate (K_2CO_3), zinc chloride ($ZnCl_2$), 4-hydroxybenzoic acid ($C_7H_6O_3$), hexadecyl trimethyl ammonium bromide (CTAB), tetraethylorthosilicate (TEOS), rhodamine B (RhB) and ammonia water (25%) were purchased from Beijing Chemical Reagent Company (China) and used as received. 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 99%) and 3-nitrophthalonitrile ($C_8H_9N_3O_2$, 99%) were purchased from Hua Teng agent company. 1,3-Diphenylisobenzofuran (DPBF, 95%) and 3-aminopropyltriethoxysilane (APTES, 99%) were obtained from ACROS and used as received.

2.2. Synthesis

2.2.1. Synthesis of 3-(4-carboxyphenoxy) phthalonitrile ***(3)***

3-Nitrophthalonitrile (2.2 g, 12.7 mmol) **1**, 4-hydroxybenzoic acid (1.75 g, 1 mmol) **2**, finely ground K_2CO_3 (7.9 g, 57 mmol) and dry DMF (10 mL) were mixed and irradiated at 400 W for 10 min under N_2 atmosphere in a microwave oven (WBFY205, 2.45 GHz, Beijing Rui Chen Wei Ye Equipment Company) equipped with a reflux condenser. Pure water (150 mL) was poured into the solution after cooling down and the pH of the mixture was adjusted to 1.00 by HCl. Flocculent precipitate was obtained and filtered to get the solid products. Methanol was used many times for product recrystallization. The yield was 62.8%.

2.2.2. Synthesis of α-tetra-(p-carboxyphenoxy) phthalocyanine zinc (ZnPc-COOH) ***(4)***

The synthetic route for ZnPc-COOH is shown in Scheme 1. 3-(4-*Carboxyphenoxy*) phthalonitrile (**3**) (450 mg, 1.67 mmol) and $ZnCl_2$ (57 mg, 0.42 mmol) were dissolved in dry DMF (4 mL) and 1, 8-diazabicyclo [5,4,0] undec-7-ene (DBU) (0.6 mL) was added. The mixture was then heated and stirred at 400 W in the microwave for 5 min under N_2 atmosphere. After reaction, the mixture was cooled to 30 °C and precipitated by adding HCl (1 M). Solid product was filtered and washed with water until the pH was 7. The product was then extracted by acetone in a Soxhlet extractor. Yield: 270 mg (58%). ^{1}H NMR (DMSO-d6) 1 ppm: 8.027 (d, 2H), 7.952 (d, 1*H*), 7.885 (m, 1*H*), 7.494 (d, 2*H*), 7.313 (d, 2*H*). Calc. for $C_{60}H_{32}N_8O_{12}Zn$: %C 64.23, %H 2.88, %N 9.99; Found: %C 64.68, %H 3.01, %N10.13. MS (ESI-MS) *m*/*z*: Calc. 1121.9; Found: 1116.5.

2.2.3. Synthesis of SiO_2/ZnPc-COOH

CTAB (0.08 g) was added into a mixture of ethanol (13 mL) and water (27.5 mL) at 30 °C. After 5 min stirring, TEOS (0.5 mL) was dropped into the mixture and then ammonia water (0.5 mL) was added. The stirring speed was kept at 700 rpm for 3 h. The product was centrifuged, washed with water and dried under vacuum at 80 °C for 12 h. The product was then calcined at 500 °C for 3 h to remove the surfactant to get the SiO_2 particles

To prepare SiO_2/ZnPc-COOH, the SiO_2 particles (1 g) was first dispersed in 50 mL toluene, and APTES (0.35 mL) was added at 80 °C. The reaction was kept for 12 h under continuous stirring, then the product was centrifuged, washed with water and dried in vacuum at 80 °C for 24 h. The modified SiO_2 particles (1 g) were dispersed by ultrasonic irridation in DMF (15 mL) for 20 min, then 0.187 g of ZnPc-COOH was added into the solution and the mixture was stirred in the dark for 6 h. The product was washed with water and ethanol for three times. After drying under vacuum at 80 °C for 6 h, the SiO_2/ZnPc-COOH was obtained. The formation of SiO_2/ZnPc-COOH composite is shown in Scheme 2.

2.3. Characterizations

2.3.1. Products characterizations

The morphologies of the synthesized particles were characterized by transmission electron microscopy (TEM) (JEM-3010, Japan) and scanning electron microscopy (SEM) (S-4700, Japan). Thermal gravimetric (TG) analysis was conducted on a thermal analysis instrument (STA-449C, Germany) in air at a scanning rate of 10 °C/min. X-ray powder diffraction (XRD) was carried out on a Rigaku 2304 diffractometer with Cu*K*a radiation (Ni-filtered). Infrared spectra (IR) were recorded on a Nicolet-8700 FT-IR spectrometer. ^{1}H NMR spectra were recorded in DMSO-d6 solutions on a AV300/AV600 spectrometer (Bruker, Germany). Elemental analyses were obtained with a vario ELcube Instrument from Elementar company (Germany).

2.3.2. Singlet oxygen quantum yield measurements

The determination of its Singlet oxygen quantum yield (Φ_Δ) determinations was performed using the chemical trapping method. 2 mL ZnPc-COOH solution that contained diphenylisobenzofuran (DPBF) with a concentration lower than $\sim 3 \times 10^{-5}$ mol/dm^3 was irradiated at 670 nm in air-saturated