



Silica microspheres functionalized with porphyrin as a reusable and efficient catalyst for the photooxidation of 1,5-dihydroxynaphthalene in aerated aqueous solution

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ABSTRACT

Silica microspheres functionalized with 5-(4-allyloxy)phenyl-10,15,20-tri(2,6-dichlorophenyl)porphyrin (APTDCPP), SiO₂-MPS-APTDCPP, have been synthesized by sol-gel process and characterized using SEM, FT-IR, UV-vis and TG. The SEM images show that the morphology of the silica microspheres is spheriform and uniform with size of 2–4 μm. Their photocatalysis activity to oxidize 1,5-dihydroxynaphthalene under visible light irradiation in aerated aqueous solution has been studied and the main product has also been identified by ¹H NMR and MS techniques. The factors affecting photocatalytic oxidation, such as oxygen concentration, initial concentration of substrate, amount of catalyst and the addition of NaN₃, have been studied in detail. The experimental results confirmed that the hybrid material is a mild, reusable and efficient heterogeneous catalyst for the photooxidation of 1,5-dihydroxynaphthalene in aerated aqueous solution.

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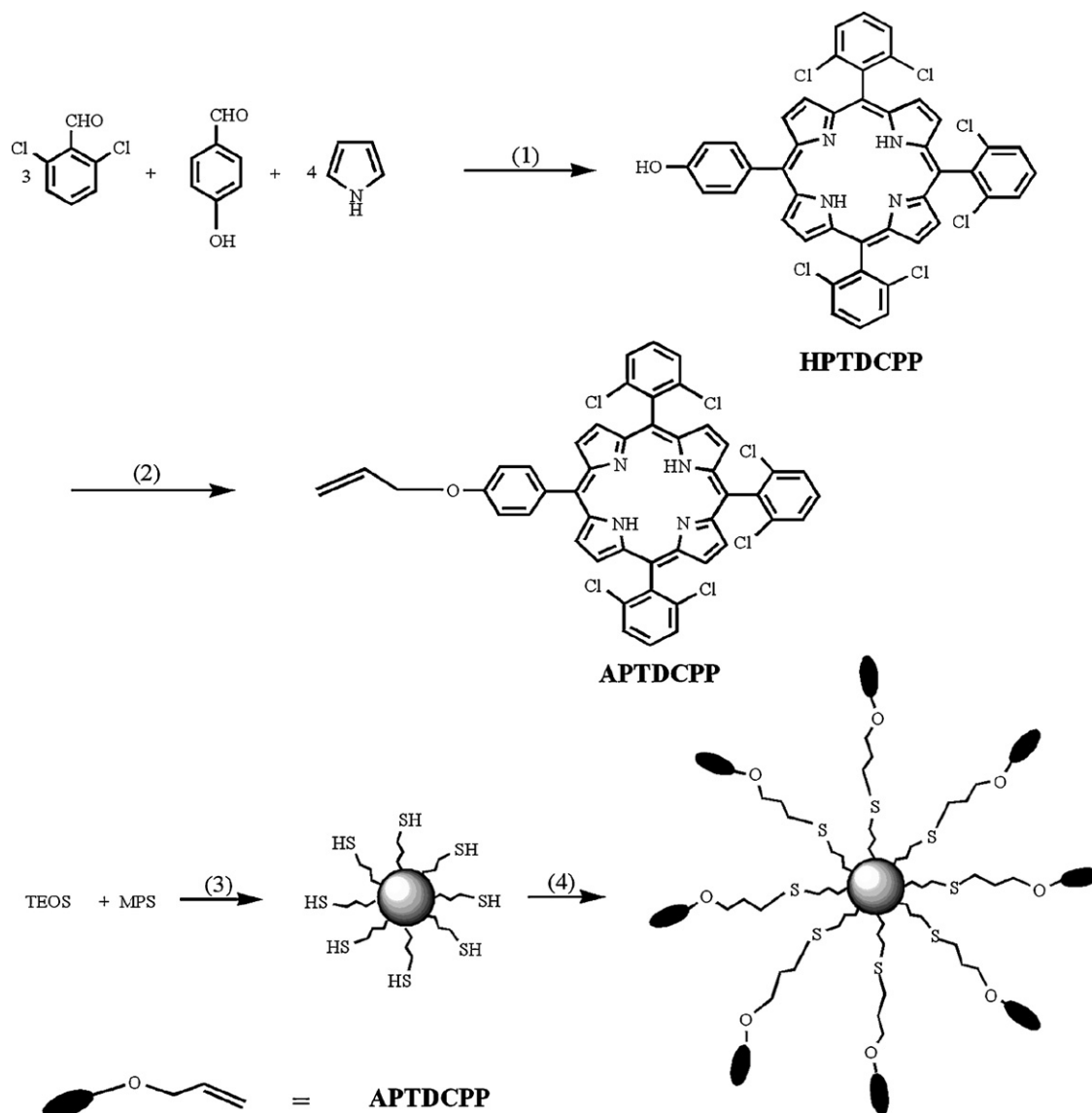
1. Introduction

In the past decades, photocatalysis has become an area of great research interest because of serious pollution in the environment from industrial and agricultural wastes water containing harmful organic compounds [1–4]. Phenolic compounds are listed among top priority pollutants for their slow degradation and high toxicity [5,6]. Several methods have been employed to degrade these pollutants. Among various strategies, dye-sensitized photooxidation of phenolic compounds involving transient singlet oxygen has been proven to be an efficient method [7–9]. In the sensitization process, the dye molecule transfers its energy to triplet oxygen and excites it to singlet state oxidizing electron-rich phenolic compounds. Undoubtedly, dye-sensitized photooxidation of phenolic compounds is one of the most important methods, since it does not liberate any additional pollutant. Porphyrins and metalloporphyrins are employed as a sensitizer [10–13] for their efficiently harvest sunlight, high molar absorption coefficients in the visible region, high quantum yields of photo-excited triplet states, and ability to generate singlet molecular oxygen. Some water soluble porphyrin deriva-

tives, such as meso-tetra(2,6-dichloro-3-sulfophenyl)porphyrin [14] and meso-tetra(4-sulfonatophenyl)porphyrin [15], have successfully used in the photooxidation of 4-chlorophenol and 2,4,6-trichlorophenol in aqueous solution. We also investigated the photooxidation of 1,5-dihydroxynaphthalene catalyzed by meso-tetra(4-sulfonatophenyl)porphyrin under visible light irradiation in aerated aqueous solution [16]. 5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrin (TDCPP) appears to be a particularly efficient photosensitizer for photooxidation of 2,3,5-trimethylphenol in acetonitrile, which is related to that the presence of chlorine atoms in meso phenyl groups increases the quantum yields of S₁-T₁ [17,18]. However, it is difficult to be used as a photosensitizer to oxidize phenolic compounds in wastes water because TDCPP is insoluble in aqueous solution.

In the last years, researches on immobilized porphyrins on hybrid materials have been sprung up by entrapment [19,20], electrostatic binding or axial ligation of metal methods [21–26], but most of them suffer from a reversible binding and the support is broken during the washing of the solvent under working conditions. A useful means to avoid these limitations is to establish the stable covalent binding between porphyrins and support materials. Kitamura et al. have reported photooxidation of phenol by silica-supported porphyrin in polymer microchannel chips [27]. Rocha Gonsalves and co-workers also studied the photocatalysis behavior of porphyrins covalently linked to polystyrene based polymers as

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Scheme 1. Synthesis route of $\text{SiO}_2\text{-MPS-APTDCPP}$. Reagents and experimental conditions: (1) acetic acid, nitrobenzene. (2) DMF, K_2CO_3 allyl bromide. (3) H_2O , $\text{C}_2\text{H}_5\text{OH}$, ammonia. (4) Toluene, AIBN, APTDCPP.

heterogeneous sensitizers [28]. Silica gel as an inorganic support material has some advantageous properties, such as excellent stability, good accessibility, and the fact that organic groups can be robustly anchored to the surface [29,30].

In order to use TDCPP as a photosensitizer to oxidize phenolic compounds in wastes water, we have synthesized a new kind of silica microspheres anchored TDCPP derivative by the thiol-ene radical polymerizations [31–33] between 3-mercaptopropyl-functionalized silica microspheres ($\text{SiO}_2\text{-MPS}$) and 5-(4-allyloxy) phenyl-10,15,20-tri(2,6-dichlorophenyl)porphyrin (APTDCPP). Their photocatalytic activity to oxidize 1,5-dihydroxynaphthalene under visible light irradiation in aerated aqueous solution has also been studied.

2. Experimental

2.1. Materials and chemicals

3-Mercaptopropyltrimethoxysilane (MPS, 95.8%), tetraethyl orthosilicate and allyl bromide (96%) were purchased from

Guangzhou Junye Chemistry plant. 1,5-Dihydroxynaphthalene and NaN_3 were obtained from Aldrich without further purification. Silica gel used to purify porphyrin by chromatograph was obtained from Qingdao. Toluene and acetonitrile were dried with calcium hydride and redistilled. All other reagents and solvents were obtained from commercial sources and used without further purification.

2.2. Instrumentation

The scanning electron microscopy (SEM) was performed with a JSM-6330F Field Emission Scanning Electron Microscope. UV-vis and IR spectra were recorded on a Shimadzu UV-3150 spectrophotometer and an EQUINOX 55 Fourier transformation infra-red spectrometer, respectively. Thermal analysis was performed with a Netzsch TG-209 Thermogravimetric Analyzer. ^1H NMR spectra were recorded on a 300 MHz Bruker-AMX spectrophotometer with tetramethylsilane (TMS) as internal reference. Mass spectrometry analysis was performed on a Thermo LCQDECA-XP spectrometer. An iodine tungsten lamp (200 W, Shanghai), ITL, was used as a light source.

2.3. Synthesis of silica microspheres functionalized with APTDCPP (SiO₂-MPS-APTDCPP)

The strategy to prepare silica microspheres functionalized with APTDCPP derivative (SiO₂-MPS-APTDCPP) is shown in Scheme 1.

2.3.1. Synthesis of HPTDCPP and APTDCPP

5-(4-Hydroxyl)phenyl-10,15,20-tri(2,6-dichlorophenyl)porphyrin (HPTDCPP) was synthesized by the method similar to [16,34]. 5.3 g dichlorobenzaldehyde (30 mmol) and 1.2 g 4-hydroxybenzaldehyde (10 mmol) were dissolved in a mixture of acetic acid (150 ml) and nitrobenzene (75 ml). After the temperature was raised to 125 °C, 2.7 g pyrrole (40 mmol) was added and the temperature was kept 125 °C for 1 h. The solution was then allowed to cool to room temperature and purple residues were obtained by filter. The crude material was purified on a silica gel chromatograph using CHCl₃ as an eluent. The second band was collected and the solvent was evaporated. Purple solid HPTDCPP was obtained in 2% yield. ESMS [CHCl₃, *m/z*]: 838 ([HPTDCPP]⁺). ¹H NMR (300 MHz, CDCl₃): 8.86 (d, 2H, β-pyrroles), 8.64 (d, 6H, β-pyrroles), 8.06 (d, 2H, 2,6-phenyl), 7.18 (d, 2H, 3,5-phenyl), 7.68 (s, 3H 4-dichlorophenyl), 7.78 (s, 6H, 3,5-dichlorophenyl), -2.51 (s, 2H, NH, pyrrole).

A mixture of HPTDCPP (0.168 g, 0.20 mmol), allyl bromide (0.0242 g, 0.20 mmol) and anhydrous K₂CO₃ (500 mg) in DMF (25 ml) was stirred for 12 h at room temperature. Then the reaction mixture was poured into water (80 ml) and filtered. The residue was submitted to column chromatography on silica gel using the chloroform as an eluent. The first band was collected and the solvent was evaporated. Purple solid 5-(4-allyloxy)phenyl-10,15,20-tri(2,6-dichlorophenyl)porphyrin (APTDCPP) was obtained in 90% yield. ESMS [CHCl₃, *m/z*]: 877 ([APTDCPP]⁺). ¹H NMR (300 MHz, CDCl₃): 8.83 (d, 2H, β-pyrroles), 8.61 (d, 6H, β-pyrroles), 8.07 (d, 2H, 2,6-phenyl), 7.25 (d, 2H, 3,5-phenyl), 7.64 (s, 3H, 4-dichlorophenyl), 7.73 (s, 6H, 3,5-dichlorophenyl), 6.16–6.28 (s, 1H, =CH-), 5.59 (d, 1H, H-C=C-), 5.41 (d, 1H, H-C=C-), 4.78 (s, 2H, =C-CH₂-O), -2.54 (s, 2H, NH, pyrrole).

2.3.2. Synthesis of SiO₂ microspheres modified by MPS (SiO₂-MPS)

The silica microspheres were prepared using a modified Stöber procedure that involved the hydrolysis of TEOS. A total of 5 ml TEOS, 300 mg polyvinyl pyrrolidone (K-30) (PVP K-30), 30 ml ethanol and 70 ml H₂O were mixed in a 250 ml round-bottomed flask under vigorous stirring until the oil (TEOS) droplets completely disappeared and a transparent solution was obtained. 2 ml ammonia was added to the mixture solution and the solution was stirred vigorously for 12 h at room temperature. Then 5 ml MPS was added dropwise into the mixture and the solution was stirred vigorously another 12 h at room temperature. After completion of the reaction, the resulting precipitate was collected by centrifugation, washed repeatedly with alcohol, and then dried in a vacuum and white powder was obtained.

2.3.3. Synthesis of SiO₂-MPS-APTDCPP composite

The silica microspheres functionalized with porphyrin were prepared by stirring a mixture solution containing 30 ml toluene, 4.4 g SiO₂-MPS, 50 mg APTDCPP and 30 mg 2,2'-azo-bis-isobutyronitrile (AIBN) at 75 °C for 15 h under N₂ atmosphere. The product was washed with CHCl₃ in a Soxhlet extractor overnight to remove unbound APTDCPP. The solids were dried for 5 h at 100 °C. Unbound APTDCPP was quantified through spectrophotometric measurement at 514 nm, by using a calibration curve obtained by using a suitably diluted solution. Thus, the amounts of bound porphyrins were determined by difference between the two measurements. The amount of APT-

DCPP in SiO₂-MPS-APTDCPP was 0.0128 mmol/g obtained by this method.

2.4. Photooxidation experiments of 1,5-dihydroxynaphthalene

Photooxidation experiments of 1,5-dihydroxynaphthalene were carried out in a 30 ml self-designed jacketed reactor maintained at a certain temperature by circulation of thermostated water. In a typical experiment, an oxygen atmosphere was achieved by continuous bubbling of pure oxygen into a suspension containing 20 ml 1,5-dihydroxynaphthalene solution and a certain amount of photocatalyst (pH 4.5). Because SiO₂-MPS-APTDCPP was able to complex 1,5-dihydroxynaphthalene, SiO₂-MPS-APTDCPP was saturated with 1,5-dihydroxynaphthalene until constant concentration in solution before light irradiation and the concentration of 1,5-dihydroxynaphthalene were used as the initial value of the further kinetic treatment of the photooxidation process. In the process of photooxidation experiment, keeping the reaction mixture magnetically stirred. A 200 W iodine tungsten lamp located at 5 cm side the reactor provided the irradiation light, which was filtered by a 410 nm cut filter to assure cut-off of the UV light. A typical incident light intensity was measured to be about 60 mW/cm² in the wavelength range of 420–550 nm. After a few minutes of oxygen purging and irradiation, the orange color of the products became clearly visible within the reactor tube and further deepened with progressing.

At given intervals of irradiation, a sample of the suspension was collected, centrifuged and filtered. The solutions were analyzed by UV-vis spectroscopy. Because Beer-Lambert law is obeyed for the concentration of 1,5-dihydroxynaphthalene on the absorption at 329 nm in the concentrations ranging from 0.01 to 0.18 mM, we can use the changes of the absorbance of 1,5-dihydroxynaphthalene at 329 nm to calculate photodegradation percentage of 1,5-dihydroxynaphthalene [18].

The reaction products were purified by extraction from the reaction mixtures with CHCl₃, chromatographing on a silica gel column using CHCl₃ as eluent and then concentrating the extracts under reduced pressure to give the pure products. ESMS [CHCl₃, *m/z*]: 173 ([M-1]⁻). ¹H NMR (300 MHz, CDCl₃): 6.94 (2H, s, H-naph.), 7.26 (1H, d, H-naph.), 7.28 (1H, d, H-naph.), 7.61 (2H, m, H-naph.), 11.87 (1H, s, OH). All these indicate that the mainly product is 5-hydroxy-1,4-naphthoquinone [18].

3. Results and discussion

3.1. Characterization of SiO₂-MPS-APTDCPP

The morphology of SiO₂-MPS and SiO₂-MPS-APTDCPP was obtained by scanning electron micrograph as shown in Fig. 1. A smooth surface could be observed on these microspheres accompanied by a satisfying uniformity and spherical morphology with an average diameter of ca. 2–4 μm in Fig. 1a and b shows that no change has happened in the diameter of SiO₂-MPS, while the surface of the silica microspheres becomes rough after APTDCPP bonding on it.

The presence of APTDCPP in the silica microspheres was confirmed by the solid state UV-vis spectra of the catalyst. Typical absorption spectra of porphyrin with Soret band (422 nm) and four Q bands (516, 547, 595, 657 nm) was observed in the solid state UV-vis spectra of SiO₂-MPS-APTDCPP (Fig. 2). Comparing these spectra with that of the APTDCPP, A 3 nm red-shift could be found in the Soret band (Fig. 2, inset), which can be attributed to the distortion of the porphyrin rings and the red-shift is usually observed when porphyrins are immobilized on solid supports [35–37].

Fig. 3 displays the FT-IR spectra of APTDCPP and SiO₂-MPS-APTDCPP. No IR band located at approximately 3075 and

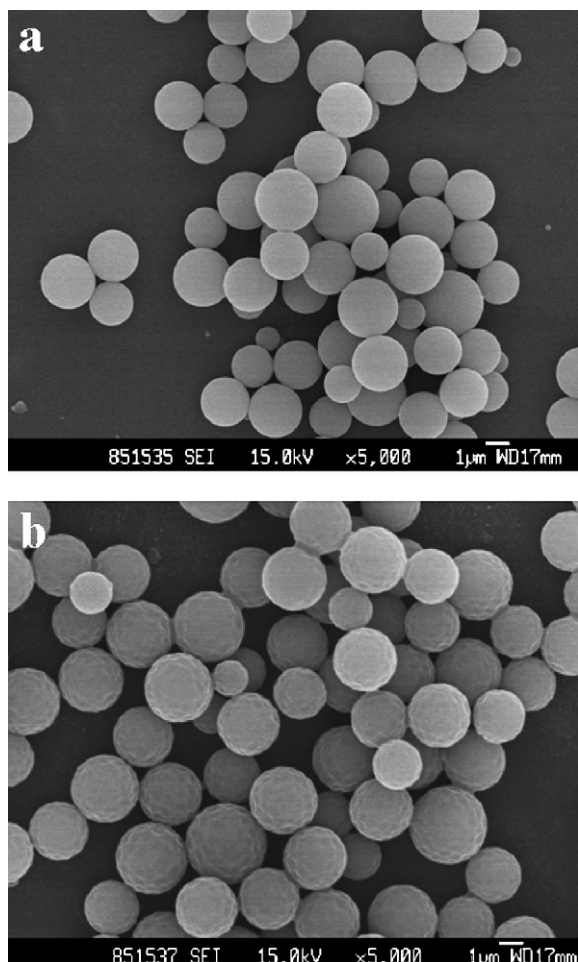


Fig. 1. Scanning electron micrograph of SiO₂-MPS (a) and SiO₂-MPS-APTDCPP (b).

1645 cm⁻¹ assigned to the vibration of the =C–H and the CH₂CH=CH₂ group of APTDCPP can be observed, indicating the completion of grafting reactions. The broad IR band at 1094 and 798 cm⁻¹ assigned to the asymmetric and symmetric stretching of Si–O–Si unit can be also observed, which indicates the formation of siloxane bonds. The IR bands between 1300 and 1600 cm⁻¹ (Fig. 3b) attributed to the pyrrole C=N stretching

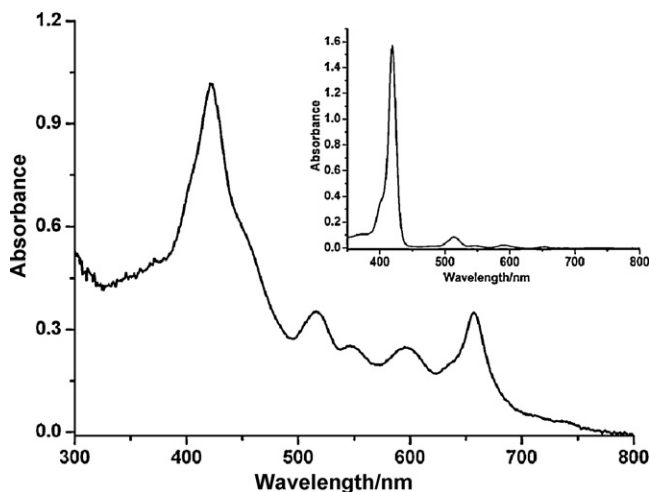


Fig. 2. Solid state UV-vis spectra of SiO₂-MPS-APTDCPP. Inset: absorption spectra of APTDCPP.

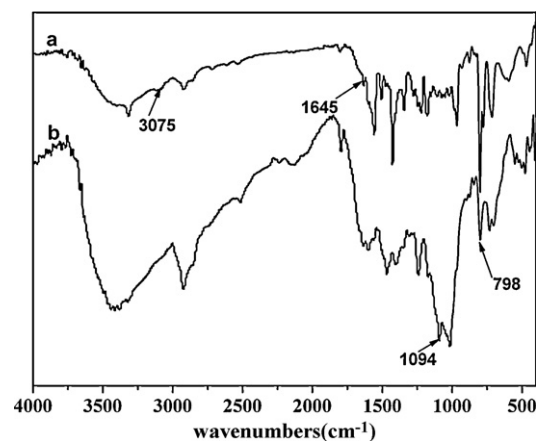


Fig. 3. FT-IR spectra for APTDCPP (a) and SiO₂-MPS-APTDCPP (b).

also indicated that the presence of porphyrin in the silica microspheres.

TG-DTG curves of SiO₂-MPS-APTDCPP are shown in Fig. 4. It can be seen that the catalyst is apparently stable up to about 260 °C and the organic ligand beginning to break off from the silica microspheres in the region of 260–650 °C. Experimental residue in the sample is about 43.29%.

3.2. Catalytic activity of SiO₂-MPS-APTDCPP

3.2.1. 1,5-Dihydroxynaphthalene photooxidation

The catalytic activity of SiO₂-MPS-APTDCPP in the photooxidation of 1,5-dihydroxynaphthalene was studied. 1,5-Dihydroxynaphthalene degradation occurred promptly in the visible irradiation under the adding of the SiO₂-MPS-APTDCPP as confirmed by the UV-vis spectra changes of 1,5-dihydroxynaphthalene (Fig. 5). The absorption spectrum of 1,5-dihydroxynaphthalene in water was characterized by three bands in the UV-vis region located at 298, 314 and 329 nm attributed to the naphthalene rings of 1,5-dihydroxynaphthalene. As observed in Fig. 5, the intensity of the 298, 314 and 329 nm absorption band decreased rapidly under visible light irradiation, indicating the degradation of 1,5-dihydroxynaphthalene in the presence of SiO₂-MPS-APTDCPP microspheres. Concomitantly, two new absorption bands (251 and 422 nm) appeared in the UV-vis region, which results from the production of 5-hydroxy-1,4-naphthoquinone in the reaction [18]. For comparison, blank experiments, in which the photooxidation experiment of 1,5-dihydroxynaphthalene was performed in dark

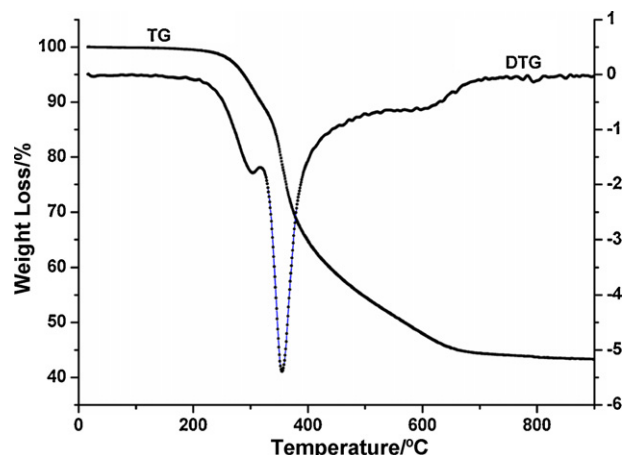


Fig. 4. TG-DTG curves of SiO₂-MPS-APTDCPP.

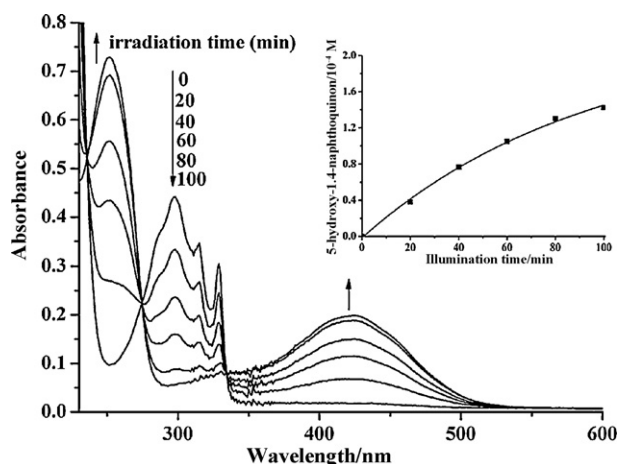


Fig. 5. UV-vis spectral changes of 1,5-dihydroxynaphthalene (1.0×10^{-4} M, pH = 4.5) during photooxidation catalyzed by SiO₂-MPS-APTDCPP (2.0 mg/ml). The insets show corresponding product.

in the presence of SiO₂-MPS-APTDCPP or irradiated with visible light without SiO₂-MPS-APTDCPP, were done and no obvious catalytic results were observed. It believes that both visible light and SiO₂-MPS-APTDCPP were indispensable to the photooxidation of 1,5-dihydroxynaphthalene. Moreover, no obvious catalytic result was observed in the controlled experiment irradiated with visible light in the presence of SiO₂-MPS.

3.2.2. Effect of initial concentration of 1,5-dihydroxynaphthalene

It is well known that the substrate concentration is an important parameter in photocatalytic processes. The effect of initial concentration of 1,5-dihydroxynaphthalene on the photooxidation percentage of 1,5-dihydroxynaphthalene was investigated in the cases that the initial concentrations of 1,5-dihydroxynaphthalene are 0.1–0.4 mM and the adding amount of photocatalyst is 2.0 mg/ml. Fig. 6a demonstrates the relationship between initial concentrations of 1,5-dihydroxynaphthalene and time.

It can be seen from Fig. 6a that the photooxidation percentage of 1,5-dihydroxynaphthalene decreased with the increasing initial concentration. 54% of 1,5-dihydroxynaphthalene remained in the solution even after 100 min irradiation for the initial concentration of 0.4 mM, which is lower than that for the initial concentration of 0.1 mM. Re-plotting Fig. 6a in the $\ln(C_0/C_t)$ - t coordinates (Fig. 6b), It is found that 1,5-dihydroxynaphthalene's photodegradation following the pseudo-first-order kinetic expression can be seen from Fig. 6b. Table 1 shows the pseudo-first-order rate constant k and half-life $t_{1/2}$ for photocatalytic degradation of 1,5-dihydroxynaphthalene at different initial concentrations. Many researchers have confirmed that the kinetic model for heterogeneous photocatalysis is in accordance with the Langmuir-Hinshelwood kinetic expression [38,39]

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$

Table 1
Pseudo-first-order kinetic parameters of 1,5-dihydroxynaphthalene photooxidation in three different concentration.

$C_{\text{int}} (\times 10^{-4} \text{ M})$	R^2	$k (\text{min}^{-1})$	$t_{1/2} (\text{min})$
1.0	0.9992	0.0164	42.2561
2.0	0.9972	0.0126	55.0000
4.0	0.9894	0.0052	133.2692

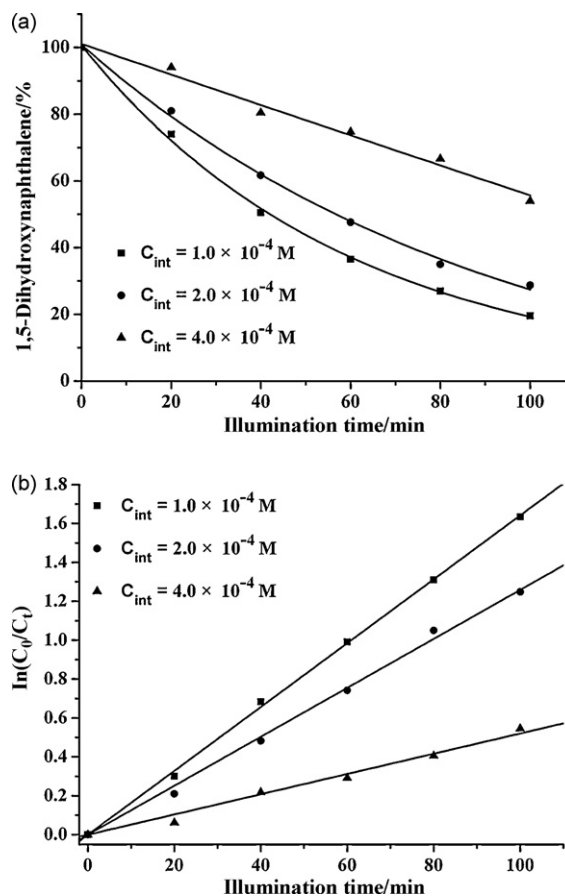


Fig. 6. (a) Photooxidation of 1,5-dihydroxynaphthalene with different initial concentrations (C_{int}) assisted by SiO₂-MPS-APTDCPP (2.0 mg/ml). (b) The plot of $\ln(C_0/C_t)$ versus t with different initial concentration of 1,5-dihydroxynaphthalene.

yielding half-life, $t_{1/2}$ (in min) is

$$t_{1/2} = \frac{0.693}{k}$$

where C_t/C_0 is the normalized 1,5-dihydroxynaphthalene concentration and k is the apparent reaction rate in term of min^{-1} .

Table 1 shows that the apparent reaction rate k decrease with the increasing initial concentration. It is obvious that the dependence of apparent reaction rate k on initial concentration of 1,5-dihydroxynaphthalene relate to the reactive species ($^1\text{O}_2$) formed at the surface of the catalyst. When the irradiation time and the amount of catalyst are constant, the reactive species ($^1\text{O}_2$) formed at the surface of the catalyst is also constant. So the apparent reaction rate k decreased with increase in the concentration of 1,5-dihydroxynaphthalene.

3.2.3. Effect of catalyst amount on the photocatalytic activity

In order to study the effect of the catalyst amount on the photooxidation of 1,5-dihydroxynaphthalene, a series of experiments were conducted employing different amount of SiO₂-MPS-APTDCPP microspheres varying from 0.5 to 4.0 mg/ml at fixed 1,5-dihydroxynaphthalene concentration (2.0×10^{-4} M). The results are shown in Fig. 7a. The reaction rate k was calculated from the data in Fig. 7a and summarized in Table 2. Fig. 7b shows that the photocatalytic oxidation follows the pseudo-first-order kinetic in the lower initial SiO₂-MPS-APTDCPP amount (0.5–2.0 mg/ml). However, when SiO₂-MPS-APTDCPP amount was greater than 2.0 mg/ml, the photocatalytic oxidation would deviate from the pseudo-first-order kinetic with respect to SiO₂-MPS-APTDCPP

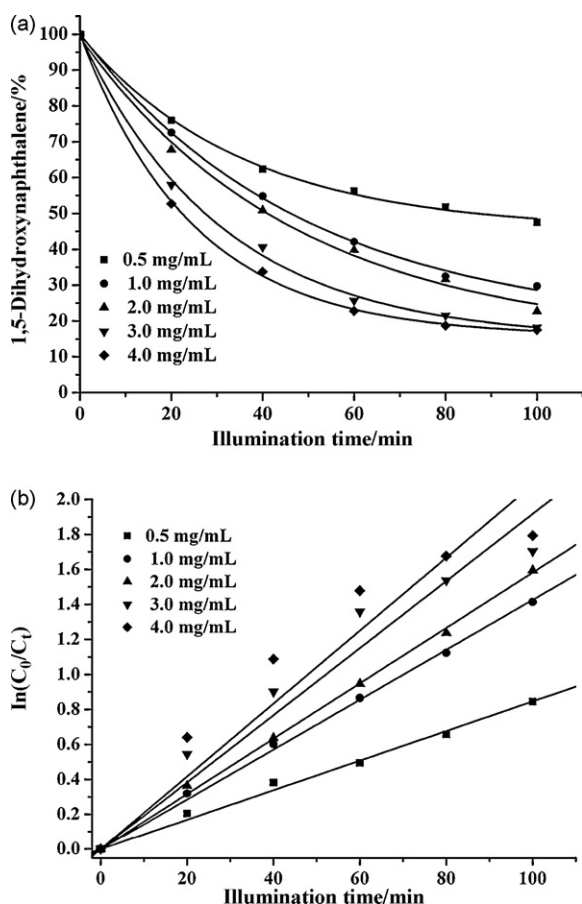


Fig. 7. (a) Effect of SiO_2 -MPS-APTDCPP amount on the photooxidation of 1,5-dihydroxynaphthalene (2.0×10^{-4} M, pH = 4.5) under visible light irradiation. (b) The plot of $\ln(C_0/C_t)$ versus t with different SiO_2 -MPS-APTDCPP amount.

amount. It seems that the deviation of the photocatalytic oxidation response to the pseudo-first-order kinetic in the case of higher SiO_2 -MPS-APTDCPP amount results from the refractive dispersion of the light irradiated by iodine tungsten lamp in the silica microspheres. The refractive dispersion of the light in the silica microspheres directly affect on the number of photons absorbed in catalytic system. When the amount of catalyst is in the range of 0.5–2.0 mg/ml, the number of photons absorbed in catalytic system can satisfy a requirement of photochemical reaction and the photocatalytic oxidation follows the pseudo-first-order kinetic. When the amount of catalyst is higher than 2.0 mg/ml, the number of photons absorbed in catalytic system does not satisfy a requirement of photochemical reaction and the photocatalytic oxidation deviate from the pseudo-first-order kinetic. In fact, only a little difference in photooxidation percentage of 1,5-dihydroxynaphthalene can be observed when the amount of catalyst is higher than 2.0 mg/ml. For example, the photooxidation percentage of 1,5-dihydroxynaphthalene is almost the same after 100 min irradiation when catalyst amount is 3.0 and 4.0 mg/ml. Usually, deviation of the photocatalytic oxidation

Table 2

Effect of catalyst amount on the pseudo-first-order parameters of 1,5-dihydroxynaphthalene photooxidation.

C_{cat} (mg/ml)	R^2	k (min^{-1})	$t_{1/2}$ (min)
0.5	0.9945	0.0085	81.5294
1.0	0.9987	0.0143	48.4615
2.0	0.9985	0.0158	43.8608
3.0	0.9587	0.0192	36.0938
4.0	0.9339	0.0208	33.3173

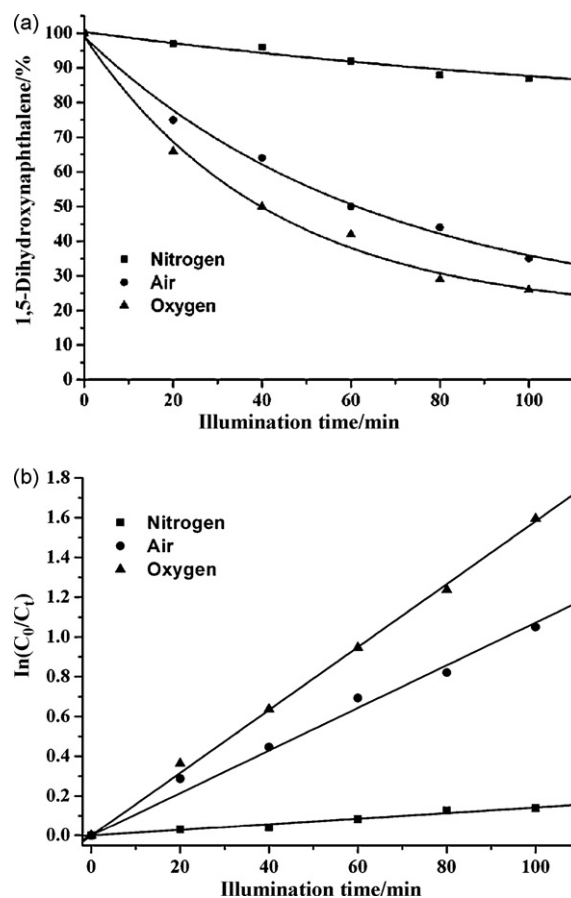


Fig. 8. (a) Effect of oxygen concentration on the photooxidation of 1,5-dihydroxynaphthalene (2.0×10^{-4} M, pH = 4.5) under visible light irradiation in the presence of SiO_2 -MPS-APTDCPP (2.0 mg/ml). (b) The plot of $\ln(C_0/C_t)$ versus t with different concentration of oxygen.

response to the pseudo-first-order kinetic can be observed in some heterogeneous catalytic systems [40,41].

3.2.4. Effect of oxygen concentration

Oxygen plays an important role in photocatalytic processes employing several types of photocatalysts [42]. In order to examine the effect of oxygen concentration on photooxidation of 1,5-dihydroxynaphthalene in our system, nitrogen, air and pure oxygen, which have different oxygen concentrations, are used in the photocatalytic processes. Fig. 8 clearly shows that oxygen concentration-dependent for the photooxidation of 1,5-dihydroxynaphthalene exists in our system. The photooxidation percentage of 1,5-dihydroxynaphthalene in the case bubbling of pure oxygen into the reaction mixture is higher than that bubbling of air into the reaction mixture. Only 12% 1,5-dihydroxynaphthalene has been oxidized under nitrogen condition, which is more likely due to some residual oxygen left in the solution. Fig. 8b indicates that the reactions of photocatalytic oxidation of 1,5-dihydroxynaphthalene in the case of blowing air or pure oxygen at the same rate accord with the first-order kinetics. The rate constant in the case of pure oxygen (0.0254 min^{-1}) is higher than that in the case of air (0.0107 min^{-1}).

3.2.5. Effect of sodium azide

Pereira and co-workers [18] have reported that the reactive species responsible for the photooxidation of 1,5-dihydroxynaphthalene in acetonitrile-dichloromethane (50%, v/v) solutions by oxygen using visible light activation of porphyrin

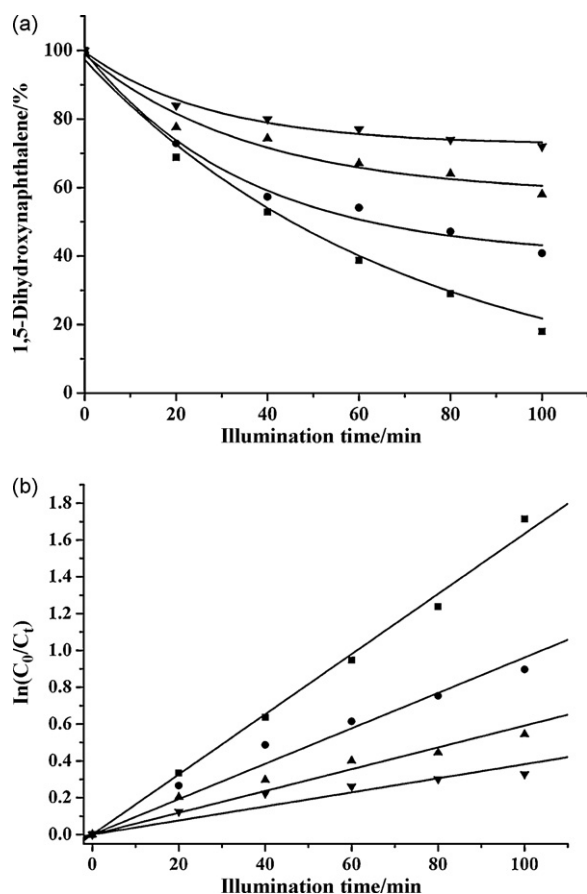


Fig. 9. (a) Effect of NaN₃ on the photooxidation of 1,5-dihydroxynaphthalene (2.0×10^{-4} M, pH=4.5) under visible light irradiation in the presence of SiO₂-MPS-APTDCPP (2.0 mg/ml). (b) The plot of $\ln(C_0/C_t)$ versus t with different concentration of NaN₃. [NaN₃]: 0 (■); 6.0×10^{-3} M (●); 1.2×10^{-2} M (▲); 1.8×10^{-2} M (▼).

involve singlet oxygen (¹O₂) generated. We also reported that the mechanism for the photodegradation of 1,5-dihydroxynaphthalene by meso-tetra(4-sulfonatophenyl)porphyrin under visible light irradiation in aerated aqueous solution is thought to involve singlet oxygen processes [18]. In order to identify whether ¹O₂ is involved in the photooxidation of 1,5-dihydroxynaphthalene in our heterogeneous catalytic system, NaN₃, a physical quencher of ¹O₂, has been used and its influence of on the photooxidation of 1,5-dihydroxynaphthalene are shown in Fig. 9 and Table 3. The results indicate that the kinetic of the photocatalytic oxidation depends on the concentration of NaN₃ and the photocatalytic oxidation also follows the pseudo-first-order kinetic in the addition of NaN₃. Table 3 shows that the rate of photooxidation decreases with the increase of NaN₃. It is obvious that the decrease of the photooxidation percentage of 1,5-dihydroxynaphthalene results from the quenching of singlet oxygen ¹O₂ by NaN₃. We believe that the photooxidation of 1,5-dihydroxynaphthalene photocatalyzed by SiO₂-MPS-APTDCPP in aerated aqueous solution also involve singlet oxygen processes.

Table 3
Effect of NaN₃ on the pseudo-first-order parameters of 1,5-dihydroxynaphthalene photooxidation.

C _{NaN₃} ($\times 10^{-3}$ M)	R ²	k (min ⁻¹)	t _{1/2} (min)
0	0.9975	0.0134	51.7164
6.0	0.9950	0.0076	91.1842
12.0	0.9911	0.0044	157.5000
18.0	0.9734	0.0028	247.5000

3.2.6. Stability and reusability of the catalysts

Immobilization of porphyrins on solid supports can offer several advantages over traditional solution-phase chemistry. For example, the solid supported porphyrins have higher stability, and can be recovered from reaction mixtures and reused. The stability of SiO₂-MPS-APTDCPP in photooxidation process of 1,5-dihydroxynaphthalene has also been investigated by repeated experiments. When a photooxidation experiments of 1,5-dihydroxynaphthalene was finished, the suspension containing 1,5-dihydroxynaphthalene, reaction product and SiO₂-MPS-APTDCPP was centrifuged and the residues (SiO₂-MPS-APTDCPP) were collected, washed with ethanol and dried carefully. No APTDCPP was found in the filtrate by UV-vis spectra, which indicated that no APTDCPP lost from the silica. Meanwhile, the UV-vis and IR spectra of the recovered SiO₂-MPS-APTDCPP did not show any substantial change comparing with those of the fresh ones. Using the recovered SiO₂-MPS-APTDCPP as catalyst to catalyze 1,5-dihydroxynaphthalene photooxidation in the same conditions, they retain their high catalytic activity after being recycled five times. For example, the photooxidation percentage of 1,5-dihydroxynaphthalene for five consecutive experiments are as follows: 81, 79, 75, 76 and 71% in the same conditions (2 mg/ml SiO₂-MPS-APTDCPP, 2.0×10^{-4} M 1,5-dihydroxynaphthalene, 100 min). These results indicate that SiO₂-MPS-APTDCPP has high chemical stability and is recoverable and reusable. We propose that these silica microspheres functionalized with porphyrin are excellent potential candidates for recoverable and reusable catalysts to catalyze photooxidation of 1,5-dihydroxynaphthalene.

4. Conclusion

We have successfully constructed silica microspheres functionalized with APTDCPP (SiO₂-MPS-APTDCPP) through a modified Stöber technique and thiol-ene polymerization. The studies on their photocatalysis activity to oxidize 1,5-dihydroxynaphthalene under visible light irradiation in aerated aqueous solution show that the functionalized silica microspheres are reusable and highly efficient photosensitizers for the photooxidation of 1,5-dihydroxynaphthalene. The photooxidation of 1,5-dihydroxynaphthalene involves singlet oxygen processes.

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