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Mesopolymer modified with palladium phthalocyaninesulfonate as a versatile photocatalyst for phenol and bisphenol A degradation under visible light irradiation

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Abstract

A novel versatile photocatalyst, FDU-PdPcS, was prepared by immobilizing palladium phthalocyaninesulfonate (PdPcS) onto the FDU-15 mesopolymer via multi-step chemical modification processes involving chloromethylation of the FDU-15 mesopolymer first with chloromethyl methyl ether, a subsequent amination reaction with ethylenediamine, and finally modification with palladium phthalocyaninesulfonate via ionic interaction. The obtained FDU-PdPcS photocatalyst was characterized by the X-ray diffraction (XRD), UV-Vis spectrosopy and inductively coupled plasma (ICP) techniques. This photocatalyst not only affords a high dispersion of monomeric PdPcS molecules, which may further be stabilized by the π-electron of benzene rings of FDU-15, but also provides a number of diamino groups inside the mesopores, which could be advantageous for the photodegradation of phenolic pollutants. In photodegradation studies of phenolic pollutants, the FDU-PdPcS catalyst exhibited excellent visible light photocatalytic activity and reusability. The photodegradation products of phenol and bisphenol A were investigated by the gas chromatoghraphy-mass spectrometry (GC-MS) technique. The results showed that the photodegradation products were composed of carboxylic acids and CO_2. Isopropanol, sodium azide and benzoquinone were used as hydroxyl radical (OH•), singlet oxygen ($^1O_2$) and superoxide radical ($O_2^{\bullet-}$) scavengers, respectively. The results suggested that $^1O_2$ and $O_2^{\bullet-}$ were the prominent active species during the photodegradation process. A possible mechanism for the photodegradation of phenol was also discussed.

Key words: mesopolymer; phthalocyanine; photocatalysis; visible light; phenolic pollutants

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Introduction

Phenol and its derivatives are typical organic pollutants in the environment generated from pesticides, herbicides, paints, leathers, and the textile and paper manufacturing industries (Ahmaruzzaman, 2008; Ahmed et al., 2010). Most of those pollutants can remain in the environment for long periods and cause serious environmental problems since they have high toxicity and poor biodegradability. Thus, the efficient removal of phenol and its derivatives from wastewater has attracted extensive attention. The methods for the removal of phenolic pollutants from wastewater include chemical oxidation (Hamoudi et al., 1998; Inchaurrondo et al., 2012; Muhammad et al., 2012; Zeng et al., 2012), photocatalytic degradation (Bazaga-Garcia et al., 2012; Chowdhury et al., 2012; Luenloi et al., 2011) and physical adsorption (He et al., 2009; Huang et al., 2012; Zeng et al., 2010; Zhao et al., 2010), etc. Photocatalysis, an energy-saving and environmentally friendly process, is a promising technique for pollutant removal, especially using visible light as an energy source, which constitutes 45% of solar energy. Metallophthalocyanines (MPcs) are some of the most efficient and promising photosensitizers or/and photocatalysts due to their ability to absorb visible light and produce highly active singlet oxygen species (Ishii, 2012; Meunier and Sorokin, 1997; Rawling and McDonagh, 2007). The use of metallophthalocyanines as photocatalysts in the degradation of organic pollutants has been extensively investigated because of their unique photophysical properties and photochemical stability. However, water-insoluble metallophthalocyanines generally exhibit a low efficiency for the photodegradation

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of organic pollutants in aqueous media, while water-soluble metallophthalocyanines suffer from difficulty in separation from reaction mixtures and also tend to aggregate in aqueous media, which leads to self-quenching of the excited species and brings about deactivation of the photocatalysts. To overcome these drawbacks, a variety of suitable supports for MPcs such as carbon materials (Lu et al., 2009; Xu et al., 2011), TiO_2 (Guo et al., 2012; Mekprasart et al., 2012), clays (Xiong et al., 2005), resins (Wu et al., 2007), zeolites (Mohamed and Mohamed, 2008; Yahiro et al., 2005) and mesoporous silicas (Shen et al., 2011; Silva et al., 2012) have been developed. Among these mentioned supports, mesoporous materials with extremely high surface area and well-ordered mesopores are particularly suitable for supporting the MPc molecules, which can be well dispersed into confined mesopores.

In comparison with silica-based mesoporous materials, the FDU-type mesopolymer materials not only possess high physicochemical stability in acidic or alkaline aqueous medium but also can efficiently adsorb phenolic pollutants from wastewater through π–π interactions and hydrogen bonding between the phenolic pollutants (e.g. phenol, nitrophenol, bisphenol A, etc.) and the aromatic species in the framework walls. For this reason, the FDU-type mesopolymer materials were considered to serve as ideal supports for anchoring the MPc molecules via multi-step chemical modification processes. In the present study, we prepared a novel photocatalyst of palladium(II) phthalocyaninesulfonate (PdPcS) supported and stabilized with a mesopolymer. The water-soluble PdPcS has proved to be an excellent photocatalyst, but in aqueous media it tends to aggregate with consequent self-quenching of the excited species (Xiong and Xu, 2007). Earlier we have reported that FDU-type mesopolymers were converted readily into diamine-functionalized mesopolymers (FDU-ED) through chloromethylation and amination procedures, respectively (Xing et al., 2008, 2009). Possessing the textural porosities of mesopolymer materials and the advantage of diamino groups, the FDU-ED material can be used as an ideal scaffold for the dispersion and stabilization of monomeric PdPcS molecules confined within the mesopore channels. The PdPcS molecules can be further stabilized by the π-electron of the benzene ring moieties in the mesopolymer material, which can prevent the PdPcS molecules from agglomerating and also increase the quantum yield of singlet oxygen. In addition, FDU-ED shows a good wettability in water and provides a number of diamino groups inside the mesopores, which could be advantageous for the photodegradation of phenolic pollutants in aqueous solution. The obtained novel mesopolymer-supported PdPcS photocatalyst exhibited high photoactivity in the degradation of phenol and bisphenol A in the presence of H_2O_2 under visible light irradiation. This method may provide a versatile way for the design and fabrication of novel mesopolymer-supported MPc photosensitizers that are useful for the rapid degradation of organic pollutants using solar light as an energy source, as well as other applications.

1 Materials and methods

1.1 materials

The FDU-15 mesopolymer and diamine-functionalized FDU-15 (FDU-ED) were synthesized as our group previously reported (Xing et al., 2008, 2009). PdPcS was synthesized according to a published method (Spiller et al., 1998). Phenol and bisphenol A were purchased from Shanghai Chemicals Inc, and were used as received.

1.2 Preparation of PdPcS-functionalized FDU-15

FDU-ED containing a number of diamino groups can form a homogeneous suspension in water. Therefore FDU-ED (1.0 g) was stirred directly into 100 mL of PdPcS dilute solution (corresponding to 0.1 wt% loading) at room temperature for 6 hr. The solution turned from blue to colorless after the modification reaction. The solid product was collected by filtration and washed with distilled water until the filtrate turned colorless. It was finally dried at 60°C for 12 hr, leading to mesopolymer-supported PdPcS, which is denoted as FDU-PdPcS.

1.3 Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu-$K\alpha$ radiation (λ = 1.5418 Å) at 35 kV and 25 mA (Rigaku, Japan). UV-Visible spectra of the FDU-15 and FDU-PdPcS were recorded on a PerkinElmer Lambda 35 UV/Vis spectrometer with in diffusion reflectance mode using polytetrafluoroethene as a reference (PerkinElmer, USA), and UV-Visible spectra of the PdPcS aqueous solution were recorded on a SPECORD-S600 (Jena, Germany), equipped with 1.0 cm quartz cells. The amount of Pd in the photocatalyst was quantified by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer (Thermo Scientific, USA).

1.4 Photocatalytic test

The photocatalytic reaction was performed in a glass reactor using a Halogen lamp (500 W, Yamin Shanghai, China) through a glass filter ($\lambda \geqslant 450$ nm) as irradiation source. In a typical experiment, 100 mL of a phenolic compound solution and 0.02 g of catalyst were stirred in an air-saturated aqueous solution at room temperature under darkness overnight until reaching adsorption equilibrium. An appropriate amount of H_2O_2 was then added into the reactor and the suspension was irradiated to start the photoreaction. During the irradiated photoreaction, a proportion of the reaction mixture (ca. 2 mL) was

sampled. After removing the solid catalyst by filtration through a membrane (0.45 μm), the amount of phenolic compound remaining in the solution was analyzed by high performance liquid chromatography (Waters 2695-2489 HPLC, C18 reverse column, 5 μm, 250 mm × 4.6 mm) using CH_3OH-H_2O (60% : 40%, pH 5 by acetic acid) as eluent. The photodegradation intermediates were identified by GC-MS on an Agilent Technologies 7890A instrument equipped with a DB-624 capillary column (60 m × 0.25 mm × 1.4 μm). The reaction filtrate was acidified to pH 1–2 and then the volume of filtrate was reduced to about 5 mL via rotary evaporation. Then 5 mL of CH_3OH and 0.5 mL of concentrated sulfuric acid were added to the residue. After the resulting mixture was refluxed for 3–4 hr, it was saturated with NaCl and further extracted with dichloromethane. The organic liquor was dried over anhydrous $MgSO_4$ and then evaporated to about 2 mL under reduced pressure before GC-MS analysis. Carbon dioxide was detected by the $Ba(OH)_2$ method. Isopropanol, sodium azide and benzoquinone were used as OH·, $^1O_2$ and $O_2^{\bullet-}$ scavengers, respectively, in the photodegradation reactions. The used catalyst was washed with hot distilled water, and dried at 80°C. The FDU-PdPcS recycling experiments were carried out under the above mentioned conditions.

2 Results and discussion

Figure 1 shows the strategy for preparing the novel photocatalyst of FDU-15 mesopolymer modified with palladium phthalocyaninesulfonate (FDU-PdPcS). First, the modification processes to create the diamine-functionalized mesopolymer were carried out as in our previous studies (Xing et al., 2008, 2009), where the FDU-15 (hexagonal P6mm) mesopolymer was modified with diamino groups (FDU-ED) through successive chloromethylation and amination reactions. Second, the obtained FDU-ED was added into the PdPcS aqueous solution. The hydrophilic diamino groups enabled FDU-ED to form a homogeneous suspension in the blue PdPcS aqueous solution. Then, the PdPcS ions were captured rapidly by the diamino groups through protonation and ionic interaction to lead to a colorless filtrate, giving rise to the mesopolymer-supported PdPcS, FDU-PdPcS.

2.1 Characterization of FDU-PdPcS

The samples were characterized by UV-Vis spectroscopy to track the chemical modification. **Figure 2a** presents the

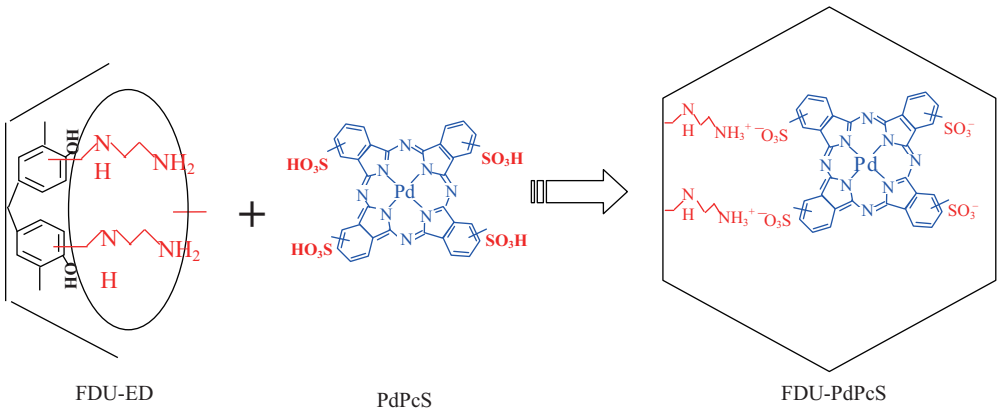

Fig. 1 Schematic illustration of the synthesis of FDU-PdPcS photocatalyst.

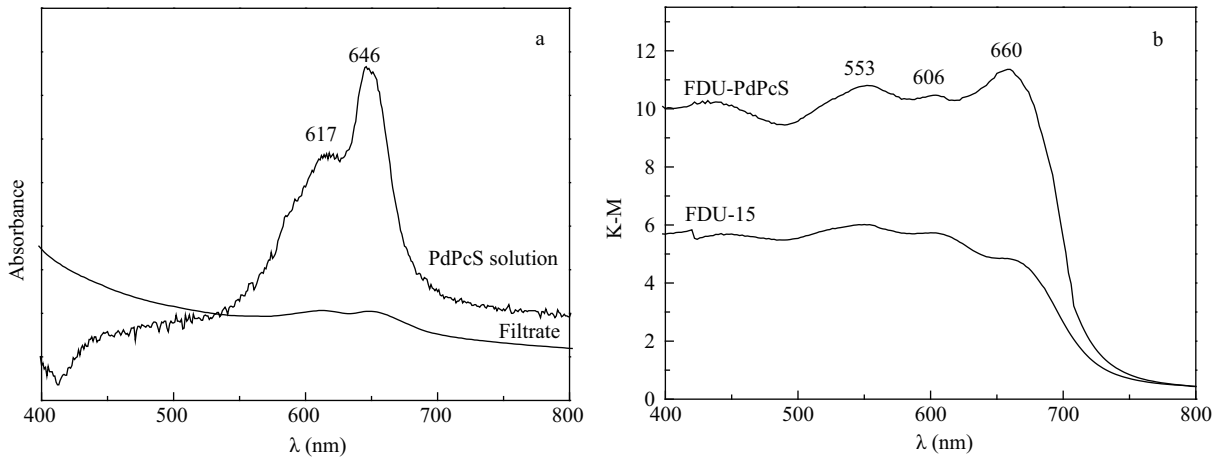

Fig. 2 UV-Vis spectra of PdPcS solution and the filtrate (a), an FDU-15 and FDU-PdPcS (b).

diffuse reflectance UV-Vis spectra of the PdPcS aqueous solution before and after the modification reaction. The distinct feature of the parent PdPcS solution was the presence of two absorption bands at 646 and 617 nm attributed to the monomer and aggregated form, respectively. After the modification reaction, these two adsorption bands disappeared notably, indicating that PdPcS ions had been completely incorporated into the mesopolymer through protonation and ionic interaction. **Figure 2b** shows the UV-Vis spectra of the FDU-15 before and after grafting. For the bare FDU-15, no obvious absorption band was found. After the modification reaction, the FDU-PdPcS developed three distinctly new absorption bands. The band at 660 nm corresponding to the PdPcS monomer was red-shifted due to the π–π interaction between PdPcS and the mesopolymer, which is in good agreement with the literature (Xiong and Xu, 2007), while the shoulder peaks at 606 and 553 nm were assigned to the aggregate forms of PdPcS. The above results suggested that most of the monomeric PdPcS molecules were successfully introduced inside the mesopores of FDU-15, and a small portion of the larger aggregate forms may be located on the outer surface of FDU-15. The loading level of PdPcS was ca. 1 mg/g, which was determined by inductively coupled plasma (ICP) analysis.

The low-angle powder XRD patterns of the parent FDU-15 and FDU-PdPcS are shown in **Fig. 3**. Both the samples exhibit three diffraction peaks, which can be ascribed to the characteristic peaks of the [10], [11] and [20] planes, based on a well-ordered 2D hexagonal structure with a P6mm space group. The results suggested that the mesostructure of the FDU-PdPcS was not destroyed after multi-step chemical modification. All the diffraction peaks for the FDU-PdPcS shifted slightly to lower angles since the unit cell increased from 88.1 to 92.5 Å after the chemical modification. This result further indicated that PdPcS molecules with bulky dimensions were successfully attached on the FDU-15 mesopolymer walls.

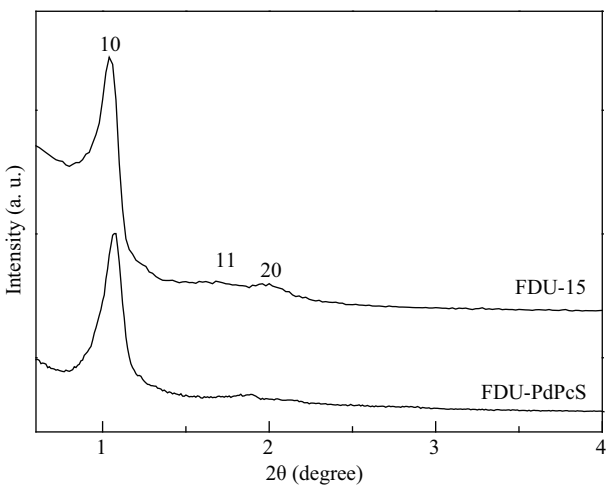

Fig. 3 XRD patterns of FDU-15, FDU-PdPcS.

2.2 Photocatalytic decomposition of phenol

It is well known that pH value plays an important role during the photooxidation reaction and greatly influences the dominant species of phenol (Gerdes et al., 1997; Xiong et al., 2005) in aqueous solution. Therefore, we first investigated the effect of the pH on the photocatalytic degradation of phenol. **Figure 4** shows the photodegradation of phenol under different pH conditions using FDU-PdPcS as photocatalyst. The degradation rates of phenol (60 mg/L) aqueous solution were about 61% and 69% after 7 hr at pH 5 and neutral aqueous solution, respectively, while almost 98% of phenol was degraded after 6 hr in an alkaline solution. The degradation rate of phenol increased with increasing pH value of the reaction mixture. Accordingly, phenolic pollutants in alkaline solution are more easily degraded than in neutral or acidic solution because the alkaline media enhances the deprotonation of phenol to form phenolate, and thus it is more oxidizable by singlet oxygen (Gerdes et al., 1997; Xiong et al., 2005). The subsequent degradation reactions were carried out at the optimum pH value (pH 11).

Figure 5 shows the concentration changes of phenol with time under various reaction conditions. In control experiments with H_2O_2 in the dark or under visible light irradiation without photocatalyst, the degradation of phenol hardly occurred, indicating that direct photolysis of H_2O_2 is impossible under visible light irradiation. The result showed that H_2O_2 could not oxidize phenol alone in the dark or under visible light irradiation. In the experiments without visible light irradiation, FDU-PdPcS also failed to catalyze the degradation of phenol in the presence of H_2O_2, and only adsorbed about 7% of phenol from the solution (**Fig. 5 line c**). However, FDU-PdPcS exhibited a high photocatalytic activity for the degradation of phenol under visible light irradiation. In the presence and absence of H_2O_2, phenol was degraded 98% and 56% after irradiation for 6 hr using FDU-PdPcS as photocatalyst, respectively

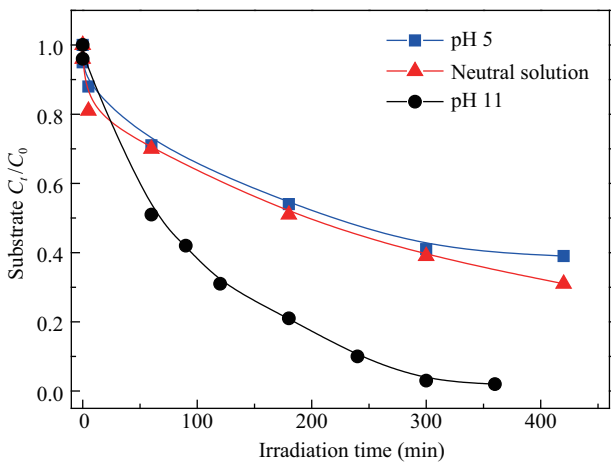

Fig. 4 Effect of pH value on the photodegradation rate of phenol. Reaction conditions: 0.02 g FDU-PdPcS, 100 mL phenol (60 mg/L), H_2O_2 (0.25 mmol/L).

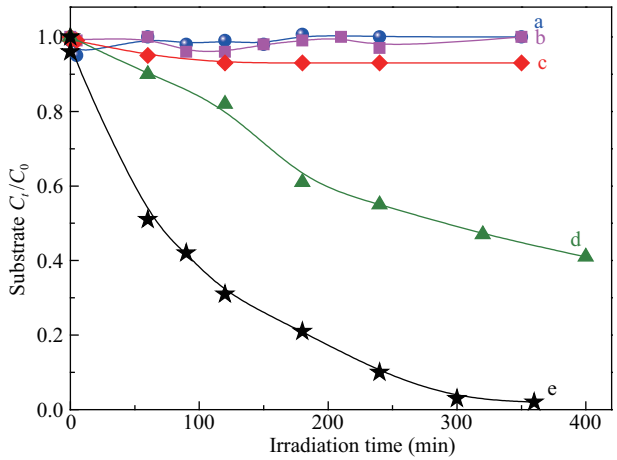

Fig. 5 Changes of phenol concentration with reaction time under various conditions. line a: H_2O_2 in dark; line b: H_2O_2 in Vis-light; line c: FDU-PdPcS + H_2O_2 in dark; line d: FDU-PdPcS in Vis-light; line e: FDU-PdPcS + H_2O_2 in Vis-light. Reaction conditions: 0.02 g FDU-PdPcS, 100 mL phenol (60 mg/L), H_2O_2 (0.25 mmol/L), pH 11.

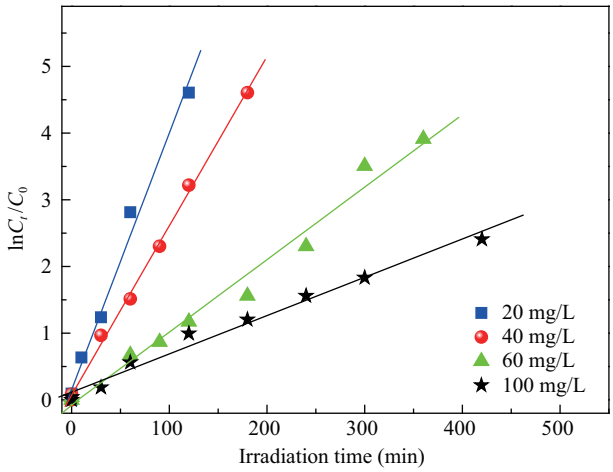

Fig. 6 Effect of initial concentration on the photodegradation of phenol.

Table 1 Rate constant (k_{obs}), half-life ($t_{1/2}$) at various concentrations of phenol

Concentration (mg/L)	R^2	k_{obs} (min^{-1})	$t_{1/2}$ (min)
20	0.9883	0.0385	18.00
40	0.9974	0.0254	27.26
60	0.9814	0.0109	63.59
100	0.9832	0.0057	121.60

(**Fig. 5 lines d** and **e**). The control experiment with FDU-PdPcS in the presence or absence of H_2O_2 demonstrated that H_2O_2 can accelerate the reaction rate under visible light irradiation and eliminate the colored intermediates during the photodegradation reactions, which was in good agreement with the reported literature (Hu et al., 2004). The above results suggested that the FDU-PdPcS photocatalyst and visible light were essential for the degradation of phenol. It is noteworthy that the FDU-PdPcS catalyst showed high photoactivity in the photodegradation of the phenol at low molar ratio of PdPcS/phenol. This can be explained by the fact that the FDU-PdPcS catalyst not only afforded a high dispersion of monomeric PdPcS molecules, which would be further stabilized by the π-electrons of the FDU-15 mesopolymer, but also provided a number of diamino groups inside the mesopores, which could be advantageous for the photodegradation of phenol.

The photocatalytic degradation of phenol can be assumed to follow first-order kinetics, which can be represented by the equation:

$$\ln(C_0/C_t) = k_{obs}t$$

where, C_0 is initial concentration and C_t is the concentration at reaction time (t), k_{obs} is the apparent rate constant, obtained from the slopes in **Fig. 6** for different concentrations of phenol. **Table 1** lists the rate constant (k_{obs}) and half-lives at initial phenol concentrations ranging from 20 to 100 mg/L. The values of k_{obs} decreased from 0.0385 to 0.0057 min^{-1} with increasing initial concentration from 20 to 100 mg/L. The results clearly showed that the photodegradation of phenol was faster in more dilute phenol solution. This was attributed to the adsorption and/or diffusion limitation of molecular oxygen in the mesopores at higher concentrations during the photodegradation reaction process (Hu et al., 2004). The variation of k_{obs} indicated that the photodegradation of phenol mainly occurred on the surface of PdPcS owing to its ability to absorb the visible light and generate the active species in situ nearby, which then oxidized the phenol.

In order to detect photodegradation intermediates of phenol, gas chromatography-mass spectrometry (GC-MS) analysis was employed. According to the previous reports, the intermediates in the degradation of phenolic pollutants consisted mainly of carboxylic acids (Kluson et al., 2007; Tai et al., 2005; Wu et al., 2007). Therefore the intermediates needed to be esterified with methanol using concentrated sulfuric acid as the catalyst, and then the obtained products were analyzed by GC-MS (**Fig. 7**). A mixture of dimethyl oxalate, dimethyl malonate, dimethyl D-malate and dimethyl maleate was identified as the methyl ester derivatives of the intermediates, suggesting that the photodegradation intermediates were composed of oxalic acid, malonic acid, malic acid and maleic acid. Besides those organic acids, carbon dioxide was also observed using the $Ba(OH)_2$ method as final products of the mineralization of phenol (Gerdes et al., 1997; Iliev et al., 2002).

To investigate the mechanism for the photodegradation processes, isopropanol, sodium azide and benzoquinone were used as hydroxyl radical (OH·), singlet oxygen ($^1O_2$) and superoxide radical ($O_2^{\bullet-}$), scavengers, respectively. This would give information concerning the reactive species during the photodegradation process. In comparison with a typical photocatalysis (**Fig. 8 line d**), the addition of benzoquinone or sodium azide distinctly retarded the degradation rate (**Fig. 8 lines a** and **b**), while the addition of isopropanol showed little influence on the

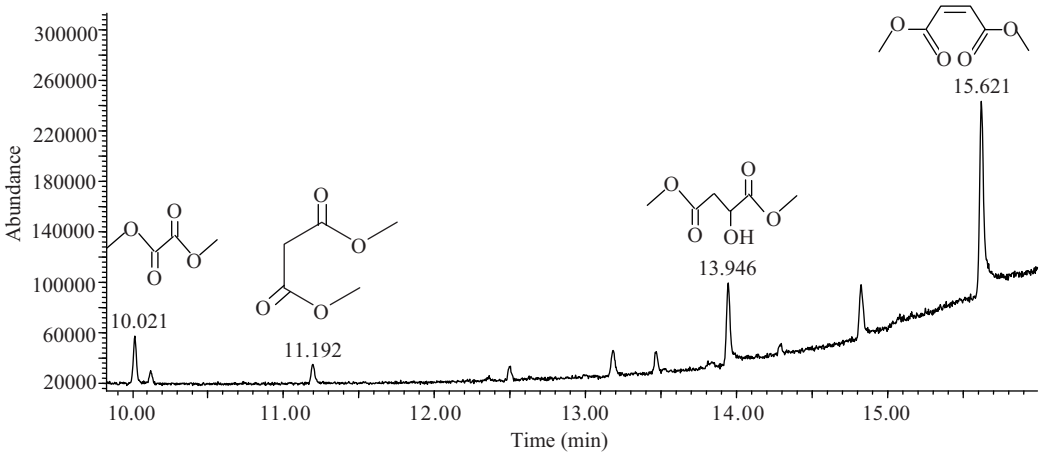

Fig. 7 GC-MS chromatogram of photodegradation of phenol. Reaction conditions: 0.02 g FDU-PdPcS, 100 mL phenol (60 mg/L), H_2O_2 (0.25 mmol/L), pH = 11, irradiation 5 hr.

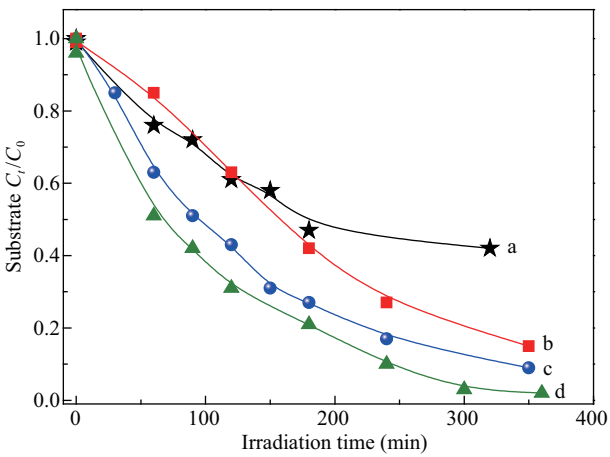

Fig. 8 Effect of scavengers on the photodegradation of phenol. (line a) benzoquinone, (line b) NaN_3, (line c) isopropanol and (line d) no scavenger.

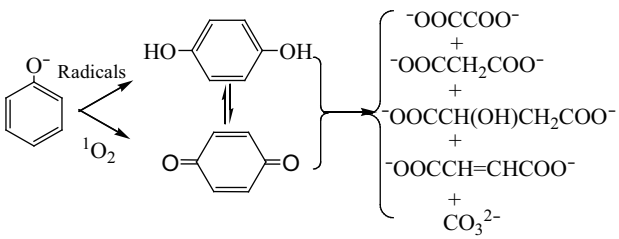

Fig. 9 Possible mechanism for the photodegradation of phenol under visible light.

degradation rate (**Fig. 8 line c**). The above experiments indicated that both $^1O_2$ and $O_2^{\bullet-}$ are probably the prominent active species during the photodegradation process under visible light irradiation, and a small amount of OH· possibly participated in the photodegradation of phenol. It has been reported that the photodegradation of phenolic pollutants may proceed through Type I and/or Type II mechanisms (Zanjanchi et al., 2010; Zugle et al., 2012). The Type I mechanism involves radicals during the photodegradation process, while the Type II mechanism starts with $^1O_2$ under visible light irradiation. Based on the above results, the photodegradation of phenol took place through both Type I and II mechanisms. The possible reaction mechanism for the photocatalytic degradation of phenol is shown in **Fig. 9**. Radicals ($O_2^{\bullet-}$, OH·) interacted with phenolate to form the hydroquinone intermediate, while $^1O_2$ reacted with phenolate to produce the benzoquinone intermediate (Ogunbayo et al., 2011). Subsequently, these intermediates generated were finally oxidized to CO_2, H_2O and various carboxylic acids.

The stability and recyclability of a heterogeneous catalyst is very important for its practical application. As shown in **Fig. 10**, after four cycles for photodegradation of phenol under the same experimental conditions, the photocatalyst exhibited similar photocatalytic activity. The high reusability of the FDU-PdPcS photocatalyat can be attributed to the high stability of FDU-15 in alkaline aqueous solution and tight attachment of PdPcS molecules inside the confined mesopores, which be further stabilized by the π-electrons of the FDU-15 mesopolymer.

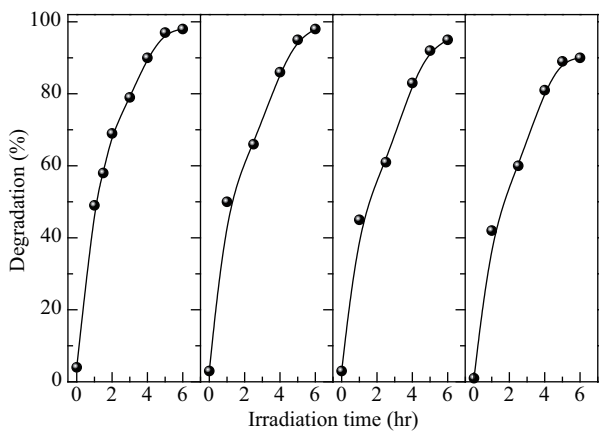

Fig. 10 Cyclic use of FDU-PdPcS for the photodegradation of phenol.

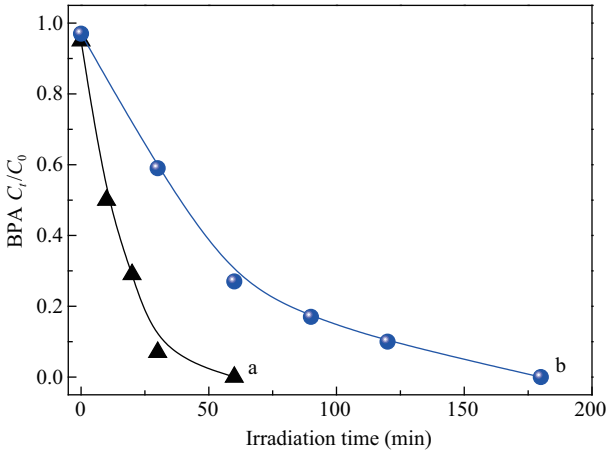

Fig. 11 Changes of BPA concentration with reaction time. The initial concentration of BPA was 0.04 mmol/L (line a) and 1.0 mmol/L (line b). Reaction conditions: 0.02 g FDU-PdPcS, 100 mL BPA, H_2O_2 (20 mmol/L), pH 11.

2.3 Photodegradation of bisphenol A

Bisphenol A (BPA) has been frequently used as a raw material in the manufacture of epoxy resins, polycarbonate resins, pesticides, etc. However, BPA is an endocrine disrupter if it is released into the environment, and can cause various diseases (Staples et al., 1998). The FDU-PdPcS catalyst was further applied to the degradation of BPA. As shown in **Fig. 11**, BPA with an initial concentration 0.04 and 1.0 mmol/L was degraded completely in the presence of H_2O_2 after irradiation for 1 and 3 hr, respectively. The organic intermediates of BPA after esterification reaction with methanol were identified by GC-MS (**Fig. 12**). A mixture of dimethyl malonate, dimethyl D-malate and dimethyl oxalate was identified as the methyl ester derivatives of intermediates. CO_2 was also observed among the final products of degradation of BPA. The above results showed that the photodegradation products of BPA, composed of carboxylic acids and CO_2, are similar to those of phenol. All the above experiments on the photodegradation of both phenol and BPA suggest that the FDU-PdPcS catalyst is an efficient heterogeneous photocatalyst and could be further applied to the photodegradation of most common organic pollutants.

3 Conclusions

A novel efficient photocatalyst, FDU-PdPcS, was prepared by efficient electrostatic interactions. The FDU-PdPcS exhibited excellent visible light photocatalytic activity and reusability in the degradation reactions of both phenol and BPA owing to the advantages of a high dispersion of monomeric PdPcS molecules in a well-ordered mesoporous, pure organic framework containing a number of diamino groups. Control experiments using isopropanol, sodium azide and benzoquinone gave evidence that $^1O_2$ and $O_2^{\bullet-}$ were probably the main active species during the photodegradation processes. FDU-PdPcS is able to act as an eco-friendly photocatalyst, and has the potential to be used for efficient removal of organic pollutants using sunlight as the energy source.

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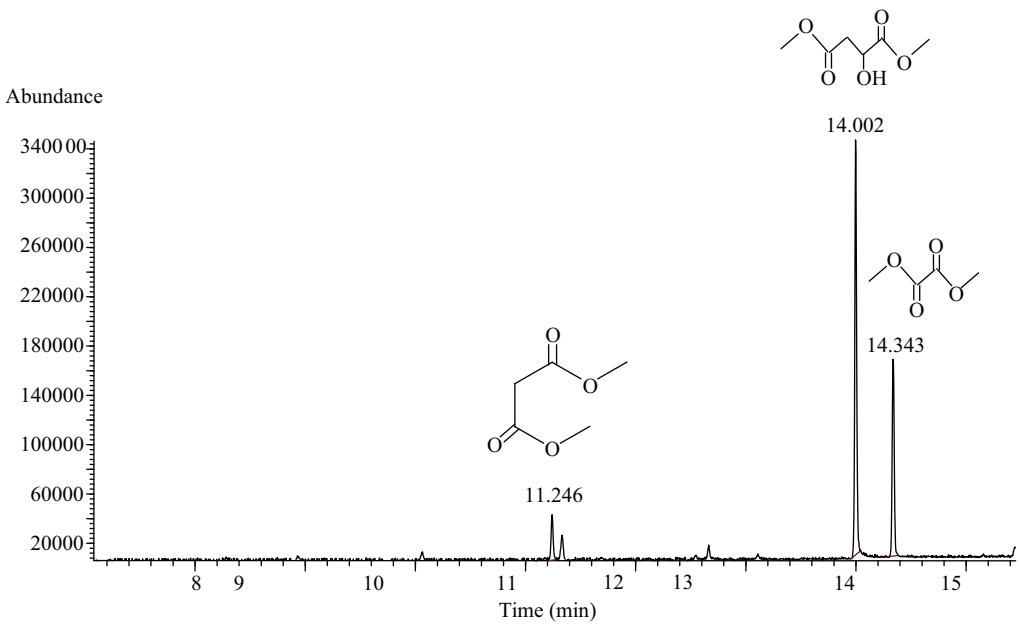

Fig. 12 GC-MS chromatogram of photodegradation of BPA. Reaction conditions: 0.02 g FDU-PdPcS, 100 mL BPA (1.0 mmol/L), H_2O_2 (20 mmol/L), pH 11, 2 hr irradiation.

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References

Ahmaruzzaman M, 2008. Adsorption of phenolic compounds on low-cost adsorbents: A review. *Advances in Colloid and Interface Science*, 143(1-2): 48–67.

Ahmed S, Rasul M G, Martens W N, Brown R, Hashib M A, 2010. Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments. *Desalination*, 261(1-2): 3–18.

Bazaga-Garcia M, Cabeza A, Olivera-Pastor P, Santacruz I, Colodrero R M P, Aranda M A G, 2012. Photodegradation of phenol over a hybrid organo-inorganic material: iron(II) hydroxyphosphonoacetate. *The Journal of Physical Chemistry C*, 116(27): 14526–14533.

Chowdhury P, Moreira J S, Gomaa H, Ray A K, 2012. Visible-Solar-Light-Driven photocatalytic degradation of phenol with dye-sensitized TiO_2: parametric and kinetic study. *Industrial & Engineering Chemistry Research*, 51(12): 4523–4532.

Gerdes R, Wohrle D, Spiller W, Schneider G, Schnurpfeil G, Schulz-Ekloff G, 1997. Photo-oxidation of phenol and monochlorophenols in oxygen-saturated aqueous solutions by different photosensitizers. *Journal of Photochemistry and Photobiology A: Chemistry*, 111(1-3): 65–74.

Guo Z C, Chen B, Mu J B, Zhang M Y, Zhang P, Zhang Z Y et al., 2012. Iron phthalocyanine/TiO_2 nanofiber heterostructures with enhanced visible photocatalytic activity assisted with H_2O_2. *Journal of Hazardous Materials*, 219-220: 156–163.

Hamoudi S, Larachi F, Sayari A, 1998. Wet oxidation of phenolic solutions over heterogeneous catalysts: Degradation profile and catalyst behavior. *Journal of Catalysis*, 177(2): 247–258.

He J G, Ma K, Jin J, Dong Z P, Wang J J, Li R, 2009. Preparation and characterization of octyl-modified ordered mesoporous carbon CMK-3 for phenol adsorption. *Microporous and Mesoporous Materials*, 121(1-3): 173–177.

Hu M Q, Xu Y M, Zhao J C, 2004. Efficient photosensitized degradation of 4-chlorophenol over immobilized aluminum tetrasulfophthalocyanine in the presence of hydrogen peroxide. *Langmuir*, 20(15): 6302–6307.

Huang J H, Jin X Y, Deng S G, 2012. Phenol adsorption on an N-methylacetamide-modified hypercrosslinked resin from aqueous solutions. *Chemical Engineering Journal*, 192: 192–200.

Iliev V, Mihaylova A, Bilyarska L, 2002. Photooxidation of phenols in aqueous solution, catalyzed by mononuclear and polynuclear metal phthalocyanine complexes. *Journal of Molecular Catalysis A: Chemical*, 184(1-2): 121–130.

Inchaurrondo N S, Massa P, Fenoglio R, Font J, Haure P, 2012. Efficient catalytic wet peroxide oxidation of phenol at moderate temperature using a high-load supported copper catalyst. *Chemical Engineering Journal*, 198-199: 426–434.

Ishii K, 2012. Functional singlet oxygen generators based on phthalocyanines. *Coordintion Chemistry Reviews*, 256(15-16): 1556–1568.

Kluson P, Drobek M, Strasak T, Krysa J, Karaskova M, Rakusan J, 2007. Sulphonated phthalocyanines as effective oxidation photocatalysts for visible and UV light regions. *Journal of Molecular Catalysis A: Chemical*, 272(1-2): 213–219.

Lu W Y, Chen W X, Li N, Xu M H, Yao Y Y, 2009. Oxidative removal of 4-nitrophenol using activated carbon fiber and hydrogen peroxide to enhance reactivity of metallophthalocyanine. *Applied catalysis B: Environmental*, 87(3-4): 146–151.

Luenloi T, Chalermsinsuwan B, Sreethawong T, Hinchiranan N, 2011. Photodegradation of phenol catalyzed by TiO_2 coated on acrylic sheets: Kinetics and factorial design analysis. *Desalination*, 274(1-3): 192–199.

Mekprasart W, Vittayakorn N, Pecharapa W, 2012. Pecharapa, ball-milled CuPc/TiO_2 hybrid nanocomposite and its photocatalytic degradation of aqueous Rhodamine B. *Materials Research Bulletin*, 47(11): 3114–3119.

Meunier B, Sorokin A, 1997. Oxidation of pollutants catalyzed by metallophthalocyanines. *Accounts of Chemical Research*, 30(11): 470–476.

Mohamed R M, Mohamed M M, 2008. Copper (II) phthalocyanines immobilized on alumina and encapsulated inside zeolite-X and their applications in photocatalytic degradation of cyanide: A comparative study. *Applied Catalysis A: General*, 340(1): 16–24.

Muhammad S, Shukla P R, Tadé M O, Wang S, 2012. Heterogeneous activation of peroxymonosulphate by supported ruthenium catalysts for phenol degradation in water. *Journal of Hazardous Materials*, 215-216: 183–190.

Ogunbayo T B, Antunes E, Nyokong T, 2011. Investigation of homogeneous photosensitized oxidation activities of palladium and platinum octasubstituted phthalocyanines: oxidation of 4-nitrophenol. *Journal of Molecular Catalysis A: Chemical*, 334(1-2): 123–129.

Rawling T, McDonagh A, 2007. Ruthenium phthalocyanine and naphthalocyanine complexes: Synthesis, properties and applications. *Coordination Chemistry Reviews*, 251(9-10): 1128–1157.

Shen C S, Wen Y Z, Shen Z L, Wu J, Liu W P, 2011. Facile, green encapsulation of cobalt tetrasulfophthalocyanine monomers in mesoporous silicas for the degradative hydrogen peroxide oxidation of azo dyes. *Journal of Hazardous Materials*, 193: 209–215.

Silva M, Calvete M J F, Gonçalves N P F, Burrows H D, Sarakha M, Fernandes A et al., 2012. Zinc(II) phthalocyanines immobilized in mesoporous silica Al-MCM-41 and their applications in photocatalytic degradation of pesticides. *Journal of Hazardous Materials*, 233-234: 79–88.

Spiller W, Kliesch H, Wohrle D, Hackbarth S, Roder B, Schnurpfeil G, 1998. Singlet oxygen quantum yields of different photosensitizers in polar solvents and micellar solutions. *The Journal of Porphyrins and Phthalocyanines*, 2(2): 145–158.

Staples C A, Dorn P B, Klecka G M, O'Block S T, Harris L R, 1998. A review of the environmental fate, effects, and exposures of bisphenol A. *Chemosphere*, 36(10): 2149–2173.

Tai C, Jiang G B, Liu J F, Zhou Q F, Liu J Y, 2005. Rapid degradation of bisphenol A using air as the oxidant catalyzed by

polynuclear phthalocyanine complexes under visible light irradiation. *Journal of Photochemistry and Photobiology A: Chemistry*, 172(3): 275–282.

Wu L, Li A M, Gao G D, Fei Z H, Xu S R, Zhang Q X, 2007. Efficient photodegradation of 2,4-dichlorophenol in aqueous solution catalyzed by polydivinylbenzene-supported zinc phthalocyanine. *Journal of Molecular Catalysis A: Chemical*, 269(1-2): 183–189.

Xing R, Liu Y M, Wu H H, Li X H, He M Y, Wu P, 2008. Preparation of active and robust palladium nanoparticle catalysts stabilized by diamine-functionalized mesoporous polymers. *Chemical Communications*, (47): 6297–6299.

Xing R, Wu H H, Li X H, Zhao Z L, Liu Y M, Chen L et al., 2009. Mesopolymer solid base catalysts with variable basicity: preparation and catalytic properties. *Journal of Materials Chemistry*, 19(23): 4004–4011.

Xiong Z G, Xu Y M, 2007. Immobilization of palladium phthalocyaninesulfonate onto anionic clay for sorption and oxidation of 2,4,6-trichlorophenol under visible light irradiation. *Chemistry of Materials*, 19(6): 1452–1458.

Xiong Z G, Xu Y M, Zhu L Z, Zhao J C, 2005. Photosensitized oxidation of substituted phenols on aluminum phthalocyanine-intercalated organoclay. *Environmental Science & Technology*, 39(2): 651–657.

Xu Z W, Li H J, Cao G X, Zhang Q L, Li K Z, Zhao X N, 2011. Electrochemical performance of carbon nanotube-supported cobalt phthalocyanine and its nitrogen-rich derivatives for oxygen reduction. *Journal of Molecular Catalysis A: Chemical*, 335(1-2): 89–96.

Yahiro H, Naka T, Kuramoto T, Kurohagi K, Okada G, Shiotani M, 2005. An EPR study on oxygen molecule adduct of Co(II)-phthalocyanines encapsulated into zeolites. *Microporous Mesoporous Materials*, 79(1-3): 291–297.

Zanjanchi M A, Ebrahimian A, Arvand M, 2010. Sulphonated cobalt phthalocyanine-MCM-41: An active photocatalyst for degradation of 2,4-dichlorophenol. *Journal of Hazardous Materials*, 175(1-3): 992–1000.

Zeng X W, Yu T J, Wang P, Yuan R H, Wen Q, Fan Y G et al., 2010. Preparation and characterization of polar polymeric adsorbents with high surface area for the removal of phenol from water. *Journal of Hazardous Materials*, 177(1-3): 773–780.

Zeng Z Q, Zou H K, Li X, Sun B C, Chen J F, Shao L, 2012. Ozonation of phenol with O_3/Fe(II) in acidic environment in a rotating packed bed. *Industrial & Engineering Chemistry Research*, 51(31): 10509–10516.

Zhao G H, Li Y F, Liu X X, Liu X L, 2010. Preparation of capsules containing 1-nonanol for rapidly removing high concentration phenol from aqueous solution. *Journal of Hazardous Materials*, 175(1-3): 715–725.

Zugle R, Antunes E, Khene S, Nyokong T, 2012. Photooxidation of 4-chlorophenol sensitized by lutetium tetraphenoxy phthalocyanine anchored on electrospun polystyrene polymer fiber. *Polyhedron*, 33(1): 74–81.

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