Palladium phthalocyaninesulfonate functionalized mesoporous polymer: A highly efficient photocatalyst for degradation of 4-chlorophenol under visible light irradiation

Rong Xing [a,*], Lin Wu [a], Zhenghao Fei [a], Peng Wu [b,*]

[a] Jiangsu Provincial Key Laboratory of Coastal Wetland Bioresources and Environmental Protection, Yancheng Teachers University, Kaifang Dadao Rd. 50, Yancheng City, Jiangsu Province 224002, China
[b] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, North Zhongshan Rd. 3663, Shanghai 200062, China

ARTICLE INFO

ABSTRACT

A novel sulfonated palladium phthalocyanine (PdPcS) modified FDU-15 mesoporous polymer (FDU-PdPcS) has been prepared by rationally chemical modification process. The PdPcS molecules were highly dispersed inside the confined mesopores, and were further stabilized through a π–π interaction with mesopolymer, which may prevent the PdPcS molecules from agglomerating and deactivating in photodegradation reactions. The physicochemical properties of thus prepared FDU-PdPcS material were characterized by XRD, N_2 adsorption-desorption, UV–vis and inductively coupled plasma techniques. FDU-PdPcS proved to be highly efficient heterogeneous photocatalyst for the degradation of 4-chlorophenol (4-CP) in the presence of H_2O_2 under visible light irradiation. The photodegradation of 4-CP with an initial concentration 0.6 mM was completed within 5 h at pH 11 using a dose of 0.2 g/L of the 0.12 wt% FDU-PdPcS photocatalyst. The photodegradation intermediates were identified by GC-MS. A possible mechanism involved in the photodegradation of 4-CP has also been discussed.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Ordered mesoporous materials with high surface area, large-pore volumes and uniform mesopores have attracted significant attention due to their potential applications in the fields of separation, adsorption, catalysis and host-guest chemistry [1–6]. Compared with the microporous zeolites, the mesoporous materials provide good opportunity for anchoring bulky functional molecules (such as enzymes, dyes, complexes, ionic liquids, etc.) into confined mesopores (2–50 nm) for practical applications [7–11]. These functional materials are expected to combine the advantages of mesoporous materials and functional molecules. For example, metalloporphyrins modified periodic mesoporous organosilica was prepared to show a high catalytic activity in the Baeyer–Villiger oxidation reaction [12].

From the viewpoint of developing energy-saving and environmentally benign chemical processes, photocatalysis is a promising technique especially using visible light as an energy source, which contains 45% solar energy. As one of the most efficient and promising photosensitizers or/and photocatalysts, metallophthalocyanines (MPcs) with unique photophysical properties and photochemical stability, are extensively investigated in photodegradation of organic pollutants due to their ability to absorb the visible light and generate highly active singlet oxygen species [13,14]. However, MPcs are a class of macrocyclic compounds, and tend to aggregate in aqueous media, which leads to self-quenching of the excited species and brings about photocatalyst deactivation. To overcome these inherent limitations, a variety of heterogeneous MPc catalysts have been developed by supporting MPc molecules on mesoporous silicas [15], zeolites [16], TiO_2 [17,18], carbon nanotubes [19,20], clays [21] and polymers [22,23], etc. Among these mentioned supports, the mesoporous materials are particularly suitable for supporting the MPc molecules because of their extremely high surface area and well-ordered mesopores, which may make the MPc molecules highly dispersed in a monomeric form in confined mesopores. Recently, Zanjanchi et al. [24] reported that the sulfonated cobalt phthalocyaninne-functionalized MCM-41 exhibited good photocatalytic activities for the degradation of 2,4-DCP in the presence of H_2O_2 at pH of 5 under UV light irradiation. According to the literatures [25,26], the degradation of chlorophenol was often carried out in a basic solution since chlorophenolate was more easily oxidized than in neutral form. However, the applications of silica-based mesoporous materials are considered to suffer a rapid degradation of mesostructure in basic solution. Thus, more promising supports are needed for practical applications.

---

* Corresponding authors. Fax: +86 515 88233188.
  E-mail addresses: xingrr@126.com (R. Xing), pwu@chem.ecnu.edu.cn (P. Wu).

Within the family of the mesoporous materials, the mesopolymers with both the mesostructures and the organic framework of polymers are considered to solve partially the disadvantages of pure silica materials owing to high physicochemical stability in acidic or basic medium as well as numerous opportunities for designing novel catalysts through co-condensation or post-graft method. So the mesopolymer materials may serve as ideal supports for anchoring the MPc molecules by taking advantage of their organic framework and regular mesopores. Moreover, different from silica-based materials, phenolic pollutants could be efficiently adsorbed onto the photocatalytic active sites on mesopolymer through π–π interaction and hydrogen bonding between the phenolic pollutants (e.g. phenol, chlorophenol and bisphenol A) and the aromatic species in the framework walls. The MPc molecules can be easily bonded to the mesopolymer by rationally chemical modification, dispersing in a monomeric form in confined mesopores and being further stabilized by the π-electron of the benzene ring moieties in mesopolymer material, which can prevent the MPc molecules from agglomerating and also increase the quantum yield of singlet oxygen.

The PdPc compound is usually chosen as a photocatalyst since it shows higher singlet oxygen yields and photostability in comparison to other metal phthalocyanines [27,28]. We have verified that the FDU-15 mesopolymers were converted readily into diamine-functionalized materials (FDU-ED) through chloromethylation and amination procedures [29,30]. Herein, we report for the first time that FDU-ED serves as ideal scaffolds for the dispersion and stabilization of the palladium phthalocyaninesulfonate molecules (PdPcS) confined within the mesopores. This mesopolymer-supported PdPcS photocatalyst proves to be highly photoactive in the degradation of 4-CP under visible light irradiation. It may provide a versatile way for designing various mesopolymer-supported MPc photocatalysts that are useful for a rapid degradation of organic pollutants using solar light.

2. Experimental

2.1. Materials

The FDU-15 mesoporous polymer and diamine-functionalized FDU-15 (FDU-ED) were synthesized as previously reported [29,30]. Palladium (II) phthalocyanine sulfonate (PdPcS) was prepared according to the literature method [31]. 4-chlorophenol was purchased from Shanghai Chemicals Inc, and was used as received.

2.2. Preparation of PdPcS-functionalized FDU-15

FDU-ED (0.50 g) was stirred in 210 mL of PdPcS solution (2.9 μg/g) at room temperature until the suspension turned to be colorless. The obtained material was washed with distilled water. It was finally dried under vacuum at 60 °C for 12 h, leading to mesopolymers supported PdPcS, which is denoted as FDU-PdPcS.

2.3. Measurements

The X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å) at 35 kV and 25 mA. Nitrogen adsorption–desorption isotherms were recorded at 77 K on a BELSORP-MAX instrument after activating the sample under vacuum at 373 K at least for 10 h. The specific surface area was evaluated using Brunauer–Emmett–Teller (BET) method. UV–visible spectra were recorded on a PerkinElmer Lambda 35 UV/VIS spectrometer with a mode of diffusion reflectance using polytetrafluoroethene as a reference. 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.

2.4. Photocatalytic test

The photocatalytic reaction was performed in a glass reactor using a Halogen lamp (500 W, Shanghai Yamin) through a glass filter ($\lambda \geq 450$ nm) as irradiation source. In a typical experiment, 50 mL of 4-CP solution and 0.01 g of catalyst were stirred in an air-saturated aqueous solution at room temperature under dark overnight until reaching an adsorption equilibrium. 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 reaction mixture (ca. 2 mL) was sampled. After removing the solid catalyst by filtration through a membrane (0.45 μm), the amount of 4-CP remaining in the solution was analyzed by high performance liquid chromatography (Waters 2695-2489 HPLC, C 18 reverse column, 5 μm, 250 mm × 4.6 mm) using CH_3OH-H_2O (60%: 40%, pH 5 by acetic acid) as an 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 it volume reduced to about 5 mL via rotatory 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 h, 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. The chloride ion analyses were performed using 0.2% $AgNO_3$ solution. The carbon dioxide was detected by $Ba(OH)_2$ method. Isopropanol, sodium azide and benzoquinone were used as OH$^\bullet$, $^1O_2$ and $O_2^{\bullet-}$ scavenger, respectively in the photodegradation reactions. The used catalyst was washed with distilled water, and dried at 353 K. The recycling experiments of FDU-PdPcS were carried out under the above mentioned conditions.

3. Results and discussion

A schematic illustration of the pathways for preparing the photocatalyst is shown in Scheme 1. First, the chloromethyl groups were successfully introduced into the benzene ring moieties of the FDU-15 (hexagonal $P6mm$) mesopolymers through the chloromethylation reaction (denoted as FDU-CH$_2$Cl).
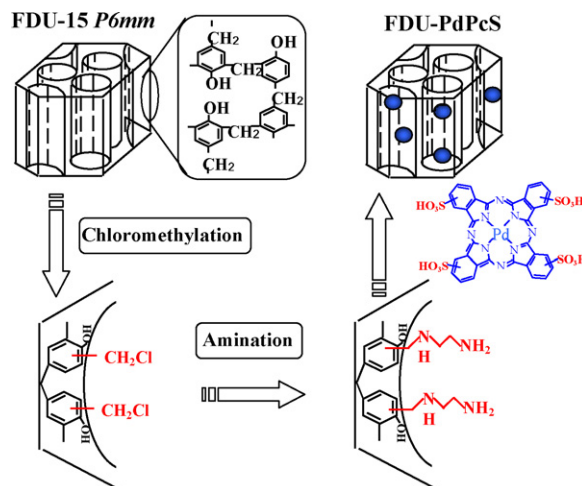
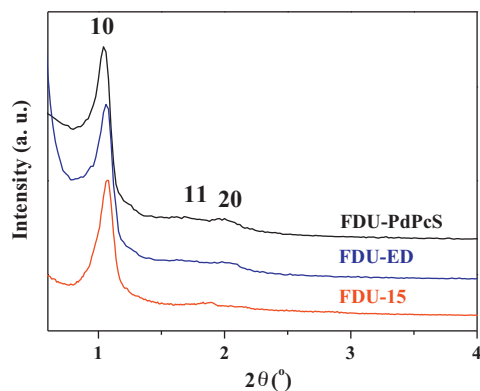**Scheme 1.** Schematic illustration for preparing PdPcS-functionalized mesopolymer materials.

Fig. 1. XRD patterns of FDU-15, FDU-ED and FDU-PdPcS.

Fig. 3. UV–vis spectra of FDU-15, FDU-PdPcS and PdPcS solution (inset).

Table 1
Textural properties of the FDU-15 before and after various modifications.

Samples	Unit cell (Å)[a]	N$_2$ adsorption		
		S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})	D_p (nm)
FDU-15	88.1	422	0.35	3.6
FDU-ED	91.9	316	0.26	3.1
FDU-PdPcS	92.8	297	0.23	2.8

[a] Calculated using d_{100} according to $a_0 = 2d_{100}/\sqrt{3}$ for FDU-15.

Secondly, FDU-CH$_2$Cl subsequently reacted with ethylenediamine (ED) solution to produce diamine-functionalized products (denoted as FDU-ED). We have well addressed these two-step functionalizations elsewhere [29,30]. Finally, FDU-ED was added to PdPcS aqueous solution, and stirred at room temperature. The PdPcS ions were captured rapidly by the diamino groups through protonation and ionic interaction, giving rise to the mesopolymers supported PdPcS, FDU-PdPcS.

3.1. Characterization of PdPcS-functionalized mesopolymers

Fig. 1 shows the powder XRD patterns of the parent FDU-15 and the modified samples. The samples all exhibited three diffraction peaks indexed as the [10], [11] and [20] planes, based on a well-ordered 2D hexagonal structure with a P6 mm space group, suggesting that the mesostructure was not destroyed after post-modification. The diffraction peaks of the modified samples shifted slightly to lower 2θ angle due to increased unit cells in the functionalized materials. This provides a further evidence for immobilizing successfully the organic groups with bulky dimensions on the mesopolymer walls. Some typical textural parameters of the FDU-15 and the modified samples are listed in Table 1.
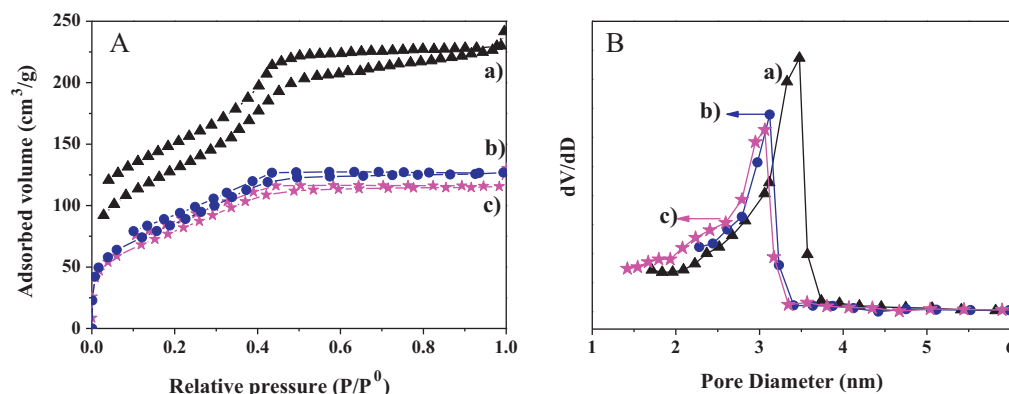
The N$_2$ adsorption–desorption isotherms and the corresponding pore size distributions of the samples are shown in Fig. 2. The samples exhibited a typical IV type isotherm and a clear H2 hysteresis loop, typical of a mesoporous structure. The pore size distributions all exhibited sharp peaks, indicating the uniform pores remained even after the multi-step chemical functionalizations. According to our previous study [30,32], the modified samples exhibited a greatly decreased N$_2$ uptake in the adsorption and desorption branches in comparison with FDU-15. This is probably because that the organic groups were anchored on the inner surface of mesopores, which may cause a slight decrease in the pore size, pore volume and surface area (Table 1). Moreover, the adsorption and desorption branches of all samples did not close completely in the region of low relative pressure due to a typical nature of these mesopolymers [33].

The diffuse reflectance UV–vis spectra of PdPcS (inset), FDU-15 and FDU-PdPcS are shown in Fig. 3. For PdPcS aqueous solution, the absorption band at 646 nm attributed to the monomer was lower than the band at 612 nm attributed to the aggregated form. It is considered that the PdPcS molecules were highly aggregated in aqueous solution. The blank FDU-15 showed no obvious absorption band, while the FDU-PdPcS developed distinctly three new absorption bands. Band at 661 nm corresponding to monomer was red-shifted due to the π–π interaction between PdPcS and FDU-15, which is well consistent with the literature [27]. The shoulder peaks at 606 and 553 nm were assigned to the aggregate forms of PdPcS. The results suggest that most of the monomeric PdPcS was successfully introduced inside the channels of FDU-15, and a small portion of the larger aggregate forms may be located on the external surface of FDU-15.

The palladium content of the FDU-PdPcS catalyst analyzed with inductively coupled plasma (ICP) was 0.014 wt% (corresponding to

Fig. 2. N$_2$ adsorption–desorption isotherms (A) and BJH pore size distribution curves (B) of (a) FDU-15, (b) FDU-ED and (c) FDU-PdPcS.
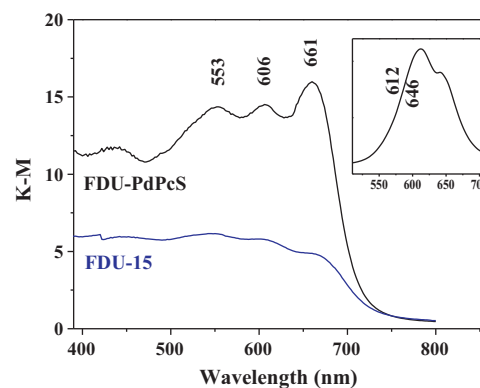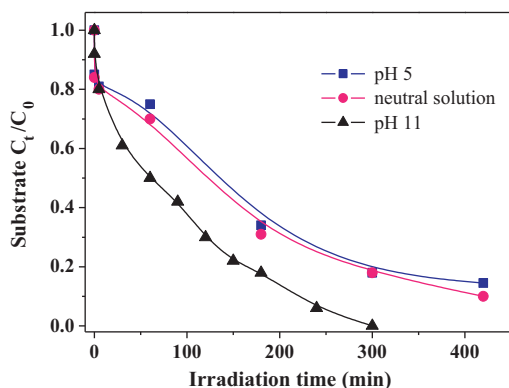
Fig. 4. Effect of pH value on the photodegradation rate of 4-CP. Reaction conditions: 0.01 g FDU-PdPcS, 50 mL 4-CP (0.6 mM), H_2O_2 (29 mM).

0.12 wt% PdPcS loading), which indicated that more than 99% of the added PdPcS was sucked into the mesopolymer.

3.2. Photocatalytic decomposition of 4-CP

3.2.1. The effect of pH

4-Chlorophenol was selected as the representative pollutant for the investigation of photodegradation since it is a typical toxic and recalcitrant pollutant in industrial wastewater which is difficult to be biodegraded due to its high chemical stability. It is well known that the pH value influences greatly the degradation rate of 4-CP in solution and the catalytic properties of the catalysts. Therefore, the effect of the pH of 4-CP solution was first investigated. Fig. 4 shows the degradation of the 4-CP in slightly acidic, basic and neutral aqueous solution (pKa of 4-CP = 9.34). After 5 h of irradiation, no significant differences were observed in acidic and neutral aqueous solution, while the degradation rate of 0.6 mM 4-CP aqueous solution was about 81% and 82% at pH = 5 and neutral aqueous solution, respectively. In a basic aqueous solution (pH = 11), 4-CP was completely degraded within 5 h, indicating that the basic media favors the photodegradation of 4-CP. This is because that the basic media enhances the deprotonation of 4-CP to form chlorophenolate, which are more oxidizable by singlet oxygen [26,34]. The results show that the optimum pH value was 11, hence the following degradation reactions were carried out under this pH value.

3.2.2. Photodegradation of 4-CP

Fig. 5 shows the concentration change of 4-CP with time under various reaction conditions. It can be seen from the experimental results that the oxidation of 4-CP could hardly occurred in the presence of H_2O_2 in the dark or ever under visible light irradiation, indicating that H_2O_2 could not generate free radicals along with visible light irradiation. FDU-PdPcS also failed to catalyze the degradation of 4-CP in the presence of H_2O_2 in the dark, and only adsorbed about 8% of 4-CP (Fig. 5c). However, FDU-PdPcS exhibited a high photocatalytic activity for the degradation of 4-CP under visible light irradiation. 4-CP was degraded completely and 61% using FDU-PdPcS as photocatalyst in the presence and absence of H_2O_2, respectively (Fig. 5d and e) after irradiation for 5 h. The blank FDU-15 was not photoactive under same reaction conditions. Above experiments suggest that FDU-PdPcS photocatalyst and visible light are crucial for degradation of 4-CP. In addition, the control experiment with FDU-PdPcS in the presence or absence of H_2O_2 showed that H_2O_2 can accelerate the reaction rate under visible light irradiation and eliminate the colored intermediates during the photodegradation reactions, which was well consistent with the reported literature [35]. It is noteworthy that at low photocatalyst/4-CP molar ratio, FDU-PdPcS catalyst shows higher
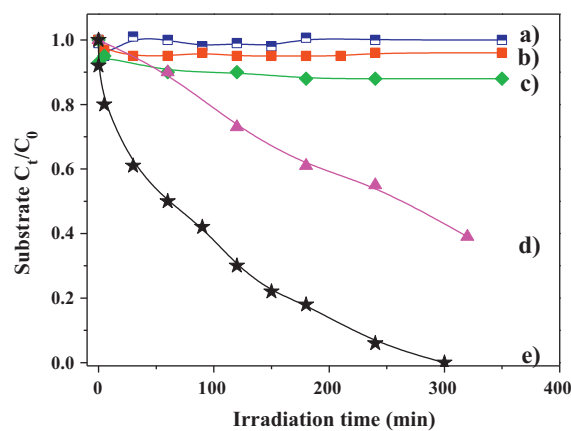

Fig. 5. The changes of 4-CP concentration with reaction time under various conditions: (a) H_2O_2 + dark, (b) H_2O_2 + vis-light, (c) FDU-PdPcS + H_2O_2 + dark, (d) FDU-PdPcS + vis-light and (e) FDU-PdPcS + H_2O_2 + vis-light. Reaction conditions: 0.01 g FDU-PdPcS, 50 mL 4-CP (0.6 mM), H_2O_2 (29 mM), pH 11.
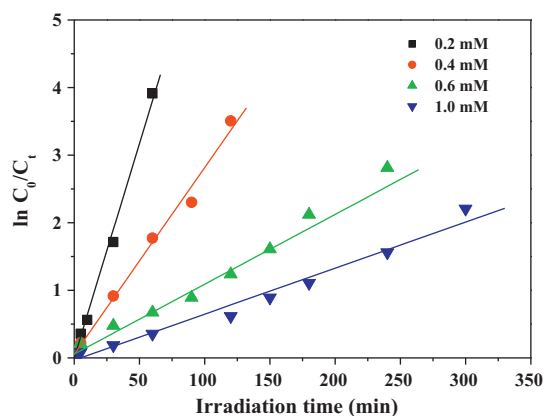

Fig. 6. Effect of initial concentration on the photodegradation of 4-CP.

photocatalytic activity in the photodegradation of the chlorinated phenols compared to CoPcS functionalized MCM-41 reported in a recent literature under similar experimental conditions [24]. This can be explained that PdPcS molecules were highly dispersed inside the confined mesopores, and further be stabilized by π-electron of mesopolymer. Moreover, FDU-PdPcS catalyst containing the hydrophilic diamino groups would form a homogeneous suspension in water and more effectively facilitates the diffusion and/or adsorption of molecular oxygen and 4-CP to the catalytic active sites

3.2.3. The effect of 4-CP concentration

The effect of the initial concentration on the degradation of 4-CP was investigated (Fig. 6). The 4-CP degradation fitted quite well into the first-order kinetics which can be represented by 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 and obtained from the slope of the plot of $\ln(C_0/C_t)$ versus reaction time t. Table 2 lists the rate constant and half-life at initial 4-CP

Table 2
The rate constant (k_{obs}), half-life ($t_{1/2}$) at various concentrations of 4-CP.

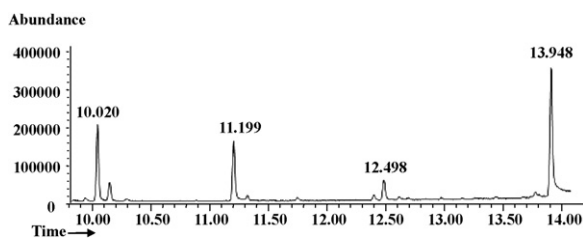| Concentration (mM)	R^2	k_{obs} (min^{-1})	$t_{1/2}$ (min)
0.2	0.9943	0.0636	10.90
0.4	0.992	0.0276	25.11
0.6	0.9877	0.0111	62.45
1.0	0.9883	0.0071	97.63

Fig. 7. GC-MS chromatogram of photodegradation of 4-CP. Reaction conditions: 0.01 g FDU-PdPcS, 50 mL 4-CP (0.6 mM), H_2O_2 (29 mM), pH = 11, 4 h.

concentrations ranging from 0.2 to 1.0 mM. The rate constant decreased from 0.0636 to 0.0071 min^{-1} with increasing the initial concentration from 0.2 to 1.0 mM. The photodegradation of 4-CP with an initial concentration 0.2 mM and 1.0 mM was completed within 1.5 h and 7.5 h, respectively. The efficiency of 4-CP photodegradation decreased with increasing initial 4-CP from 0.2 mM to 1.0 mM. This was attributed to adsorption and/or diffusion limitation of molecular oxygen in the mesopores at higher concentrations during the photodegradation process [35]. The results clearly show that the photodegradation of 4-CP was faster in more dilute 4-CP solution.

3.3. Products and mechanism of 4-CP photodegradation

To confirm the highly polar and small molecules of degradation process, the products were esterified with methanol using concentrated sulfuric acid as the catalyst. The esterified products were identified by GC–MS. The results are shown in Fig. 7 and listed in Table 3. A mixture of dimethyl oxalate, dimethyl malonate, dimethyl maleate and dimethyl D-malate was identified as the methyl ester derivatives of intermediates, suggesting that the photodegradation products were composed of oxalic acid, malonic acid, maleic acid and malic acid. Moreover, in the final products, the chloride ions and carbon dioxide were detected by using $AgNO_3$ and $Ba(OH)_2$ method, respectively.

To investigate the mechanism for the photodegradation process, isopropanol, sodium azide and benzoquinone were used as hydroxyl radicals ($OH^•$), singlet oxygen ($^1O_2$) and superoxide radicals ($O_2^{•-}$) scavenger, respectively. This would give information concerned with the reactive species during photodegradation process. In comparison to a typical photocatalysis (Fig. 8e), the addition of isopropanol showed a little influence on the degradation of 4-CP

Table 3
Intermediates of the 4-CP photodegradation determined by GC–MS.

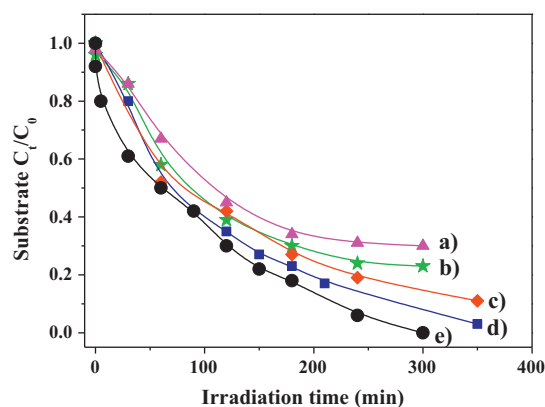| Retention time (min)	Identified intermediate	Molecular structure
10.020	Dimethyl oxalate	
11.190	Dimethyl malonate	
12.498	dimethyl maleate	
13.948	Dimethyl D-malate	

Fig. 8. Effect of scavengers on the photodegradation of 4-CP. (a) NaN_3 (0.01 M) + benzoquinone (0.025 mM), (b) benzoquinone (0.025 mM), (c) NaN_3 (0.01 M), (d) isopropanol (0.05 M) and (e) no scavenger.

(Fig. 8d), indicating that a small amount of $OH^•$ participated in the photodegradation of 4-CP under visible light irradiation. However, the addition of benzoquinone or sodium azide retarded distinctly the photodegradation rate (Fig. 8b and c). The lowest degradation rate was observed in the presence of both sodium azide and benzoquinone (Fig. 8a). The results imply that both $^1O_2$ and $O_2^{•-}$ are probably the prominent active species in the photodegradation of 4-CP in the presence of FDU-PdPcS with H_2O_2 under visible light irradiation. In the previous studies [25,36], the superoxide radical ($O_2^{•-}$) is produced via electron transfer process, which is part of the Type I mechanism. The singlet oxygen ($^1O_2$) is generated via energy transfer from triplet state of the sensitizer to ground state oxygen and initiates the reaction, which belongs to the Type II mechanism. Based on the above results, the photodegradation of 4-CP might proceed through Type I and II mechanisms. Fig. 9 shows the possible mechanism for the photocatalytic degradation of 4-CP. Hydroquinone formed in Type I reaction process is similar to the photodegradation of 4-nitrophenol [37], while benzoquinone generated in Type II reaction process is consistent to the reported for the degradation of 2,4,6-trichlorophenol [38]. The obtained intermediates were further oxidized to various carboxylic acids.

3.4. Catalysts recycling

From the viewpoint of environmental application, the recyclability of heterogeneous catalyst is very important. In the kinetic and recycling experiments under the same experiment conditions, the photodegradation rate of 4-CP was very comparable to the results achieved on the fresh catalyst after reused for 4 times (Fig. 10). As evidenced by XRD analysis, the reused FDU-PdPcS catalyst showed the diffraction peaks very similar to those of the parent FDU-PdPcS
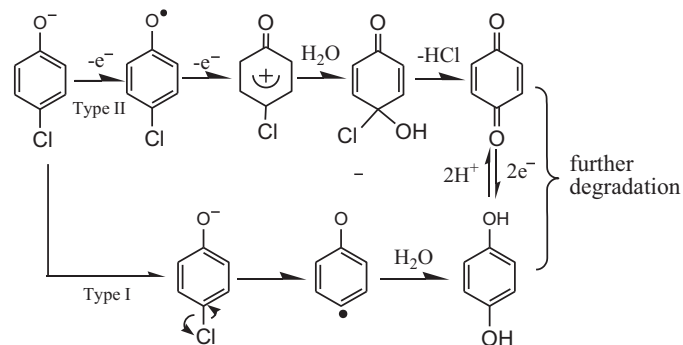

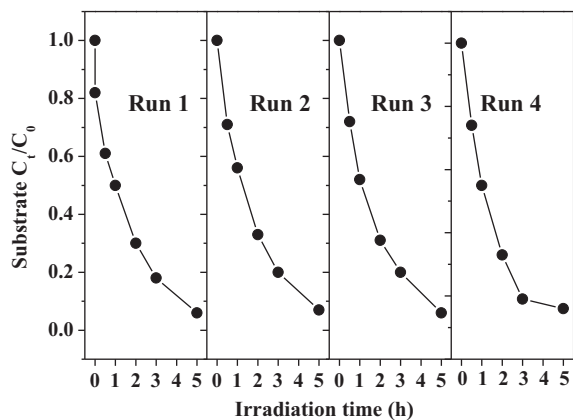Fig. 9. Possible mechanism for the photodegradation of 4-CP under visible light.

Fig. 10. Cyclic use of FDU-PdPcS for the photodegradation of 4-CP.
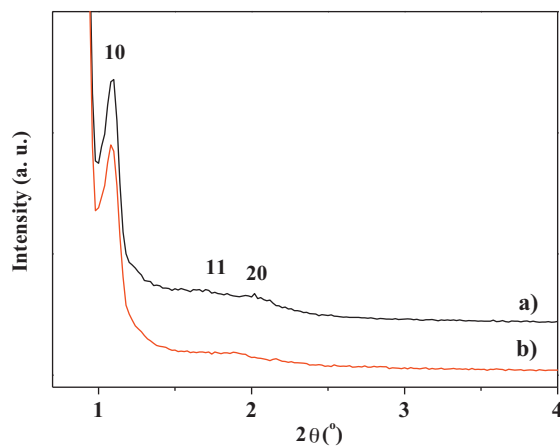

Fig. 11. XRD patterns of (a) fresh FDU-PdPcS and (b) FDU-PdPcS catalyst after 4 runs.

(Fig. 11), indicating that the ordered mesostructure was retained in repeated reactions. FDU-PdPcS was thus confirmed to a highly reusable catalyst.

4. Conclusions

A novel PdPcS-functionalized mesopolymer photocatalyst has been prepared readily through the effective electrostatic interactions. The monomeric PdPcS molecules were highly dispersed inside mesopores and further stabilized by the π-electrons of the benzene rings in mesopolymer, which could avoid the aggregation of PdPcS. The FDU-PdPcS exhibits a high visible light photocatalytic activity and reusability in the degradation of 4-CP reaction, and is expectable for efficient removal of organic pollutants using the sunlight as the energy source. The method could be usable as a valid way for designing and preparing mesopolymers supported other MPcs photocatalysts.

References

[1] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615–3640.
[2] Z. Wu, P.A. Webley, D. Zhao, Langmuir 26 (2010) 10277–10286.
[3] K. Sugino, N. Oya, N. Yoshie, M. Ogura, J. Am. Chem. Soc. 133 (2011) 20030–20032.
[4] D. Xiang, L. Yin, J. Mater. Chem. 22 (2012) 9584–9593.
[5] C. Gao, H. Zheng, L. Xing, M. Shu, S. Che, Chem. Mater. 22 (2010) 5437–5444.
[6] L. Feng, H. Li, Y. Qu, C. Lü, Chem. Commun. 48 (2012) 4633–4635.
[7] L. Wang, D. Dehe, T. Philippi, A. Seifert, S. Ernst, Z. Zhou, M. Hartmann, R.N.K. Taylor, A.P. Singh, M. Jia, W.R. Thiel, Catal. Sci. Technol. 2 (2012) 1188–1195.
[8] M. Hartmann, D. Jung, J. Mater. Chem. 20 (2010) 844–857.
[9] V. Lykourinou, Y. Chen, X. Wang, L. Meng, T. Hoang, L. Ming, R.L. Musselman, S. Ma, J. Am. Chem. Soc. 133 (2011) 10382–10385.
[10] K. Mori, M. Tottori, K. Watanbe, M. Che, H. Yamashita, J. Phys. Chem. C 115 (2011) 21358–21362.
[11] C. Cai, H. Wang, J. Han, Appl. Surf. Sci. 257 (2011) 9802–9808.
[12] E. Jeong, M.B. Ansari, S. Park, ACS Catal. 1 (2011) 855–863.
[13] B. Meunier, A. Sorokin, Acc. Chem. Res. 30 (1997) 470–476.
[14] T. Rawling, A. McDonagh, Coord. Chem. Rev. 251 (2007) 1128–1157.
[15] C. Shen, Y. Wen, Z. Shen, J. Wu, W. Liu, J. Hazard. Mater. 193 (2011) 209–215.
[16] M. Alvaro, E. Carbonell, M. Esplá, H. Garcia, Appl. Catal. B: Environ. 57 (2005) 37–42.
[17] V. Iliev, J. Photochem. Photobiol. A 151 (2002) 195–199.
[18] X. Zhao, Z. Li, Y. Chen, L. Shi, Y. Zhu, Appl. Surf. Sci. 254 (2008) 1825–1829.
[19] T.B. Ogunbayo, T. Nyokong, J. Mol. Catal. A: Chem. 337 (2011) 68–76.
[20] A. Morozan, S. Campidelli, A. Filoramo, B. Jousselme, S. Palacin, Carbon 49 (2011) 4839–4847.
[21] Z. Xiong, Y. Xu, L. Zhu, J. Zhao, Environ. Sci. Technol. 39 (2005) 651–657.
[22] Z. Guo, C. Shao, J. Mu, M. Zhang, P. Zhang, Catal. Commun. 12 (2011) 880–885.
[23] L. Wu, A. Li, G. Gao, Z. Fei, S. Xu, Q. Zhang, J. Mol. Catal. A: Chem. 269 (2007) 183–189.
[24] M.A. Zanjanchi, A. Ebrahimian, M. Arvand, J. Hazard. Mater. 175 (2010) 992–1000.
[25] R. Zugle, E. Antunes, S. Khene, T. Nyokong, Polyhedron 33 (2012) 74–81.
[26] R. Gerdes, D. Wohrle, W. Spiller, G. Schneider, G. Schnurpfeil, G.J. Schulz-Ekloff, J. Photochem. Photobiol. A 111 (1997) 65–74.
[27] Z. Xiong, Y. Xu, Chem. Mater. 19 (2007) 1452–1458.
[28] A. Sun, Z. Xiong, Y. Xu, J. Hazard. Mater. 152 (2008) 191–195.
[29] R. Xing, Y. Liu, H. Wu, X. Li, M. He, P. Wu, Chem. Commun. 47 (2008) 6297–6299.
[30] R. Xing, H. Wu, X. Li, Z. Zhao, Y. Liu, L. Chen, P. Wu, J. Mater. Chem. 19 (2009) 4004–4011.
[31] W. Spiller, H. Kliesch, D. Wohrle, S. Hackbarth, B. Roder, G. Schnurpfeil, J. Porphyr. Phthalocya. 2 (1998) 145–158.
[32] R. Xing, N. Liu, Y. Liu, H. Wu, Y. Jiang, L. Chen, M. He, P. Wu, Adv. Funct. Mater. 17 (2007) 2455–2461.
[33] F. Zhang, Y. Meng, D. Gu, Y. Yan, C. Yu, B. Tu, D. Zhao, J. Am. Chem. Soc. 127 (2005) 13508–13509.
[34] K. Ozoemena, N. Kuznetsova, T. Nyokong, J. Photochem. Photobiol. A 139 (2001) 217–224.
[35] M. Hu, Y. Xu, J. Zhao, Langmuir 20 (2004) 6302–6307.
[36] T.B. Ogunbayo, T. Nyokong, J. Mol. Catal. A: Chem. 350 (2011) 49–55.
[37] T.B. Ogunbayo, E. Antunes, T. Nyokong, J. Mol. Catal. A: Chem. 334 (2011) 123–129.
[38] A. Sorokin, B. Meunier, Chem. Eur. J. 2 (1996) 1308–1317.