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Preparation and photo-oxidative functions of poly(ethylene-*co*-methacrylic acid) (PE-*co*-MAA) nanofibrous membrane supported porphyrins

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Surface functionalized poly(ethylene-*co*-methacrylic acid) (PE-*co*-MAA) nanofibrous membranes were successfully prepared and applied as solid supports to immobilize photosensitizers. Several activation agents were used to facilitate the surface functionalization of PE-*co*-MAA nanofibrous membranes, and PCl₅ was found to be the most efficient one to activate surface carboxylic acid groups. Three spacers with variable lengths were introduced to the membrane surfaces prior to immobilizations of protoporphyrin IX (PPIX), a photosensitizer. The results revealed that the membranes with longer spacer chain incorporated more photoactive macrocyclic compounds, and the supported PPIX provided a more powerful catalytic effect on the photo-oxidation of 1,5-dihydroxynaphthalene. After five times of repeated catalytic reactions, the catalytic activity of the solid supported PPIX was maintained at 80% of the original power, and the membrane morphology was intact. The nanofibrous membrane supported photosensitizer provided high catalytic activity, easy handling, good durability and reusability.

Introduction

Singlet oxygen induced photo-oxidation reactions in the presence of visible light, oxygen and photosensitizers have attracted much attention due to the effective, economical and environmentally friendly reaction pathway.¹⁻³ By efficiently capturing and transferring radiant energies from light to molecular oxygen, nonmetallated porphyrins as organic photosensitizers are capable of generating high quantum yields of singlet oxygen. As a result, a variety of photo-oxidation reactions mediated by porphyrin derivatives were extensively studied.⁴ However, the key challenge for using these homogeneous catalysts is the reusability of the porphyrin compounds owing to the difficult recovering processes from reaction media.

Immobilization of the photosensitizers onto solid support materials provides a simple and effective way to circumvent the limitation mentioned above. A variety of support media including beads, gels and membranes have been developed for this purpose.⁵⁻¹⁰ The resulting products of support media and organic photosensitizers as heterogeneous catalysts exhibited synergetic benefits of easy recovery, ready reusability and improved flexibility for various working solvents. However, these advantages are usually accompanied by undesired weakening of catalytic activity, as a direct result of decreased quantum yield of singlet oxygen.¹¹ Inspired by their intrinsic properties, considerable efforts have been devoted to utilize nanoscaled materials



(mesoporous materials, nanoparticles, nanotubes, nanosheets and nanofibrous membranes) as support media for organic photosensitizers.¹²⁻¹⁶ In comparison with conventional support media, the enormous high specific surface areas of nanoscaled materials provide more sites and enhanced accessibility of immobilized photoactive molecules, thus enabling higher quantum yield of singlet oxygen for improved activities. Despite these superiorities, a major issue related to mesoporous media is low oxygen diffusion rates into and out of the solid matrices, which is especially important for oxygen involved reactions. In addition, solvent dependent dispersion properties and difficult isolation processes of nanoparticles and nanotubes also limited the practical applications of these nanosized media. In the absence of the abovementioned drawbacks, nanofibrous membranes serve as an attractive alternative to achieve high amounts of immobilized photosensitizers as well as well-maintained catalytic activity. Composite nanofibrous membranes with porphyrin moieties have been fabricated by an electrospun method from solutions of mixed photosensitizers and target polymers. However, leaching of coordinatively bound porphyrins from the mixture media limited the applications.14,15 Furthermore, Xu et al. reported the synthesis of copolymers of vinyl porphyrins with acrylonitrile and the subsequent electrospinning of the resulting copolymer into porphyrin containing nanofibers. The polymer matrices may block light exposure of the embedded photosensitizers, which may have caused a reduced photocatalytic activity,16 whereas covalently immobilized porphyrins on the surface of nanofibrous membranes as catalysts for photo-oxidation reactions have not received much attention yet.

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Recently, a high throughout procedure to fabricate thermoplastic nanofibers was developed by melt extrusion of an immiscible polymer blend of the target polymer with a sacrificial matrix, in which the fiber size was controllable via varied polymer blend ratios.17,18 Poly(ethylene-co-methacrylic acid) (PE-co-MAA) nanofiber was successfully prepared by using this method.¹⁹ The resulting PE-co-MAA nanofibers possess good thermal and chemical stability due to the polyethylene backbones. The carboxylic acid groups from the methacrylic acid units are available for chemical attachment of various functional groups. Most importantly, the inherent high specific surface area from the open porous structure and ultrafine fiber size of nanofibrous membranes are beneficial for possessing high density of surface functional groups as well as being easily accessible to the incorporation of the macrocyclic porphyrins. Considering these advantages, PE-co-MAA nanofibrous membranes are envisioned as ideal solid media for supporting the photosensitizers.

In this study, PE-co-MAA nanofibrous membranes were prepared and surface functionalized to examine the feasibility as solid support media. Protoporphyrin IX (PPIX), a widely studied photosensitizer to generate singlet oxygen, was selected as a model photosensitizer and covalently immobilized onto the activated PE-co-MAA nanofibrous membranes (Scheme 1). Due to the close adjacency to solid surfaces, the performance of immobilized photoactive molecules could be directly influenced by the nature of the support material.²⁰ Therefore, three diamine spacers with different lengths were employed to anchor PPIX to PE-co-MAA polymer backbones. The catalytic activity of the supported PPIX was evaluated through a photo-oxidation reaction of 1,5-dihydroxynaphthalene in organic solutions with irradiation of visible light. And the effects of spacers, substrate/catalyst ratio, solvent media and oxygen concentration in this catalytic system were also investigated.

Experimental

1. Materials

Poly(ethylene-*co*-methacrylic acid) (PE-*co*-MAA; methacrylic acid 15 wt%), phosphorus pentachloride (PCl₅), thionyl chloride, oxalyl chloride, *N*-hydroxybenzotriazole (HOBt), *N*,*N*-diisopropylethylamine (DIPEA), 1,3-diaminopropane, 1,8-diamine-3,6-dioxaoctane, 4,9-dioxa-1,12-dodecanediamine, protoporphyrin IX (PPIX), 1,5-dihydroxynaphthalene, *O*-(benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HBTU), *N*-(9-fluorenylmethoxycarbonyl)-glycine (Fmoc-Gly-OH) and methyl piperidine were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Cellulose acetate butyrate (CAB; butyryl content 35–39%), carbonyldiimidazole (CDI), diisopropylcarbodiimide (DIC), acetone, acetonitrile (MeCN), dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF), chloroform and tetrahydrofuran (THF) were obtained from Acros Chemical (Pittsburgh, PA, USA). All chemicals were used as received.

2. Fabrication of PE-co-MAA nanofibrous membranes

PE-*co*-MAA nanofibers were prepared according to a previously published procedure.¹⁹ Briefly, CAB as a sacrificial matrix was mixed with PE-*co*-MAA in a blend ratio of CAB/PE-*co*-MAA = 85/15, which was gravimetrically fed into a Leistritz co-rotating twin-screw (18 mm) extruder (Model MIC 18/GL 30D, Nurnberg, Germany) at a feed rate of 12 g min⁻¹. The blends were extruded into composite fibers through a two strand



Scheme 1 Surface functionalization and PPIX immobilization on PE-co-MAA nanofibrous membranes.

(2 mm in diameter) rod die, hot-drawn by a take-up device with a drawing ratio of 25 (the area of cross-section of the die to that of the extrudates) and air cooled to room temperature. And then, PE-*co*-MAA nanofibers were obtained *via* Soxhlet extraction of acetone to remove CAB from the CAB/PE-*co*-MAA composite fiber. The prepared nanofibers were subsequently made into stable suspensions and deposited onto a polyester monofilament fabric as a releasing surface. After evaporation of solvents, the PE-*co*-MAA nanofibrous membrane was formed. The quantification of loading capacity of surface carboxylic acid groups on the prepared membrane was evaluated by an acid/base titration method described before.²¹

3. Surface functionalization of PE-*co*-MAA nanofibrous membranes

Variable activation agents, PCl₅, thionyl chloride, oxalyl chloride, CDI, DIC/HOBt and HBTU, were first used to activate the surface carboxylic acid groups on PE-*co*-MAA nanofibrous membranes, respectively. Typically, 0.2 mmol of PCl₅ was dissolved in 20 mL DCM, and then 40 mg of PE-*co*-MAA nanofibrous membranes was immersed in this solution. This mixture was gently shaken for 4 h at room temperature, and then the resulting membranes were washed with DCM (20 mL \times 3). A similar reaction condition was used for other activation agents except the reaction time for CDI was 12 h.

To attach spacers onto membrane surfaces, 40 mg of the activated membranes were immersed into 20 mL DCM, in which 1 mmol of a diamine spacer was previously dissolved. For the membranes activated by PCl₅, thionyl chloride and oxalyl chloride, 1.5 mmol of DIPEA was also added into the reaction solution. After shaking overnight at room temperature, aminated membranes were washed with DCM (20 mL \times 2), MeCN (20 mL \times 2) and distilled water (20 mL \times 2), and then dried in a vacuum. The prepared membranes from 1,3-diaminopropane, 1,8-diamine-3,6-dioxaoctane and 4,9-dioxa-1,12-dodecanediamine were assigned to PE-*co*-MAA1, PE-*co*-MAA2 and PE-*co*-MAA3, respectively.

The total amount of amine groups on the aminated PE-co-MAA nanofibrous membrane was determined by element analysis of total nitrogen content with the original PE-co-MAA membrane as a control. The quantification of accessible primary amine loading on the membrane surfaces was tested by Fmoc analysis.^{21,22} Specifically, 5 mmol Fmoc-Gly-OH in 20 mL DMF was activated by equal amounts of DIC and HOBt for 30 min at room temperature, followed by adding 50 mg of aminated PE-co-MAA nanofibrous membrane. The mixture was shaken overnight to couple all accessible primary amine on membrane surfaces with N-terminal protected amino acid. At the end of this coupling reaction, the resulting membrane was washed with DMF (20 mL \times 2) and MeCN (20 mL \times 2). After being dried in a vacuum to a constant weight, 50 mg of Fmoc-protected glycine attached dry PE-co-MAA membranes were treated by 10 mL methyl piperidine/DMF solution (volume ratio 1:4) for 4 h, from which 50 µL of the reaction solution was collected and diluted to 4 mL. UV absorbance (300 nm) of the diluted solution was measured with a UV spectrometer (Evolution 600, Thermo, USA). And the primary amine loading was calculated from eqn (1):

Primary amine loading (mmol g⁻¹) =
$$\frac{1000 \times A}{M \times 7800 \times D}$$
 (1)

where A is the UV absorbance, M is the weight of membranes in the unit of mg and D is the dilution factor which is determined as 0.00125 in this study. Meanwhile, the original PE-co-MAA nanofibrous membrane treated under the same procedure was tested as a control.

4. Immobilization of PPIX onto aminated PE-co-MAA nanofibrous membranes

To incorporate photosensitizers onto membrane surfaces, 0.15 mmol of PPIX was first mixed with an equal amount of CDI in 5 mL DMF. The mixture was heated to 60 °C and vigorously shaken for 4 h. Then, 20 mg of the aminated membranes was added, and the reaction continued overnight. After that, the PPIX immobilized membranes were extensively washed with DMF (20 mL \times 3) and MeCN (20 mL \times 3) to remove physically absorbed PPIX and any other unreacted chemical. Element analysis was also used to determine the total nitrogen content of the PPIX immobilized membranes and the loading capacity of immobilized PPIX was calculated from the difference of nitrogen content before and after PPIX immobilization.

5. Characterization

Morphologies of nanofibrous membranes were observed by using a scanning electron microscope (SEM) (XL 30-SFEG, FEI/ Philips, USA) at 5 kV accelerating voltage on gold sputter coated samples. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were measured by a Nicolet 6700 spectrometer (Thermo Fisher Scientific, USA). A laser Raman microscope (Renishaw RM1000) with excitation at 514 nm was used to obtain Raman spectra. A PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) was employed for element analysis. ¹H NMR was measured using an Avance DRX-500 MHz NMR spectrometer (Bruker BioSpin, Billerica, MA) with XWINNMR software (version 3.5). Mass spectrometry analysis was performed with a Waters Micromass ZQ 2000 (ESI-MS) mass spectrometer.

6. Photo-oxidation reactions catalyzed by supported protoporphyrin IX (PPIX)

1 mmol of 1,5-dihydroxynaphthalene was dissolved in 20 mL of MeCN in which oxygen gas was purged for 10 min. According to the desired substrate/catalyst ratio, a certain amount of free or supported PPIX was added into the mixture, respectively, to initiate the photo-oxidation reaction. And the reaction media were irradiated by three 50 W lamps which were filtered by a 410 nm cut filter to shield UV light. The reaction rate was monitored by a UV-vis spectroscope at 420 nm. After the reaction was completed, the supported PPIX was removed and washed thoroughly with MeCN until no substrate in the washing solutions was detected by the measurement of UV-vis absorbance. At the end, the reaction solution and all washing solutions were collected and evaporated, the subsequent residue was separated by flash chromatography on a Combi-flash column (Isco, Inc., Nebraska, USA) with chloroform/MeCN mixture (volume ratio 9 : 1) as an eluent. The resulting oxidative product was characterized *via* ¹H NMR, mass spectra, and FTIR, respectively, and identified as 5-hydroxy-1,4-naphthalenedione. This reaction was also carried out in chloroform or THF to study the solvent effect. Moreover, air gas or nitrogen gas was purged into the reaction solution to study the effect of oxygen concentration. To achieve a reliable result, each test was repeated three times at least and all of the results reported were the average value of the replicated tests.

5-Hydroxy-1,4-naphthalenedione. $m/z = 174 [M + H]^+$; ¹H NMR (500 MHz, CDCl₃)/ppm: 7.59 (1H, d, H-naph.), 7.61 (1H, d, H-naph.), 7.92–7.97 (3H, m, H-naph.), 12.22 (1H, s, OH); FTIR (KBr): 1601 cm⁻¹ (aromatic bond), 1664 and 1640 cm⁻¹ (aromatic ketone).

Results and discussion

1. Preparation of PE-*co*-MAA nanofibrous membrane supported protoporphyrin IX

1.1. Fabrication of nanofibrous membranes. Poly(ethylene-*co*-methacrylic acid) (PE-*co*-MAA), a random copolymer consisting of ethylene and methacrylic acid segments with a weight blend ratio of 85/15, was fabricated into nanofibers by using a recently developed high throughput production process.¹⁷ The resultant nanofibers were dispersed into stable suspensions and then deposited onto releasable substrates to form PE-*co*-MAA nanofibrous membranes. The morphologies of the membrane surfaces were observed *via* SEM, and the results are presented in Fig. 1. The original PE-*co*-MAA nanofibrous membranes possessed an open porous non-woven like structure with uniform and continuous nanofibers. The average diameter of these nanofibers was measured as 210.76 nm. In addition, the unique



Fig. 1 SEM images of original PE-*co*-MAA nanofibrous membranes (a), PPIX immobilized PE-*co*-MAA nanofibrous membranes (b), PPIX immobilized PE-*co*-MAA nanofibrous membranes after 5 repeated cycles of photo-oxidation reactions (c) and the distribution of fiber size of original PE-*co*-MAA nanofibrous membranes (d).

membrane morphology remained intact after photosensitizer immobilization and catalytic photo-oxidation reactions, distinctly shown in Fig. 1(b) and (c), suggesting that PE-co-MAA nanofibrous membranes were chemically stable for surface functionalizations and as support media for catalytic applications.

The amount of carboxylic acid groups from PE-*co*-MAA polymers was calculated as 1.74 mmol g^{-1} based on the weight percentage of methacrylic acid segments. However, the actual surface density of these carboxylic acid groups on PE-*co*-MAA nanofibrous membranes was only around 0.72 mmol g⁻¹, measured by an acid/base titration method. The reduced value was probably due to a result that certain carboxylic acid groups were embedded inside the polymer after the formation of the nanofibrous membranes, leading to only 41.38% of the existing carboxylic acid groups accessible. Also, the hydrophobic nature of PE-*co*-MAA polymer provided unfavorable contact between the membrane surfaces and aqueous solution, enabling some reactive sites inside the membranes undetectable by the titration method mentioned above.

1.2. Activation of nanofibrous membranes. The surface density of reactive sites, their reactivity and accessibility on nanofibrous membranes have major impacts on the efficiency of surface functionalization. To enhance the reactivity of carboxylic acid groups on the surfaces of PE-co-MAA nanofibrous membranes, six activation agents were initially employed to activate the carboxylic acid groups which further reacted with 1,3-diaminopropane. And the activation efficiencies on the acid groups were evaluated based on the amount of resulting primary amines determined by Fmoc analysis. As Fig. 2 shows, PCl₅ was found to be the most effective activation agent, which can efficiently and rapidly convert carboxylic acid into acid chloride, the most reactive acid derivative with amine groups. Thionyl chloride and oxalyl chloride, as agents that can form acid chlorides, also afforded a relatively high amount of primary amine loadings on the membranes in comparison to three other common coupling agents, which proceeded by forming intermediates with the catalysts and then having nucleophilic substitution by amino



Fig. 2 Primary amine loadings of PE-*co*-MAA nanofibrous membranes activated by different activation agents.

groups. Having determined the superior performance of PCl₅, this activation method was used in the following studies.

The direct adjacency of carboxylic acid groups to their polymer backbones leads to steric hindrance from the polymer chain, limiting the accessibility of these reactive sites to macrocyclic porphyrins. The introduction of spacers was a promising strategy to circumvent this drawback.23 In this study, three diamine spacers with various molecular lengths were used to investigate their influence on the surface functionalization and subsequent catalytic performance (Table 1). The chemical structure changes of PE-co-MAA nanofibrous membranes during the activation with PCl₅ and amination with spacers were observed via ATR-FTIR (Fig. 3). The characteristic peak of carboxylic acid groups at 1701 cm⁻¹ from the original membrane disappeared after the activation reaction, instead, the specific peak for acid chloride groups was found around 1798 cm⁻¹. For all three aminated membranes with different spacer chains, two strong peaks appeared at 1641 and 1528 cm⁻¹, assigned to C=O stretching (Amide I) and N-H bending (Amide II), respectively, which indicated the covalent amide linkage between the membrane surfaces and diamine spacers.24 In addition, the new peaks around 1120 cm⁻¹ were assigned to C-O stretching from alkyloxide groups of longer spacer chains. The ATR-FTIR spectra demonstrated the presence of diamine spacers covalently bonded to the membrane surfaces.

To further investigate the effect of the spacers on surface functionalization, the total amounts of amine groups on the aminated PE-co-MAA nanofibrous membranes were assessed via elemental analysis. The total amine loading values from Table 2 were found to be inversely related to the molecular lengths of the used spacer chains, possibly due to the fact that the long spacer chains might have lost reactivity because of potential inter- or intramolecular entanglement. Basically, each activated carboxylic acid group on the membrane surface should react with one end-amine group from each diamine spacer to give one free end-amine group for subsequent reactions. As a result, the amount of the expected primary amine groups can be calculated as half the amount of total amine groups that were reacted on the membranes with values of 0.365, 0.216 and 0.186 mmol g^{-1} for PE-co-MAA1, PE-co-MAA2 and PE-co-MAA3, respectively. However, the measured amounts of accessible primary amine, by the Fmoc analysis, were found to be lower than the ones as expected. Also shown in Table 2, the retention rates (measured primary amine/calculated primary amine) of the primary amines followed the order: PE-co-MAA1 (85.2%) > PE-co-MAA2 (72.6%) > PE-co-MAA3 (70.0%). This was ascribed to the fact of crosslinking effect from the reactions between both two endamine groups and two surface acid chloride groups. And the



Fig. 3 ATR-FTIR spectra of: original PE-*co*-MAA nanofibrous membranes (a), PCl_5 activated PE-*co*-MAA nanofibrous membrane (b), 1,3-diaminopropane aminated membranes (PE-*co*-MAA1) (c), 1,8-diamine-3,6-dioxaoctane aminated membrane (PE-*co*-MAA2) (d), and 4,9-dioxa-1,12-dodecanediamine aminated membrane (PE-*co*-MAA3) (e).

chance of this crosslinking reaction increased with the increment of molecular length of the spacer chains.²⁰

1.3. Covalent immobilization of protoporphyrin IX (PPIX). The utilization of the prepared membranes as solid support media for photosensitizers was demonstrated by using protoporphyrin IX (PPIX). According to Scheme 1, PPIX was covalently attached to the aminated PE-co-MAA nanofibrous membranes via nucleophilic substitution reaction between carboxylic acid groups of PPIX and the primary amine groups on the membrane surfaces. A coupling agent, N,N'-carbonyldiimidazole (CDI), was used to facilitate this reaction by activating the carboxylic acid groups to imidazole carboxylic ester and then enabling the subsequent substitution reaction with the primary amine groups. The resulting PE-co-MAA nanofibrous membrane supported PPIXs with three different diamine spacer lengths, 1,3-diaminopropane, 1,8-diamine-3,6-dioxaoctane and 4,9-dioxa-1,12-dodecanediamne, are referred to as PE-co-MAA-PPIX1, PE-co-MAA-PPIX2 and PE-co-MAA-PPIX3, respectively. Due to the symmetric molecular structure of PPIX,

 Table 1
 Various spacers used for surface activation of PE-co-MAA nanofibrous membranes

Spacers	Chemical structures	Length	Activated membranes	
1,3-Diaminopropane	H ₂ N NH ₂	5 atoms	PE-co-MAA1	
1,8-Diamine-3,6-dioxaoctane		10 atoms	PE-co-MAA2	
4,9-Dioxa-1,12- dodecanediamine		14 atoms	PE-co-MAA3	

 Table 2
 Surface functionalization of PE-co-MAA nanofibrous membranes with spacers and PPIX

Aminated membranes	$\frac{\text{Total amine loading}^a}{\text{mmol g}^{-1}}$	$\frac{\text{Primary amine loading}^{b}}{\text{mmol g}^{-1}}$	$\frac{\text{Retention rate}^{c}}{\%}$	PPIX loading mmol g ⁻¹	$\frac{\text{Yields}^d}{\%}$	Supported photosensitizer
PE-co-MAA2	0.432 ± 0.041	0.157 ± 0.011	72.6	0.063 ± 0.008	40.1	PE-co-MAA-PPIX2
PE-co-MAA3	0.372 ± 0.034	0.139 ± 0.008	70.0	0.067 ± 0.009	48.2	PE-co-MAA-PPIX3
^{<i>a</i>} Total amine loading v amine loading/(total am	vas determined by elementation $\log \log(2)$	ntal analysis. ^b Primary ami ^d Yields = (PPIX loading/i	ine loading was det	termined by Fmo	c analysis.	^c Retention rate = [primary

Raman spectroscopy was used to observe the changes of chemical structures during the PPIX immobilization (Fig. 4). In the case of pure PPIX, two pairs of specific peaks around 1600 and 1350 cm⁻¹ were assigned to the vinyl groups and pyrrole rings from the macrocyclic molecule,^{25,26} respectively, which were not found from the aminated PE-co-MAA nanofibrous membranes. However, the presence of these characteristic peaks from the PPIX immobilized membranes illustrated the successful immobilization of PPIX onto the nanofibers. Also, the quantitative amounts of the immobilized PPIX on the membrane surfaces were evaluated by elemental analysis of total nitrogen atoms (Table 2). In comparison with other aminated membranes, a low value of immobilized PPIX was found for PE-co-MAA1 with the shortest spacer chain in spite of the high value of accessible primary amine groups. This can be related to the possibility that, due to the close proximity of primary amine groups to the membrane surfaces, high steric hindrance blocked the approach of the macrocyclic compound, PPIX, to these reactive sites, leading to low reaction efficiency. In contrast, the amounts of



Fig. 4 Raman spectra of pure PPIX (a), PPIX immobilized on 4,9dioxa-1,12-dodecanediamine aminated membrane (PE-*co*-MAA-PPIX3) (b) and 4,9-dioxa-1,12-dodecanediamine aminated membrane (PE-*co*-MAA3) (c).

immobilized PPIX significantly enhanced by using longer spacers, and the values were about 0.063 and 0.067 mmol g⁻¹ for PE-*co*-MAA2 and PE-*co*-MAA3, respectively. Furthermore, the reaction efficiency of the primary amines on the membrane surfaces also improved proportionately to the increase of chain length of the three used spacers. These results further revealed that a longer spacer chain was preferred for the immobilizations of the macrocyclic molecule onto the surfaces of the nanofibrous membranes.

2. Photo-oxidation reactions catalyzed *via* the supported protoporphyrin IX (PPIX)

2.1. Photo-oxidation of 1.5-dihydroxynaphthalene. It has been reported that PPIX as an organic photosensitizer is capable of catalyzing photo-oxidation reactions by efficiently generating singlet oxygen under light exposure.27 In this study, the catalytic performances of free PPIX and PE-co-MAA nanofibrous membrane supported PPIX were investigated based on the photo-oxidation of 1,5-dihydroxynaphthalene, which involves 1,4-cycloaddition of singlet oxygen onto a phenyl ring and of the corresponding 5-hydroxy-1,4-naphproduction thalenedione⁸ (Scheme 2). The UV-Vis absorbance spectra of 1,5-dihydroxynaphthalene in the presence of the supported photosensitizer, PE-co-MAA-PPIX3 (substrate/catalyst molar ratio 100:1), under irradiation of a visible light source as a function of exposure time are presented in Fig. 5. The intensities of three major peaks from 1,5-dihydroxynaphthalene, 298, 316 and 330 nm, gradually decreased with correspondingly increased intensities of new peaks around 249 and 428 nm, which are the characteristics of the oxidized product. Therefore, the completion of this reaction was determined to be when the peak intensity at 428 nm ceased increasing. After 9 h of irradiation, the three original peaks from 1,5-dihydroxynaphthalene totally disappeared, and the color of the reaction solution changed from light pink to yellow. And then, the oxidized product was isolated, characterized and identified as 5-hydroxy-1,4-naphthalenedione,



1,5-dihydroxynaphthalene

5-hydroxy-1,4-naphthalenedione

Scheme 2 Photo-oxidation reaction of 1,5-dihydroxynaphthalene catalyzed by photosensitizers in the presence of oxygen and light irradiation.



Fig. 5 UV-vis spectra of 1,5-dihydroxynaphthalene in MeCN during the photo-oxidation reaction catalyzed by PE-*co*-MAA-PPIX3. The inset presents the color difference of the reaction media before and after the photo-oxidation reaction.

which was consistent with the literature.^{8,28} Furthermore, no product was found after 24 h of irradiation by using the original PE-*co*-MAA nanofibrous membrane as a blank experiment.

2.2. Effect of spacers, substrate/catalyst ratio, solvent media and oxygen concentration. The influence of spacers on catalytic activities of the supported PPIX was investigated by comparing the isolated yields of the oxidized product and the reaction time under the same conditions, and the results are illustrated in entries 1 to 4 in Table 3. Among all the supported photosensitizers, PE-co-MAA-PPIX3 containing the longest spacer exhibited the highest catalytic activity, with the performance comparable to unbound PPIX. In addition, as the spacer chain length decreases, reduced yield of the oxidized product, 5-hydroxy-1,4-naphthalenedione, and prolonged irradiation time to complete the photo-oxidation reaction were observed. For PE-co-MAA-PPIX1 with the shortest spacer arm, it took almost 20 h to reach the final yield of around 75%. Such a low activity indicated that the catalytic function of the supported PPIX was mainly dependent on the distinct structures of spacers.

Longer spacer chains enable the surface immobilized photosensitizers to act with a higher freedom, which is more similar to their free analogues in reaction solutions. Therefore, PE-*co*-MAA-PPIX3 with the highest catalytic activity was employed for further explorations.

The effect of substrate/catalyst molar ratio was further studied by adjusting the value at 500 : 1 and 1000 : 1 (entries 5 and 6, Table 3). As expected, lower yields of the oxidized product and longer time required to finish the photo-oxidation reaction were found. Furthermore, the solvent systems could have an impact on the photo-oxidation reactions, including varied oxygen solubility and different lifetimes of generated singlet oxygen.²⁹ Solvents could also swell the solid matrix and enhance contact between the supported photosensitizers with reaction media, leading to an improved catalytic performance.³⁰ Three organic solvents were used in this study in which both oxygen solubility and singlet oxygen lifetimes followed the order: chloroform > MeCN > THF. As shown in entries 4, 7 and 8 in Table 3, the solvent with the most powerful catalytic effect was chloroform, in which more than 99% of the reaction yield was achieved within 8 h. However, the solid supported photosensitizer in THF exhibited significantly lower catalytic activity than the ones observed in the other two solvents. Although chloroform and THF are more favorable to the hydrophobic PE-co-MAA nanofibrous membranes than MeCN, the remarkable difference of catalytic performances of PE-co-MAA-PPIX3 in these three solvent systems suggested that the oxygen solubility and singlet oxygen lifetimes were the predominant factors influencing this photo-oxidation reaction. Due to the oxygen involved reaction mechanism, the effect of oxygen concentration was also studied by purging pure oxygen, air and nitrogen to the reaction media, respectively (entries 4, 9 and 10 in Table 3). The dramatically reduced reaction rates and yields with the decrease of oxygen concentration indicated the crucial importance of oxygen in this

Table 4 Reusability of supported PPIX for photo-oxidation of 1,5-dihydroxynaphthalene^a

Running time	1 st	2^{nd}	$3^{\rm rd}$	4^{th}	5 th
Isolated yields (%)	97	96	93	89	80
Reaction time (h)	9	10	12	12	13

^{*a*} Photosensitizer: PE-*co*-MAA-PPIX3; substrate/photosensitizer ratio: 100/1; solvent: MeCN purged with oxygen.

 Table 3
 Photo-oxidation of 1,5-dihydroxynaphthalene catalyzed by free and supported PPIX

Entry	Photosensitizers	$R = n_{\rm s}/n_{\rm c}^{\ a}$	Solvent	Isolated yields (%)	Reaction time (h)	
1 ^b	DDIV	100 • 1	MeCN	00	5	
2^{b}	PE-co-MAA-PPIX1	100.1 $100 \cdot 1$	MeCN	75	20	
$\overline{3}^{b}$	PE-co-MAA-PPIX2	100 : 1	MeCN	93	11	
4^b	PE-co-MAA-PPIX3	100:1	MeCN	97	9	
5^b	PE-co-MAA-PPIX3	500:1	MeCN	82	11	
6^b	PE-co-MAA-PPIX3	1000:1	MeCN	61	18	
7^b	PE-co-MAA-PPIX3	100:1	Chloroform	97	6	
8^b	PE-co-MAA-PPIX3	100:1	THF	36	24	
9 ^c	PE-co-MAA-PPIX3	100:1	MeCN	46	20	
10^d	PE-co-MAA-PPIX3	100:1	MeCN	17	24	

^{*a*} Molar ratio of substrates and photosensitizers. ^{*b*} Reaction media were previously purged with oxygen. ^{*c*} Reaction media were previously purged with air. ^{*d*} Reaction media were previously purged with nitrogen.

photo-oxidation reaction, similar to the findings in the literature.³¹

2.3. Stability and reusability of supported PPIX. The solid supported photosensitizers offer several advantages in catalytic reactions in comparison with the use of the free agents, including easy handling, simple recovery, and reusability for continuous processes. In this study, PE-co-MAA-PPIX3, after one catalytic reaction, was washed extensively and dried in a vacuum, followed by immersing into another freshly prepared 1,5-dihydroxynaphthalene for repeated catalytic reactions. Table 4 shows that the yields of the oxidized product slightly decreased while the reaction time gradually increased to complete the reaction as the repetition of experiments continued, similar but better than the results of the silica bead supported porphyrins.³¹ The probable reason for the inactivation of the supported PPIX is the degradation of the macrocyclic rings during the photo-oxidation reaction, as reported.³² However, up to 5 repeated catalytic reactions were tested; the PE-co-MAA nanofibrous membrane supported photosensitizer still provided 80% catalytic efficiency, proving it is durable and reusable for photo-oxidation reactions.

Conclusion

By using melt extrusion, dispersion and depositing processes, PEco-MAA nanofibrous membranes with uniform nanofibers and open porous structure were prepared. Activated with PCl₅, the membranes were incorporated with diamine spacers with variable lengths to provide free amino groups for covalent linking with protoporphyrin IX (PPIX), a model photosensitizer. The catalytic performance of PE-co-MAA nanofibrous membrane supported PPIX was evaluated based on photo-oxidation reactions of 1,5-dihydroxynaphthalene. The length of spacer chains affected the loading capacity of PPIX on membrane surfaces and the catalytic activity of the supported PPIX. The supported PPIX still possessed 80% catalytic efficiency after 5 repeated experiments. These results indicated that the nanofibrous membrane supported photosensitizer exhibited high catalytic activity, easy handling, good durability and reusability.

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