Electrostatic Assembly of Porphyrin-Functionalized Porous Membrane toward Biomimetic Photocatalytic Degradation Dyes

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ABSTRACT: Porphyrin-based catalytic oxidation is one of the most representative biomimetic catalysis. To mimic the biomimetic catalytic oxidation of nature, a positive charged porous membrane, quaternized polysulfone (QPSf) membrane with spongelike structure, was prepared for supporting meso-tetraphenylsulfonato porphyrin (TPPS). The influence of polymer concentration, coagulation bath, and additives on the structure of the substrate membrane was explored, and the optimized membrane with porosity of 87.1% and water flux of 371 L·m⁻²·h⁻¹ at 0.1 MPa was obtained. Monolayer TPPS was adsorbed on the QPSf membrane surface by the electrostatic self-assembly approach, and the adsorption process followed the pseudo second-order kinetic model and Langmuir adsorption isotherm equation. The resulting TPPS@QPSf membrane showed excellent visible light response, and the photocatalytic performance for dyes was then enhanced dramatically after TPPS was immobilized on the membrane. The removal efficiencies for rhodamine B (RhB), methylene blue (MB), and methyl orange (MO) were 92.1, 94.1, and 92.1% under visible light irradiation, respectively. The primary photocatalytic degradation of the dye was a zero-order reaction, and the secondary reaction of degradation followed pseudo first-order kinetics. Finally, the TPPS@QPSf membrane can be reused for photocatalytic degradation of RhB for 10 cycles with no obvious change on removal efficiency, which indicated that this membrane is a promising material for dyeing water treatment coupled with visible light irradiation.

1. INTRODUCTION

The discharge of refractory organic dyes, which possess high resistance to microbial degradation, has been a great challenge for the traditional water treatment.¹ As an advanced treatment method, photocatalysis oxidation aroused broad attention in water treatment owing to its powerful oxidation ability and environmental compatibility.² TiO₂ is an extensively investigated photocatalyst due to its distinct photocatalytic efficiency, high stability, low cost, and nontoxicity.³ However, because of the wide band gap (3.0−3.2 eV),⁴ TiO₂ mainly was stimulated by UV light, and the high recombination rate of photogenerated hole−electron pairs lowers the quantum efficiency of photocatalytic processes.⁵ In addition, nanostructured TiO₂ photocatalysts were usually used in a suspension system, which resulted in difficult recovery from the treated water.⁶⁻⁷

As well known, functional photosensitizers, porphyrin and its derivatives, have high molar extinction coefficients in the region of visible light. The extensive system of delocalized π electrons results in very strong absorption in the visible region, including an intense absorption of the Soret band (400−450 nm) and four weak Q bands (500−650 nm).⁸⁻⁹ Therefore, porphyrins and their metal complexes have been used as photocatalysts irradiated by visible light.¹⁰⁻¹² For example, Kim et al.¹³ studied the photocatalytic activities of tin porphyrin under visible light and the photocatalytic activities were demonstrated successfully by the degradation of acid orange 7 and 4-chlorophenol in water. Liu et al. prepared two-dimensional (2D) and three-dimensional (3D) porphyrin-functionalized materials, such as diporphyrin honeycomb film (composed of titanium dioxide, protoporphyrin IX, and hemin),¹⁴ hemin-functionalized graphene hydrogel,¹⁵ and 5,10,15,20-tetrakis(4-carboxylphenyl) porphyrin-sensitized graphitic carbon nitride nanosheets.¹⁶ They also studied the photoelectrochemistry and photodegradation toward dyes. Moreover, porphyrins were also investigated as a sensitizer of TiO₂, which extended the absorption of TiO₂ to the visible

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region, enhanced interfacial charge transfer, and lowered the electron–hole recombination rate.\textsuperscript{17,18}

Although excellent photocatalytic performance was proved, the application of porphyrin was limited due to the aggregation of free porphyrin in the solution and the difficulty of recovery from the reaction mixture.\textsuperscript{13} Therefore, porphyrin and its derivatives loading on porous substrates had been the focus for practical use.\textsuperscript{19–25} For example, Daoud et al.\textsuperscript{23} reported a copper(II) porphyrin (\textit{meso}-tetra(4-carboxyphenyl)-porphyrinato, TCP) and TiO\textsubscript{2} complex, which was supported by cotton fabric. They found that methylene blue, stains of coffee, and wine were degraded by the cotton fabrics supported CuTCP/TiO\textsubscript{2} under visible light irradiation. In a previous work, \textit{meso}-tetraphenylsulfonato porphyrin (TPPS) was loaded on porous membranes, such as quaternized polysulfone (QPSf) membrane, ethylenevinyl alcohol graft poly(2-(dimethylamino)ethylmethacrylate) membrane, and also pH-responsive polysulfone graft poly(4-vinylpyridine) membrane.\textsuperscript{25–26} The supramolecular self-assembly and supramolecular chirality of TPPS was observed on these membranes. However, it was also found that the fluorescence intensity was decreased, which restricted the photocatalytic activity of porphyrin. Therefore, monolayer porphyrin on the solid substrates may be the key of the photocatalytic performance.

The aim of this work is to present a novel monolayer porphyrin-assembled porous membrane for dye degradation under irradiation of visible light. First, a polymer membrane with spongelike pores was fabricated from quaternized polysulfone (QPSf) membrane, ethylenevinyl alcohol graft poly(2-(dimethylamino)ethylmethacrylate) membrane, and also pH-responsive polysulfone graft poly(4-vinylpyridine) membrane.\textsuperscript{25–26} The supramolecular self-assembly and supramolecular chirality of TPPS was observed on these membranes. However, it was also found that the fluorescence intensity was decreased, which restricted the photocatalytic activity of porphyrin. Therefore, monolayer porphyrin on the solid substrates may be the key of the photocatalytic performance.

The XPS spectrum of CMPSf (Figure 1c), another new emission peak was found at 400 eV, which was ascribed to N 1s, and O 1s, respectively. In the XPS spectrum of QPSf (Figure 1c), another emission peak was found at 200 eV, which was ascribed to Cl 2p. This result suggested that chloromethyl group (CH\textsubscript{2}Cl) was introduced onto PSF by chloromethylation. In the XPS spectrum of QPSf (Figure 1c), another new emission peak was found at 400 eV, which was ascribed to N 1s. These results further confirmed that quaternized polysulfone was obtained.

2. RESULTS AND DISCUSSION

2.1. Chemophysical Characterization of QPSf. The chemical structure of QPSf was confirmed by X-ray photoelectron spectroscopy (XPS), and the XPS spectra of QPSf as well as PSf and chloromethylated polysulfone (CMPSf) are shown in Figure 1. It can be seen from Figure 1a (XPS spectrum of PSf) that three major emission peaks (167.4, 284.8, and 531.9 eV) were found, which were assigned to S 2p, C 1s, and O 1s, respectively. In the XPS spectrum of CMPSf (Figure 1b), a new emission peak at 200 eV was found, which was ascribed to Cl 2p. This result suggested that chloromethyl group (CH\textsubscript{2}Cl) was introduced onto PSF by chloromethylation. In the XPS spectrum of QPSf (Figure 1c), another new emission peak was found at 400 eV, which was ascribed to N 1s. These results further confirmed that quaternized polysulfone was obtained.

2.2. Preparation of QPSf Membrane. 2.2.1. Influence of Polymer Concentration. Polymer concentration is an important parameter for fabricating membrane by the NIPS method.\textsuperscript{27} The influences of QPSf polymer concentration on morphology of the membrane are shown in Figure 2. It can be seen that a dense top surface was obtained for all polymer concentrations from 14.0 to 22.0 wt %. On the contrary, open pores were found obviously on the bottom surface of the membrane, the pore size of which decreased with increase of polymer concentration. Furthermore, fingerlike holes could be found on the cross section when the polymer concentration was lower than 16.0 wt %, while spongelike pores were obtained at a polymer concentration higher than 16.0 wt %. The reason is that the pore structure of the membrane was directly affected by the viscosity of the casting solution. Generally, a higher viscosity was obtained at a higher concentration of polymer, which results in a delayed demixing.\textsuperscript{28} Under the driving force of a concentration gradient, slow mutual diffusion occurred between the solvent and nonsolvent during phase inversion delayed demixing.\textsuperscript{29} Therefore, the fingerlike pores in the polymeric membranes were totally substituted by the spongelike pores with increasing polymer concentration higher than 16.0 wt %. The delayed demixing resulted in a small pore size and reduced porosity.\textsuperscript{30} As a result, the pure water flux declined from 498.4 to 139.9 L·m\textsuperscript{–2}·h\textsuperscript{–1} with an increase of polymer concentration from 14 to 22 wt % (Figure 3).

2.2.2. Effect of Coagulation Bath. Thermodynamics and kinetics are two dominating mechanisms that control the formation of polymeric porous membrane by NIPS. Therefore, the composition of the coagulation bath and temperature often play an important role in the structure of the obtained membrane.\textsuperscript{31,32} As a green-friendly nonsolvent, water was used as the main coagulation bath for membrane formation. However, macroporous and fingerlike pores were obtained due to the instantaneous demixing in water. Therefore, ethanol or DMAC was introduced into the coagulation bath to control the structure of membrane, respectively.

The polarity of the nonsolvent was reduced when ethanol was added into water, which led to a change of phase separation from instantaneous demixing to delayed demixing. The delayed demixing process often resulted in a more spongelike structured membrane, as shown in Figure 4a. A dense skin layer was obviously obtained, and the thickness of the dense layer gradually decreased from 6.20 to 4.10 μm. Similarly, spongelike structured membranes were also obtained when a DMAC/water mixture was used as the coagulation bath. This was because the difference between solvent (DMAC) and nonsolvent (DMAC/water) diminished.

![Figure 1. XPS survey spectra: (a) PSF, (b) CMPSF, and (c) QPSf.](https://dx.doi.org/10.1021/acsomega.0c00135)
When DMAc was added into water, more spongelike pores were obtained with increase of DMAc content in the coagulation bath (Figure 4d), and the thickness of the membrane increased gradually (Figure 4c).

The effects of coagulation bath on the permeation of membrane are shown in Figure 5. The pure water flux increased slightly on increasing ethanol or DMAc content in water, and the flux of the membrane coagulated in ethanol/water was much higher than that in DMAc/water. Therefore, ethanol/water (50 wt %) was used as the coagulation bath in the following experiment.

2.2.3. Effect of Additive. Additive is another factor that controls the morphology and structure of polymer membrane. Typical inorganic additives include LiCl and ZnCl₂, and typical polymer additives include poly(ethylene glycol) (PEG) and poly(vinylpyrrolidone) (PVP). Because of their high solubility when DMAc was added into water. More spongelike pores were obtained with increase of DMAc content in the coagulation bath (Figure 4d), and the thickness of the membrane increased gradually (Figure 4c).

The effects of coagulation bath on the permeation of membrane are shown in Figure 5. The pure water flux increased slightly on increasing ethanol or DMAc content in water, and the flux of the membrane coagulated in ethanol/water was much higher than that in DMAc/water. Therefore, ethanol/water (50 wt %) was used as the coagulation bath in the following experiment.
in nonsolvent (usually water) and good miscibility with polymers, PEGs are widely used in preparing polymer membranes by NIPS. In this work, PEG-20000 was used and the effects of PEG-20000 on composite membrane morphologies are shown in Figure 6. It was found that the spongelike structure (cross section) of membrane was obtained. As shown in Figure 6, the micropores increased initially and decreased afterward, while the thickness of the dense layer gradually increased from 5.30 to 6.40 μm with increasing PEG-20000 content from 4 to 16 wt %. The reason can be explained by the two main mechanisms, thermodynamic stability and dynamics stability, which control the structure of membrane. As an additive, PEG reduced the compatibility of the mixtures in a casting solution, which resulted in the decrease of thermodynamic stability. On the contrary, the additive improved the viscosity of the casting solution, which led to dynamics stability of the casting solution. The phase separation process was controlled by the thermodynamic stability when the content of PEG was lower than 12 wt %. As a result, the porosity of the membrane increased from 84.6 to 87.1% with increasing PEG content from 4 to 12 wt % (Figure 7). However, it decreased to 77.6% when the PEG content was further increased to 16 wt %. This was because the phase separation process was restrained by the dynamics stability. The rapid diffusion between solvent and nonsolvent was reduced. Consequently, the spongelike structure with high porosity was substituted by a dense layer on both surfaces, as shown in Figure 6d. What is more, the increase of thickness of the dense layer further indicated the

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**Figure 4.** FE-SEM images of QPSf membranes from various coagulation baths (a) cross section of ethanol/water (ethanol content 10, 30, and 50 wt %), (b) upper cross section of ethanol/water (ethanol content 10, 30, and 50 wt %), (c) cross section of DMAc/water (DMAc content 10, 30, and 50 wt %), and (d) middle cross section of DMAc/water (DMAc content 10, 30, and 50 wt %).

**Figure 5.** Effect of coagulation bath on the permeation of the QPSf membrane.
transformation phase separation process from thermodynamic stability to dynamics stability. The influence of PEG content on pure water flux of the QPSf membrane is also shown in Figure 7. The pure water flux decreased from 548 to 327 L·m⁻²·h⁻¹ with increasing PEG content from 4 to 16 wt % in the casting solution. According to the above results, a PEG content of 4 wt % was used in the following sections.

2.3. Adsorption and Characterization of TPPS on QPSf Membrane.

2.3.1. Adsorption of TPPS on QPSf Membrane. The electronegative TPPS was immobilized on positive charged QPSf membrane by electrostatic interaction, and the FE-SEM images of the obtained TPPS@QPSf membrane are shown in Figure 8a,b. It can be seen that there are no visible aggregates on the surface and the cross section of the TPPS@QPSf membrane. Comparing with Figure 6a, no obvious changes on membrane structure were found. The pure water flux and porosity were 532 L·m⁻²·h⁻¹ and 84.0%, which were similar to the control QPSf membrane, as described in Section 2.2.3 (PEG content 4%). These results suggested that the membrane pores were not blocked and no large aggregates formed on the membrane.

The adsorption kinetics of TPPS on QPSf membrane was investigated as shown in Figure 8c. It can be seen that the adsorption capacity increased dramatically at the first 180 min; then, it reached a plateau. The fitting parameters of the adsorption kinetics are listed in Table 1. As shown, the pseudo second-order model presented a higher value of $R^2$ than that of the pseudo first-order model. The calculated $Q_e$ was consistent with the actual values from experiments. These results indicated that the adsorption kinetic model of pseudo second order was more appropriate for the adsorption process of TPPS on QPSf membrane.

The adsorption thermodynamic of TPPS on QPSf membrane was also investigated, as shown in Figure 8d.

Figure 6. FE-SEM images of QPSf membranes with various concentrations of PEG (a) 4 wt %, (b) 8 wt %, (c) 12 wt %, and (d) 16 wt %.

Figure 7. Effect of PEG content on pure water flux and porosity of the QPSf membrane.
was found that the adsorption capacities of TPPS increased linearly to 30 mg·g⁻¹ on increasing the equilibrium concentration of TPPS. Afterward, it reached the maximum immobilization and the maximum adsorption capacity was about 39 mg·g⁻¹. The Langmuir isothermal adsorption model and Freundlich adsorption model were used to characterize the adsorption thermodynamic process, and the resulting parameters are presented in Table 2; the Langmuir constant $K_L$ was 13.82 mg·L⁻¹ and the calculated maximum adsorption capacity $Q_m$ was 40.84 mg·g⁻¹, which was in agreement with the experiment result. The regression coefficient $R^2$ for the Langmuir model and Freundlich model were 0.9924 and 0.8487, respectively. This indicates that the Langmuir isothermal adsorption model yields a relatively good fitting and the TPPS adsorption on QPSf membrane was monolayer adsorption immobilization.

The desorption of TPPS from the TPPS@QPSf membrane was carried out to illustrate the stability of TPPS on QPSf membrane. The TPPS@QPSf membrane was immersed in deionized water, and the concentration of TPPS (desorbed from TPPS@QPSf membrane) was determined by UV spectra. The desorption amount (DA) and desorption efficiency (DE) were calculated from eqs 1 and 2.

$$\text{DA} = \frac{C_t \times V_3}{m_2}$$

$$\text{DE} = \frac{\text{DA}}{Q} \times 100\%$$

where $C_t$ is the concentration of TPPS at a given time (mg·L⁻¹), $V_3$ is the volume of DI water, $m_2$ is the mass of membrane (g), and $Q$ is the adsorption capacity of TPPS on QPSf membrane (mg·g⁻¹). The desorption efficiency of TPPS was only 2.72% after the TPPS@QPSf membrane was soaked in DI water for 5 h, and it hardly increased after being soaked for 72 h. These results indicate that TPPS was adsorbed strongly on the QPSf membrane by electrostatic interaction and positive charged QPSf membrane is an excellent support for electronegative TPPS.

2.3.2. Characterization of TPPS@QPSf Membrane. The UV–vis diffuse reflectance adsorption spectra of the TPPS@QPSf membrane and control QPSf membrane are shown in Figure 9a. To illustrate the assembly behavior of TPPS on QPSf membrane, the UV–vis spectra of TPPS in an aqueous solution at pH 7.0 and 1.0 are also presented. As can be seen, there were no adsorption peaks in the visible light region for the pristine QPSf membrane. However, strong adsorptions
were found for the TPPS@QPSf membrane from 300−700 nm and the characteristic absorption peaks of Soret and Q bands of TPPS were observed on the membrane surface. This result suggested that TPPS was immobilized on the QPSf membrane successfully.

Interestingly, in the UV−vis spectra of TPPS@QPSf membrane, a broadened Soret band and four strong Q bands attracted our attention. Generally, a sharp peak of the Soret band at 413 nm and four very weak Q bands at 517, 553, 592, and 634 nm can be found for free TPPS at pH 7.0, as shown in Figure 9a. While the Soret band shifted from 413 to 434 nm, the Q band shifted to 595 and 644 due to the protonated porphyrin at pH 1.0 in an aqueous solution.35 Two new Soret bands at 490 and 708 nm appeared in Figure 9a, which resulted from the formation of J aggregates (side-by-side type self-assembly of TPPS). However, as shown in Figure 9a, four strong peaks appeared at 517, 553, 591, and 634 nm, which suggested that the porphyrin on the membrane surface was mainly monomer.36 The monodispersed porphyrins on the porous membrane substrate are desirable for the photocatalytic performance of TPPS under visible light irradiation.37

The adsorption of TPPS on QPSf membrane was further confirmed by determining the electrical properties (ζ-potential) of the membrane surface before and after adsorption. The results are shown in Figure 9b. As shown, the value of ζ-potential ranges from 9.68 to −9.58 mV for the original QPSf membrane as the pH varies from 3.0 to 10.0. The negative charged QPSf membrane is ascribed to the strong negative charge of the PSF substrate.38,39 While for the TPPS@QPSf membrane, it becomes more negative (from 3.57 to −22.45 mV) after TPPS is immobilized on the membrane surface. These results further confirmed that TPPS was immobilized on the QPSf membrane.

2.4. Photocatalytic Degradation Performance of TPPS@QPSf Membrane. 2.4.1. Photocatalytic Degradation of RhB. Batch photocatalytic degradation experiments were applied to evaluate the photocatalytic activities of free-based TPPS and the as-prepared TPPS@QPSf membrane, and the results are shown in Figure 10. It can be seen from Figure 10a that the concentration of RhB was not changed under the irradiation of visible light without photocatalyst, which indicated the stability of RhB. However, the absorbance decayed with increasing irradiation time when it was catalyzed by the TPPS@QPSf membrane under visible light irradiation, as shown in Figure 10b, which suggested that the removal efficiency of RhB increased continuously. It can be seen from Figure 10a, the removal efficiency of RhB was about 10.3% in the first 30 min (without visible light irradiation), which was due to the adsorption of RhB on the TPPS@QPSf membrane, while the removal efficiency increased rapidly under the irradiation of visible light and the final removal efficiency was up to 92.1% after 300 min. For comparison, the degradation of RhB was also carried out in a homogeneous reaction using the TPPS solution. It was found from Figure 10a that only about 40% RhB was removed under visible light irradiation for 300 min. This low removal efficiency may be due to the
aggregation of porphyrin, which usually results in the decrease of photoresponse performance.\textsuperscript{40} This result suggested that the photocatalytic performance of TPPS was aroused tremendously after it was immobilized on the QPSf membrane. This is attributed to the strong photoresponse in the visible range of the dispersed immobilized TPPS on the membrane surface, as illustrated in Section 2.3.2.

The initial RhB concentration affected the photocatalytic degradation significantly, and the results are shown in Figure 11a. It was clearly observed that the removal efficiency reduced on increasing the initial concentration of RhB. The removal efficiency was 92.1\% at a concentration of 10 mg L\(^{-1}\), while it reduced to 79.6\% on increasing the initial concentration of RhB to 16 mg L\(^{-1}\). What’s more, it was observed that the removal efficiency increased linearly with irradiation time and a turning point was found after 180 to 240 min at various initial concentrations of RhB, which indicated the change of the kinetic model, as is to be discussed in Section 2.5.

The stability and reusability performance are key characters of catalysts for practical application. The recycling experiments of the TPPS@QPSf membrane were carried out after the used membrane was rinsed by DI water, and the results are shown in Figure 11b. As can be seen from Figure 11b, there was no obvious change in the removal efficiency (>90\%) after the membrane was used for 10 cycles. These results indicated that TPPS was immobilized on the membrane firmly and the
TPPS@QPSf membrane can be reused for the next degradation experiment.

2.4.2. Photocatalytic Degradation for Other Dyes. The resultant TPPS@QPSf membrane can also be used for effective degradation of methylene blue (MB) and methyl orange (MO), and the comparison results are shown in Figure 12. Herein, the initial concentration of each dye was 10 mg·L⁻¹. As shown in Figure 12a,b, the absorbance decayed with increasing irradiation time when they were catalyzed by the TPPS@QPSf membrane, which suggested that the removal efficiencies of MB and MO kept increasing continuously. As shown in Figure 12c, the first 30 min (without visible light irradiation) was for the adsorption of dyes on the membrane surface. It was found that about 10.8 and 7.6% of MB and MO were adsorbed on the TPPS@QPSf membrane. However, the removal efficiencies of the two dyes increased rapidly when they were irradiated by visible light and the final removal efficiencies for MB and MO were 94.1 and 92.1% after irradiation for 200 and 300 min, respectively. Therefore, the TPPS@QPSf membrane can be used for various dye degradations when coupled with visible light irradiation.

2.5. Kinetics of Photodegradation by TPPS@QPSf Membrane. To determine the kinetics of photodegradation, the relationships between Cₜ and irradiation time or ln(C₀/Cₜ) and irradiation time are plotted as shown in Figure 13. It was found that the degradation process can be divided into two stages. Taking the degradation of RhB (10 mg·L⁻¹) as an example, the linear relationship between Cₜ and time in the first stage (t < 180 min as shown in Figure 13a) illustrated that the degradation of RhB was a zero-order reaction and the reaction rate constant for the zero-order reaction was 3.3 × 10⁻² mg·L⁻¹·min⁻¹, while in the second stage (t > 180 min), the linear relationship between ln(C₀/Cₜ) and t (min) suggested that the reaction rate constant was 1.2 × 10⁻² min⁻¹.

These results can be explained by the primary reaction and secondary reaction of photochemistry. First, the photodegradation took place on the membrane surface. Second, the adsorption and desorption of dye molecules on the membrane surface followed a fast equilibrium in the first stage with a high level of RhB concentration. In this case, the fraction of surface coverage was kept a constant. According to the Langmuir–Hinshelwood equation (eq 3), the reaction rate (−dCᵣ/dt) was a constant. Third, the concentration of RhB reduced after irradiation for 200 min and the surface diffusion process became the rate-determining step. Therefore, the reaction rate equation can be written as eq 4, and it can be transformed into eq 5 at a very low concentration of RhB. As a result, ln(C₀/Cₜ) had a linear relationship with irradiation time, which demonstrated that the secondary process was a pseudo first-order reaction.

\[ \frac{dC}{dt} = k_d \theta \]  
\[ \frac{dC}{dt} = k \theta = \frac{kbC_t}{1 + bC_t} \]  
\[ \frac{dC}{dt} \approx kbC_t = k_{app}C_t \]  

where Cₜ was the RhB concentration at time t, kₒ is the rate constant for zero order, b is the adsorption constant of Langmuir, and k₂ₚp is the apparent rate constant for the first order.

Similarly, the degradation kinetics of MB and MO also contained two processes, as shown in Figure 13b,c. The reaction rate constants of the primary reaction were 4.3 × 10⁻² and 7.6 mg·L⁻¹·min⁻¹ for degradation of MB and MO,
respectively, and the reaction rate constants of the secondary reaction for each were $1.1 \times 10^{-2}$ and $1.6 \times 10^{-2}$ min$^{-1}$.

2.6. Degradation of RhB by Photocatalysis Coupling with TPPS@QPSf Membrane Reactor. In industrial application, cross-flow filtration was widely applied owing to the alleviated membrane fouling by shear force. Therefore, the photocatalytic degradation of RhB was further carried on by the cross-flow filtration coupling with visible light irradiation. In the cross-flow filtration process, the transmembrane pressure was held at around $5 \times 10^{-3}$ MPa to provide sufficient contact time between RhB molecules and TPPS@QPSf membrane. As shown in Figure 14, $C_t/C_0$ in the permeate solution increased from 0.84 to 0.96 in the first 60 min when QPSf membrane was equipped in the photocatalytic membrane reactor (PMR). $C_t/C_0$ less than 1.0 was due to the adsorption of RhB on the membrane. Furthermore, $C_t/C_0$ remained 0.99, which indicated that there was almost no rejection for RhB and also no RhB degradation by QPSf membrane without immobilization of TPPS. On the contrary, $C_t/C_0$ was less than 0.10, which indicated that RhB in the permeate solution was degraded by PMR when the TPPS@QPSf membrane was equipped in PMR. The RhB removal efficiency remained around 93.0% for 300 min in the permeate under visible light irradiation. Furthermore, the total organic carbon (TOC) value was measured to evaluate the removal of RhB by photocatalysis coupling with TPPS@QPSf membrane filtration. However, the TOC removal ratio in the permeate was only 21.5%. This result indicated that partial mineralization of RhB took place during the degradation by the TPPS@QPSf membrane, which we will discuss in Section 2.7. The low TOC removal ratio can be explained as follows: On the one hand, the mineralization could only occur before the solution was discolored, as discussed in the literature, because no substrates could be excited under irradiation of visible light after the solution was discolored completely. On the other hand, the degraded RhB solution penetrates the membrane and no further degradation occurs because of no contact with the catalyst (TPPS@QPSf membrane).

2.7. Photocatalysis Degradation Mechanism of RhB. To expound the photocatalysis degradation mechanism of RhB, gas chromatography mass spectrometry (GC-MS) was used to detect the components in the permeate after degradation. The results are shown in Table 3. It can be seen from Table 3 that the degradation products mainly include benzoic acid and phenols, polyhydric fatty acids, and short-chain polyhydroxy alcohols. The degradation process can be described as follows: Photogenerated electron ($e^-$) and hole ($h^+$) pairs were generated when porphyrins on the membrane surface were excited by visible light. High-energy electrons can react with water and O$_2$ to generate active oxides, such as hydroxyl radicals ($\cdot$OH) and superoxide anion radicals ($\cdot$O$_2^{-}$). Furthermore, $\cdot$O$_2$ can also be generated through energy transfer reactions. Under an attack from these active oxides, RhB molecules were decomposed into benzoic acid, terephthalic acid, and other polycarboxylic acid compounds. Finally, these compounds containing benzene ring were further degraded into polyhydric fatty acids and polyhydric alcohols, as shown in Table 3. Other advanced oxidation methods or biochemical treatment methods are needed for further mineralization.

3. CONCLUSIONS

In this study, a positive charged quaternized polysulfone membrane for supporting electronegative porphyrin (TPPS) was successfully fabricated by the NIPS process. The morphologies and performance of the blend membrane were affected by the polymer concentration, coagulation bath, and additives. A spongelike porous structure membrane with porosity of 87.1% and water flux of 371.3 L·m$^{-2}$·h$^{-1}$ was prepared under the following conditions: QPSf polymer

![Figure 14. Photocatalytic degradation of RhB by photocatalytic membrane reactor.](https://dx.doi.org/10.1021/acsomega.0c00135)

Table 3. Detected Degradation Products of RhB by GC-MS

| Benzoic acid and phenols | Polyhydric fatty acids | Polyhydric alcohols |
|-------------------------|------------------------|---------------------|
| m/z 196                 | m/z 118                | m/z 92              |
| Structure               | Structure              | Structure           |
| ![Image](image1.png)    | ![Image](image2.png)   | ![Image](image3.png) |
| m/z 166                 | m/z 90                 | m/z 76              |
| ![Image](image4.png)    | ![Image](image5.png)   | ![Image](image6.png) |
| m/z 154                 | ![Image](image7.png)   | ![Image](image8.png) |
| m/z 122                 | ![Image](image9.png)   | ![Image](image10.png) |
concentration of 18 wt %, PEG-20k concentration of 12 wt %, and $V_{\text{ethanol}}/V_{\text{water}} = 1:1$ as the coagulation bath. Mono-dispersed TPPS was assembled on the QPSf membrane surface by electrostatic interaction, and the adsorption of TPPS on QPSf membrane followed the pseudo second-order kinetic model and Langmuir adsorption isotherm equation. The range of visible light response of porphyrin (TPPS) was expanded by electrostatic interaction, and the adsorption of TPPS on positively charged QPSf membrane by electrostatic interaction. The details can be briefly described as follows: (1) The surplus moisture on the surface of the as-prepared QPSf membrane was removed with filter paper. (2) The QPSf membrane was immersed into an aqueous solution of TPPS on a water bath oscillation at 150 rpm and 25 ± 1 °C. The anionic TPPS molecules were absorbed on the positively charged QPSf membrane by electrostatic interaction. (3) The electrostatic assembly of TPPS@QPSf membrane was rinsed by distillate water until no TPPS was detected in the traces of DMAc and additive. The e(746) composition of coagulation bath on membrane structures were explored.

The morphologies of the QPSf membrane were recorded by a Hitach S-4800 field emission scanning electron microscope (FE-SEM). The cross section of the composite membrane was obtained after being dipped into liquid nitrogen and fractured instantly. Then, the cross section as well as the surface of membranes were coated with gold by a sputter-coating machine before test.

The pure water flux ($J_w$) of the membrane was determined at 0.1 MPa by a filtration cell with an effective area of $2.2 \times 10^{-3}$ m². The membrane was compacted by DI water for 40 min at 0.15 MPa before collecting the data. The flux was calculated by eq 6:

$$J_w = \frac{V}{\Delta t \cdot A_1}$$  

where $V$ is the collected volume of permeate (L), $\Delta t$ is the effective time during the filtration (h), and $A_1$ is the active area of the membrane (m²).

The composite membrane porosity ($\rho_p$) was determined by a weighing method, and it was calculated by eq 7:

$$\rho_p = \frac{w_1 - w_2}{A_2 \cdot I \cdot d_m}$$

where $w_1$ (g) and $w_2$ (g) are the weights of the wet and dry membranes, respectively, and $A_2$ (cm²), $I$ (cm), and $d_m$ (g cm⁻³) are the effective area, thickness, and density of QPSf membrane.

4. EXPERIMENTAL SECTION

4.1. Materials. Polysulfone (PSf, MW = 80 kDa) was supplied by Solvay Co. Ltd. (Shanghai). Chloromethylated polysulfone (CMPSF) with a degree of substitution (DS) of 22% was prepared according to our previous work. Tetraphenylsulfonato porphyrin (TPPS) was purchased from J&K Scientific Ltd. Rhodamine B (RhB), methylene blue (MB), and methyl orange (MO) were purchased from Tianjin Guangfu Fine Chemical Research Institute. All other chemicals were of analytical grade and used as received.

4.2. Preparation and Characterization of Quaternized Polysulfone Membrane. QPSf polymer was prepared through the quaternization reaction, as shown in Scheme 1. Briefly, CMPSF (5 g) was dissolved in N,N-dimethylacetamide (DMAc, 50 mL). Then, excess trimethylamine was added dropwise and the mixture was stirred at room temperature for 24 h. Quaternized polysulfone polymer was precipitated in deionized water. To eliminate any unreacted trimethylamine, a Soxhlet extractor was applied with ethanol for 12 h. The anionic TPPS molecules were absorbed on the positively charged QPSf membrane by electrostatic interaction. The e(552) composition of coagulation bath on membrane structures were explored.

The quaternized polysulfone membrane was prepared by the traditional nonsolvent induced phase separation (NIPS). Quaternized polysulfone was dissolved in DMAc at 60 °C. After being degassed under vacuum, the homogeneous casting solution was cast on a clean glass plate with a gap of 200 μm by an automated membrane applicator (Elcometer 4340, England). Then, it was immersed into a coagulation bath immediately for phase separation at room temperature. The obtained membrane was soaked in DI water for 24 h to remove traces of DMAc and additive. The e(575) composition of coagulation bath on membrane structures were explored.

4.3. Preparation and Characterization of TPPS@QPSf Membrane. TPPS@QPSf membrane was fabricated by an electrostatic assembly. The details can be briefly described as follows: (1) The surplus moisture on the surface of the as-prepared QPSf membrane was removed with filter paper. (2) The QPSf membrane was immersed into an aqueous solution of TPPS on a water bath oscillation at 150 rpm and 25 ± 1 °C. The anionic TPPS molecules were absorbed on the positively charged QPSf membrane by electrostatic interaction. (3) The electrostatic assembly of TPPS@QPSf membrane was rinsed by distillate water until no TPPS was detected in the traces of DMAc and additive. The concentration of TPPS with a high extinction coefficient ($\varepsilon_{414 \text{nm}} = 5.33 \times 10^5$ L mol⁻¹ cm⁻¹) in the solution was determined according to the law of Lambert–Beer, and the adsorption capacity ($Q$, mg g⁻¹) of TPPS in porous membrane was calculated by eq 8.
where $C_0$ and $C_t$ are the concentrations ($\text{mg L}^{-1}$) of TPPS in the initial solution and at a given time, respectively, which are determined by UV spectra (Shimadzu UV 2700). $m$ is the mass (g) of the dry membrane, and $V_s$ is the volume (L) of TPPS solution.

To study the adsorption mechanism, the pseudo first-order (eq 9) and pseudo second-order adsorption (eq 10) kinetic models have been applied to describe the adsorption process.

\[
Q_t = Q_e (1 - e^{-k_1 t})
\]

\[
Q_t = \frac{Q_s t}{(1/k_2 Q_s) + t}
\]

where $k_1$ (min$^{-1}$) and $k_2$ (mg$^{-1}$·min$^{-1}$) are rate constants of the pseudo first-order and pseudo second-order models. $Q_s$ and $Q_e$ are the adsorption amounts (mg·g$^{-1}$) at equilibrium and at time $t$ (min), respectively.

The adsorption isotherm studies were also conducted to illustrate the transmission of TPPS from the solution phase to the membrane phase at equilibrium. The Langmuir isothermal adsorption model in eq 11 and the Freundlich adsorption model in eq 12 were used to characterize the adsorption thermodynamic process.

\[
Q_e = \frac{Q_m \times c_e}{k_3 + c_e}
\]

\[
Q_e = k_4 c_e^{1/n}
\]

where $Q_m$ (mg·g$^{-1}$) and $Q_m$ (mg·g$^{-1}$) are the equilibrium and maximum adsorption capacities of TPPS, respectively. $K_1$ (µmol·L$^{-1}$) and $k_1$ ((mg·g$^{-1}$)(L·µmol$^{-1}$)$^{1/n}$) are the Langmuir constant and Freundlich constant, respectively. $c_e$ (µmol·L$^{-1}$) is the equilibrium concentration of TPPS. $n$ is the empirical parameter.

The $z$-potential was measured through a streaming potential measurement unit (Surpass 3, Anton Paar, Austria) by using a 1 mmol·L$^{-1}$ KCl solution as the electrolyte, with the pH value ranging from 3.0 to 10.0.

**4.4. Photocatalytic Degradation of Dyes.** Batch photocatalytic degradation experiments were conducted in a glass beaker filled with a dye solution (10 mg·L$^{-1}$, 200 mL) and porphyrin catalysts (0.70 mg of free-based TPPS or 10 pieces of TPPS@QPSf membrane with 1 × 1 cm$^2$ size and adsorption capacity of 35 mg·g$^{-1}$) at the ambient temperature and atmospheric pressure. A schematic diagram of the experimental setup for the photocatalytic degradation is shown in Scheme 2a. A 300 W Xenon lamp (CEL-HXF300, AuLight, Beijing) was served as the visible light source right above the beaker, and a glass filter was used to block UV light to ensure illumination by visible light only. Samples (3 mL of dye solution after degradation) were taken from the reactor at given time intervals, and the concentration of the dye was determined by a UV–vis spectrophotometer. The removal efficiency of the dye was calculated by eq 13.

\[
\eta (%) = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

where $C_0$ and $C$ are the concentrations ($\text{mg L}^{-1}$) of the initial dye solution and the solution after degradation at time $t$, respectively.

To evaluate the treatment of dyeing wastewater by photocatalysis coupling with filtration, a photocatalytic membrane reactor (PMR) equipped with the TPPS@QPSf membrane was applied by a flow-through filtration model, as shown in Scheme 2b. Herein, the TPPS@QPSf membrane was equipped in the membrane cell between two module sheets. The material of the module was poly(methyl methacrylate) (PMMA) with 92% light transmittance, which ensured that the light can reach the membrane surface. A Xenon lamp (300 W) served as the visible light source above the membrane cell, and the distance between the surface of membrane and the light source was 20 cm. The photocatalytic degradation took place on the membrane surface when the aqueous solution of dye flowed through the membrane under the irradiation of visible light. The concentration of dye was determined by a UV–vis spectrophotometer. The removal efficiency of the dye in the permeate solution ($\eta_p$) was calculated by eq 14.

\[
\eta_p (%) = \left( \frac{C_0 - C_p}{C_0} \right) \times 100
\]

where $C_0$ and $C_p$ are the concentrations ($\text{mg L}^{-1}$) of the initial dye solution and permeate solution, respectively.

The total organic carbon (TOC) value of the feed and the permeate solution was measured by a TOC analysis (GE Innovox). The removal ratio of TOC ($R_{\text{TOC}}$, %) was calculated by eq 15.

\[
R_{\text{TOC}} = 1 - \left( \frac{\text{TOC}_f}{\text{TOC}_0} \right) \times 100
\]
where TOC_p is the TOC value of the permeate solution (ppm) and TOC_0 is the TOC value of the feed.

Gas chromatography mass spectrometry (GC-MS) was applied to determine the products of RhB degraded by the TPQS@QPSf membrane under visible light irradiation. It was carried out on a Thermo Finnigan Trace gas chromatograph interfaced with a Polaris Q ion trap mass spectrometer and carried out on a Thermo Finnigan Trace gas chromatographer.

The oven temperature program was set from 50 °C (2 min) to 260 °C at 5 °C·min⁻¹. The injection temperature was 260 °C. Helium was used as the carrier gas.

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES

(1) Mendret, J.; Hatat-Fraile, M.; Rivallin, M.; Broquillon, S. Hydrophilic composite membranes for simultaneous separation and photocatalytic degradation of organic pollutants. *Sep. Purif. Technol.* 2013, 111, 9–19.

(2) Chong, M. N.; Jin, B.; Chow, C. W.; Saint, C. Recent developments in photocatalytic water treatment technology: a review. *Water Res.* 2010, 44, 2997–3027.

(3) Friedmann, D.; Mendive, C.; Bahmann, D. TiO₂ for water treatment: Parameters affecting the kinetics and mechanisms of photocatalysis. *Appl. Catal., B* 2010, 99, 398–406.

(4) Yao, H.; Wang, X.; Yao, M.; Yao, X. Band structure design of semiconductors for enhanced photocatalytic activity: the case of TiO₂. *Prog. Nat. Sci.: Mater. Int.* 2013, 23, 402–407.

(5) Zheng, J.; Chang, F.; Jiao, M.; Xu, Q.; Deng, B.; Hu, X. A visible-light-driven heterojunction composite WO₃/Bi₂O₃Cl₂: Synthesis, characterization, and improved photocatalytic performance. *J. Colloid Interface Sci.* 2018, 510, 20–31.

(6) Banerjee, S.; Pillai, S. C.; Falars, P.; O’Shea, K. E.; Byrne, J. A.; Dionysiou, D. D. New Insights into the Mechanism of Visible Light Photocatalysis. *J. Phys. Chem. Lett.* 2014, 5, 2543–54.

(7) Xu, T.; Ni, D.; Chen, X.; Wu, F.; Ge, P.; Lu, W.; Hu, H.; Zhu, Z.; Chen, W. Self-floating graphitic carbon nitride/zinc phthalocyanine nanofibers for photocatalytic degradation of contaminants. *J. Hazard. Mater.* 2016, 317, 17–26.

(8) Abrahamse, H.; Hamblin, M. R. New photosensitizers for photodynamic therapy. *Biochem. J.* 2016, 473, 347–64.

(9) Jha, O.; Yadav, T. K.; Yadav, R. A. Structural and vibrational study of a neurotransmitter molecule: Dopamine [4-(2-aminoethyl) benzene-1,2-diol]. *Spectrochim. Acta, Part A* 2018, 189, 473–484.

(10) Shiragami, T.; Matsumoto, J.; Inoue, H.; Yasuda, M. Antimony porphyrin complexes as visible-light driven photocatalyst. *J. Photochem. Photobiol., C* 2005, 6, 227–248.

(11) Dong, S.; Feng, J.; Fan, M.; Pi, Y.; Hu, L.; Han, X.; Liu, M.; Sun, J.; Sun, J. Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: a review. *RSC Adv.* 2015, 5, 14610–14630.

(12) Wang, J.; Zhong, Y.; Wang, L.; Zhang, N.; Cao, R.; Khan, I.; Alarid, L.; Haddad, R. E.; Bai, F.; Fan, H. Morphology-controlled synthesis and metalation of porphyrin nanoparticles with enhanced photocatalytic performance. *Nano Lett.* 2016, 16, 6523–6528.

(13) Kim, W.; Park, J.; Jo, H. J.; Kim, H.-J.; Choi, W. Visible light photocatalysts based on homogeneous and heterogenized tin porphyrins. *J. Phys. Chem. C* 2008, 112, 491–499.

(14) Zhao, Y.; Shang, Q.; Yu, J.; Zhang, Y.; Liu, S. Nanostructured 2D diporphyrin honeycomb film: Photocatalyst, photocatalytic, and antibacterial activity. *ACS Appl. Mater. Interfaces* 2015, 7, 11783–11791.

(15) Zhao, Y.; Zhang, Y.; Liu, A.; Wei, Z.; Liu, S. Construction of three-dimensional hemin-functionalized graphene hydrogel with high mechanical stability and adsorption capacity for enhancing photocatalytic degradation of ethylene glycol. *ACS Appl. Mater. Interfaces* 2017, 9, 4006–4014.

(16) Shao, F.; Li, L.; Tian, Z.; Zheng, C.; Zhang, Y.; Li, Q.; Liu, S. Promoting Photodegradation Efficiency via a Heterojunction Photocatalyst Combining with Oxygen Direct and Fast Diffusion from the Gas Phase to Active Catalytic Sites. *ACS Appl. Mater. Interfaces* 2019, 11, 44922–44930.

(17) Zhou, W.; Sun, X. L.; Gu, L.; Bao, F. F.; Xu, X. X.; Pang, C. Y.; Gu, Z. G.; Li, Z. A green strategy for lithium isotopes separation by using mesoporous silica materials doped with ionic liquids and benzo-15-crown-5. *J. Radioanal. Nucl. Chem.* 2014, 300, 843–852.

(18) Liu, X.-E.; Qian, H.; Mele, G.; et al. Impact of different TiO₂ samples and porphyrin substrates on the photocatalytic performance of TiO₂ @copper porphyrin composites. *ChemCat. Today* 2017, 281, 45–52.

(19) Collini, E.; Ferrante, C.; Bozio, R.; Lodi, A.; Ponterini, G. Large third-order nonlinear optical response of porphyrin J-aggregates oriented in self-assembled thin films. *J. Mater. Chem.* 2006, 16, 1573–1578.

(20) Liu, Z.; Yi, Y.; Xu, H.; Zhang, X.; Ngo, T. H.; Smet, M. Cation-selective microcontact printing based on surface-molecule-imprinted layer-by-layer films. *Adv. Mater.* 2010, 22, 2689–2693.

(21) Fateeva, A.; Chater, P. A.; Ireland, C. P.; Tahir, A. A.; Khimyak, Y. Z.; Wiper, P. V.; Darwent, J. R.; Rosseinsky, M. J. A water-stable porphyrin-based metal-organic framework active for visible-light photocatalysis. *Angew. Chem., Int. Ed.* 2012, 51, 7440–7444.

(22) Heo, G.; Manivannan, R.; Kim, H.; Ryu, J. W.; Son, Y.-A. Visible light-photo-sensitized metallo-porphyrin/TiO₂ photocatalyst and its related self-cleaning effects in poly ethylene terephthalate. *J. Nanosci. Nanotechnol.* 2019, 19, 8004–8012.

(23) Afzal, S.; Daoud, W. A.; Langford, S. J. Photostable self-cleaning cotton by a copper(II) porphyrin/TiO₂ visible-light photocatalytic system. *ACS Appl. Mater. Interfaces* 2013, 5, 4753–4759.
(24) Wiederhold, J. G. Metal stable isotope signatures as tracers in environmental geochemistry. *Environ. Sci. Technol.* 2015, 49, 2606–2624.
(25) Zhao, L.; Liu, M.; Zhang, Y.; et al. Aggregation and supramolecular chirality of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin on an achiral poly(2-(dimethylamino)ethy methylacylate)-grafted ethylene-vinyl alcohol membrane. *J. Mater. Chem. C* 2015, 3, 3650–3658.
(26) Wang, M.; Yan, F.; Zhao, L.; Zhang, Y.; Sorci, M. Preparation and characterization of a pH-responsive membrane carrier for meso-tetraphenylsulfonato porphyrin. *RSC Adv.* 2017, 7, 1687–1696.
(27) Hung, W. L.; Wang, D. M.; Lai, J. Y.; Chou, S. C. On the initiation of macrovoids in polymeric membranes — effect of polymer chain entanglement. *J. Membr. Sci.* 2016, 505, 70–81.
(28) McVery, B. T.; Temple, J. A. T.; Huang, X.; Marsh, K. L.; Hoek, E. M. V.; Kaner, R. B. Fabrication of low-fluorulation ultrafiltration membranes using a hydrophobic, self-doping polyaniline additive. *Chem. Mater.* 2013, 25, 3597–3602.
(29) Darvishmanesh, S.; Jansen, J. C.; Tasselli, F.; Tocci, E.; Luis, P.; Degrève, J.; Drioli, E.; Van der Bruggen, B. Novel polyphenylsulfone membrane for potential use in solvent nanofiltration. *J. Membr. Sci.* 2011, 379, 60–68.
(30) Guillon, G. R.; Pan, Y.; Li, M.; Hoek, E. M. V. Preparation and characterization of membranes formed by nonsolvent induced phase separation: A review. *Ind. Eng. Chem. Res.* 2011, 50, 3798–3817.
(31) Thomas, R.; Guillon-Burrieza, E.; Arafat, H. A. Porous structure control of PVDF membranes using a 2-stage coagulation bath phase inversion process for application in membrane distillation (MD). *J. Membr. Sci.* 2014, 452, 470–480.
(32) Sajoughi, E.; Amirilargani, M.; Mohammadi, T. Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes. *Desalination* 2010, 262, 72–78.
(33) Kim, J. H.; Lee, K. H. Effect of PEG additive on membrane formation by phase inversion. *J. Membr. Sci.* 1998, 138, 153–163.
(34) Dai, Z.; Aboukeila, H.; Ansaloni, L.; Jing, D.; Baschetti, M. G.; Deng, L. Nafion/PEG hybrid membrane for CO2 separation: Effect of PEG on membrane micro-structure and performance. *Sep. Purif. Technol.* 2019, 67–77.
(35) Wang, M.; Ji, Y.; Zhang, Y.; Wang, S.; Long, X.; Zhao, L.; Yan, F. Preparation and the pH-sensitivity of poly(4-vinylpyridine) graft polysulfone membrane. *Polyim. Mater. Sci. Eng.* 2016, 32, 1–6.
(36) Li, M.; Zhao, L.; Zhang, Y.; Liu, M.; Ye, H.; Zhang, Y.; Chen, X. Adsorption behavior and self-aggregation of S, 10, 15, 20-tetrakis-(4-sulfonatophenyl)-porphyrin on quaternized polysulfone membrane. *Colloid Polym. Sci.* 2015, 293, 513–522.
(37) Song, Y.; Garcia, R. M.; Dorin, R. M.; Wang, H.; Qiu, Y.; Shelnutt, J. A. Synthesis of Platinum Nanocages by Using Liposomes Containing Photocatalyst Molecules. *Angew. Chem., Int. Ed.* 2006, 45, 8126–8130.
(38) Manawy, Y.; Kochkodan, V.; Mohammad, A. W.; Atieh, M. A. Arabic gum as a novel pore-forming and hydrophilic agent in polysulfone membranes. *J. Membr. Sci.* 2017, 529, 95–104.
(39) Qiu, W. Z.; Du, Y.; Ly, Y.; Yang, H. C.; Xu, Z. K. Codeposition of catechol–polyethyleneimine followed by interfacial polymerization for nanofiltration membranes with enhanced stability. *J. Appl. Polym. Sci.* 2017, 134, 45422.
(40) Lu, D. D.; Rananaware, A.; Thi, H. P. N.; Jones, L.; Bhosale, S. V. Fabrication of a TiO2@ porphyrin nanofiber hybrid material: a highly efficient photocatalyst under simulated sunlight irradiation. *Adv. Nat. Sci. Nanosci.* 2017, 8, No. 015009.
(41) Lei, P.; Chen, C.; Yang, J.; Ma, W.; Zhao, J.; Zang, L. Degradation of dye pollutants by immobilized polyoxometalate with H2O2 under visible-light irradiation. *Environ. Sci. Technol.* 2005, 39, 8466–8474.
(42) Liu, G.; Li, X.; Zhao, J.; Hidaka, H.; Serpone, N. Photooxidation pathway of sulfonrohemine-B. Dependence on the adsorption mode on TiO2 exposed to visible light radiation. *Environ. Sci. Technol.* 2000, 34, 3982–3990. 

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