Fabrication of Bioinspired Gallic Acid-Grafted Chitosan/Polysulfone Composite Membranes for Dye Removal via Nanofiltration

Jie Wang, Xin Yang,* Dayuan Zheng, Ayan Yao, Dan Hua,* Vijayan Srinivasapriyan, and Guowu Zhan*

ABSTRACT: In this work, we have developed a novel and facile method to prepare gallic acid-grafted chitosan/polysulfone (PS) composite membranes for dye removal from aqueous solutions. First, the gallic acid was grafted onto the eco-friendly chitosan through a free-radical grafting copolymerization reaction. Second, the gallic acid-grafted chitosan conjugates were codeposited onto the top surface of PS substrates by electrostatic interactions in order to transform the ultrafiltration membrane to the thin and defect-free nanofiltration membrane. The morphology and chemical composition of the as-prepared composite membranes were fully characterized by various spectroscopy and microscopy techniques. Moreover, after the optimization of preparation parameters, the obtained membrane displayed a high rejection of 97.2% for Congo red with a high permeance of 14.0 L h⁻¹ m⁻² bar⁻¹. Furthermore, the composite membranes also exhibited good rejections for other dyes with different molecular weights such as Evan blue (97.3%), Acid red 94 (97.6%), and Alcian blue 8GX (98%) on the basis of size exclusion, accompanied with good permeance of 12.9, 11.9, and 10.9 L h⁻¹ m⁻² bar⁻¹, respectively, which shows potential for scale-up industrial applications.

1. INTRODUCTION

According to incomplete statistics, there are more than 100,000 commercial synthetic dyes being produced every year in the textile industry.¹ The discharge of colorful dyes in effluent and wastewater has become a global concern because many synthetic dyes are toxic and nonbiodegradable, which poses a serious threat to aquatic ecosystems and human health.²⁻⁴ Therefore, the treatment and reuse of textile wastewater are of great significance, and developing effective approaches for dye treatment is critically important. Traditional technologies, such as coagulation,⁵⁻⁶ adsorption,⁷⁻¹⁰ advanced oxidation,¹¹⁻¹⁴ and biological degradation,¹⁵⁻¹⁹ have been reported to treat textile wastewater. Unfortunately, most of them are inadequate for the total removal of dyes in textile wastewater.²⁰ In addition, adding guest chemicals not only increases operating costs but also inevitably causes secondary pollution.²¹

Among the various strategies, membrane-based processes, such as ultrafiltration, nanofiltration, and reverse osmosis, have become an effective way for water purification and wastewater treatment, owing to their advantages such as low cost, relatively low energy consumption, good dye rejection, convenient operating conditions, and being eco-friendly.²² Among these techniques, nanofiltration becomes an attractive alternative purification technology, particularly in textile wastewater treatment, because of that it not only has a lower molecular weight cut-off (MWCO, 200–1000 Da) than ultrafiltration but also shows higher permeability and lower operating pressure than reverse osmosis.²³,²⁴

To date, most traditional commercially available nanofiltration membranes are fabricated by interfacial polymerization (IP) of diamine and acyl chloride to form a thin polyamide (PA) selective layer on the top surface of an ultrafiltration substrate.²⁵,²⁶ Although the separation performances of PA-based nanofiltration membranes are acceptable regarding the separation performance, organic solvents like n-hexane and toxic chemicals such as diamines and acyl chloride are largely used during the preparation process, which will inevitably cause serious environmental issues.²⁷,²⁸ Therefore, it is preferable to explore a greener route of preparing selective layers in terms of manufacturing thin-film composite membranes for nanofiltration.

In recent years, bio-inspired chemistry has attracted much attention, and various bio-inspired materials from naturally occurring products such as dopamine, catechol, tannin acid, catechin, gallic acid (GA), and chitosan (CS) have been demonstrated in surface modification of membranes. For
instance, Zhao and Wang have reported a novel method to fabricate the loose nanofiltration membrane by coating hydrophilic GA and polyethyleneimine (PEI) on the hydrolyzed polyacrylonitrile substrate, and the obtained composite membrane exhibited both higher flux and higher dye rejection compared to the conventional nanofiltration membranes.\textsuperscript{29} Zhang et al. fabricated novel composite membranes by IP between tannic acid and trimesoyl chloride at the water/oil interface, which exhibited excellent antifouling properties, low flux decline ratios, and high chemical stability.\textsuperscript{30} Wang et al. reported a facile strategy for fabricating loose nanofiltration membranes based on the rapid codeposition of biomimetic adhesive polydopamine and PEI by using CuSO\textsubscript{4}/H\textsubscript{2}O\textsubscript{2} as a trigger, which showed ultrahigh water permeance (26.2 L h\textsuperscript{−1} m\textsuperscript{−2} bar\textsuperscript{−1}) and distinguished rejections for negatively charged dyes (e.g., Direct red 23, Reactive blue 2, and Reactive orange 16), positively charged dyes (e.g., Rhodanine blue), and divalent salts (e.g., MgCl\textsubscript{2} and Na\textsubscript{2}SO\textsubscript{4}).\textsuperscript{31}

CS, derivative from chitin, is the second most abundant biopolymer in nature. Currently, CS has become an alternative to petroleum-based synthetic polymers because of many excellent properties, such as biocompatibility, renewability, low toxicity, low cost, and so forth.\textsuperscript{32} In addition, chitosan can be chemically functionalized easily as it contains abundant amino and hydroxyl functional groups.\textsuperscript{33} Recently, chitosan has also been applied to membrane fabrication as active layers for microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. The explored strategies include surface cross-linking,\textsuperscript{34} surface coating,\textsuperscript{35} blendings,\textsuperscript{36} layer-by-layer self-assembly,\textsuperscript{37} phase inversion,\textsuperscript{38} ultraviolet irradiation, and so forth. However, to the best of our knowledge, the grafting of

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Figure 1. (a) Schematic illustration of the fabricating procedure of GA-g-CS/PS membrane and (b) the proposed mechanism for the synthesis of GA-g-CS selective layer by the ascorbic acid/H\textsubscript{2}O\textsubscript{2} redox pair-mediated grafting method.

Figure 2. SEM images of surface and cross-section morphologies of the (a–d) PS substrate and (e,f) GA-g-CS/PS composite membrane. Note: the GA-g-CS/PS composite membrane was prepared under the following conditions: CS concentration of 1.4 wt %, GA concentration of 0.10 wt %, solution pH of 4.0, deposition time of 4 h, and heating time of 1 h.
GA onto CS for preparing the selective layer of composite membrane for nanofiltration has not yet been considered.

In this work, we first aim to prepare a thin selective layer by modifying CS via GA grafting based on ascorbic acid/hydrogen peroxide (H$_2$O$_2$) redox pairs.\textsuperscript{39–41} Specifically, the hydroxyl radical (HO\textsuperscript{•}) was produced by the reaction between ascorbic acid and H$_2$O$_2$ and then initiated the grafting reaction of GA onto CS (see Figure 1). Afterward, the obtained gallic acid-grafted chitosan (GA-g-CS) conjugates were codeposited onto polysulfone (PS) substrates to form composite nanofiltration membranes, which were then characterized for their morphological and physicochemical properties. In addition, the effects of several fabrication conditions on their separation performances were investigated in detail. The purpose of this study is to provide new insights into the designing of low-pressure composite nanofiltration membranes on the basis of bioinspired materials. The introduction of bioinspired CS and GA not only decreases fabrication costs but also alleviates the pollution problem of using toxic and expensive organic solvents. Moreover, the facile fabrication procedures with high reproducibility allow for the scale-up industrial applications of the composite membranes.

2. RESULTS AND DISCUSSION

2.1. Characterization of PS Substrates and GA-g-CS/PS Composite Membranes. 2.1.1. Morphology Observation. Figure 2 displays the scanning electron microscopy (SEM) images of the top surface and cross-section of the PS substrate and GA-g-CS/PS composite membranes. As shown, the PS substrate possessed an asymmetric structure consisting of a dense top surface, a sponge-like porous sublayer, and a bottom layer with fully developed finger-like macropores. However, its top surface showed many small pores (i.e., defects). It has been reported that the average pore size distribution of membranes can be estimated by retaining PEG with different molecular weights.\textsuperscript{42} Herein, the PS substrate showed rejections against PEG 70,000 and PEG 100,000 of 41.4\% and 62.5\%, respectively, with a pure water permeance of 947 L h$^{-1}$ m$^{-2}$ bar$^{-1}$. Accordingly, the pore size distribution of the PS substrate is plotted in Figure S1. As shown, the mean pore size of the PS substrate was about 17 nm within an ultrafiltration range (Mw: 1000–200,000 Da). On the other hand, a much denser top surface of GA-g-CS/PS composite membrane was found from the SEM images (Figure 2e,f), which showed the top surface and cross-section view of the composite membrane and indicated the successful formation of a selective layer.

The surface topology of the membranes was also observed from the three-dimensional atomic force microscopy (AFM) images. The average roughness ($R_a$) reflects the changes of flat surface in the nanoscale morphology.\textsuperscript{29} As shown in Figure 3, the AFM characterization result indicated that the $R_a$ of GA-g-CS/PS membrane was 41.5 nm, which was relatively smooth as compared with the PS substrate ($R_a = 60.2$ nm). Moreover, the variation of $R_a$ also indicated that GA-g-CS conjugates were
successfully codeposited on the external surface of the PS substrate.

2.1.2. Chemical Composition Analyses. First, UV−vis spectra of CS, GA, and GA-g-CS mixed solutions are displayed in Figure 4a. As can be seen, CS aqueous solution exhibited no absorption peak in the range from 200 to 800 nm while GA aqueous solution showed two characteristic absorption peaks at 212 nm and 261 nm, which were assigned to the \( \pi \) system of the benzene ring.\(^{43,44} \) It was observed that the absorption peak at 261 nm red-shifted to 265 nm in GA-g-CS, which is consistent with the reported literature.\(^ {43} \) In addition, the redshift might be attributed to the lower energy required for the \( n-\pi^* \) and \( \pi-\pi^* \) transition because of the formation of the covalent bonds between GA with CS.\(^ {39,43,44} \) Again, both results confirmed that GA was successfully grafted to CS.

The surface chemical properties of composite membranes were investigated by using Fourier-transform infrared spectroscopy (FTIR) at attenuated total reflection mode. Figure 4b shows the FTIR spectra of the PS substrate, CS/PS, and GA-g-CS/PS composite membrane. Compared to the spectrum of the PS substrate, an additional absorption peak at 1650 cm\(^{-1} \) was observed in both CS/PS and GA-g-CS/PS membranes. The absorption peak can be attributed to the C=O stretch vibration of amide groups,\(^ {34} \) confirming that CS species was successfully deposited on the PS substrate. It was believed that electrostatic interactions played a critical role in the deposition process. For instance, the pristine PS substrate was negatively charged\(^ {45} \) while the CS was positively charged (34.5 mV) in acidic conditions because of the abundant protonated amino groups (see Table S3). The identifications of other major characteristic bands in FTIR spectra are listed in Table S4.

Figure S. XPS spectra of (a) survey, (b) C 1s, and (c) O 1s of the PS substrate, (d) N 1s, (e) C 1s, and (f) O 1s of CS/PS sample (prepared under a CS concentration of 1.4 wt %, solution pH of 4.0, deposition time of 4 h, and heating time of 1 h), (g) N 1s, (h) C 1s, and (i) O 1s of and GA-g-CS/PS sample, which was prepared under the following conditions: CS concentration of 1.4 wt %, GA concentration of 0.10 wt %, solution pH of 4.0, deposition time of 4 h, and heating time of 1 h.
Therefore, X-ray photoelectron spectroscopy (XPS) was adopted to further analyze the surface chemistry of PS, CS/PS, and GA-g-CS/PS samples.

Figure 5a displays the XPS survey spectra of PS, CS/PS, and GA-g-CS/PS composite membranes. As can be seen, the nitrogen signal was not found in the PS substrate but in CS/PS and GA-g-CS/PS samples, which was ascribed to the NH$_3^-$ and NH-C=O groups of CS. The nitrogen contents in CS/PS and GA-g-CS/PS samples were 1.8 and 1.1%, respectively (see Table S5). Therefore, X-ray photoelectron spectroscopy (XPS) was adopted to further analyze the surface chemistry of PS, CS/PS composite membranes with different CS concentrations and the (b) GA-g-CS/PS composite membranes with different GA concentrations. Feed concentration was 30 ppm, and operating pressure was 1 bar.

2.2. Membrane Nanofiltration Performance Evaluation. On the basis of our preliminary experiments, we chose PS3 as the optimal substrate in the following study (see Table S2). It is well known that the preparation conditions of the selective layers have great influences on the chemical properties and separation performance. Thus, the effects of a series of synthetic parameters, including the concentration of CS, the concentration of GA, pH of the GA-g-CS mixed solution, deposition time, and heating time, on the separation performance were systematically studied. The first three parameters are critical to the formation of GA-g-CS conjugates while the last two parameters are expected to affect the combination manner between the PS substrate and GA-g-CS thin film.

2.2.1. Effect of the Concentration of CS. In general, the concentration of chitosan would determine the thickness of the selective layer, so composite membranes made from different concentrations of chitosan were prepared, and their separation performance toward Congo red (CR) aqueous solution was compared. The effect of chitosan concentration on the performance of the GA-g-CS/PS composite membrane was studied with other conditions being fixed (viz., GA concentration of 0.10 wt%, solution pH of 4.0, deposition time of 4 h, and heating time of 1 h). As shown in Figure 6a, when the CS concentration increased from 0.8 to 1.4 wt%, the rejection for CR increased slightly from 96.4 to 97.2% while the permeance decreased from 21.4 to 14.0 L h$^{-1}$ m$^{-2}$ bar$^{-1}$. It is likely that the increase of CS concentration promotes the formation of more concentrated GA-g-CS conjugates resulting in a denser and thicker skin layer. The result also confirms the excellent separation performance of the composite membranes.

2.2.2. Effect of the Concentration of GA. Subsequently, the effect of concentration of GA on the separation performance of the GA-g-CS/PS composite membranes was investigated with other conditions being fixed (viz., CS concentration of 1.4 wt%, solution pH of 4.0, deposition time of 4 h, and heating time of 1 h). As shown in Figure 6b, the increment of GA concentration from 0.06 to 0.12 wt% caused a continuous decline in permeance from 20.6 to 12.7 L h$^{-1}$ m$^{-2}$ bar$^{-1}$. However, dye rejection hardly changed at the expense of permeance. This could be explained by the fact that the increase of GA concentration favored the formation of GA-g-CS conjugates, which promotes the assembly of GA-g-CS conjugates onto the surface of PS substrates. The results
indicated that GA was quite suitable for the grafting of CS even at a low concentration.

2.2.3. Effect of pH of the Synthetic Solution. It is well-known that pH plays an important role in the formation of CS-based conjugates. For instance, Hu et al. reported that the pH played a critical role in determining the zeta potential and grafting degree of the conjugates.43 Therefore, the effect of the pH of the synthetic solution on the separation performance was investigated with other conditions being fixed (viz., CS concentration of 1.4 wt %, GA concentration of 0.10 wt %, deposition time of 4 h, and heating time of 1 h). As shown in Figure 7a, when the pH of the synthetic solution increased from 2.0 to 6.0, the permeance first decreased from 43.8 to 14.0 L h⁻¹ m⁻² bar⁻¹ while the rejection for CR showed an opposite trend. At the pH of 2.0, the amino groups in CS were likely to be protonated, leading to a positively charged surface,52 which was unfavorable to the synthesis of GA-g-CS conjugates. On the contrary, when the pH increased from 2.0 to 4.0, the protonation degree of CS decreased, and the amino groups became more reactive,53 which was beneficial for the formation of GA-g-CS conjugates and the followed deposition of a denser selective layer on PS substrate. However, when further increasing pH (i.e., >4), CS molecules became insoluble because of partial deprotonation,54 which is unlikely to assemble GA-g-CS conjugates onto the PS substrate. In contrast, a relatively loose membrane structure was produced with large permeance but negligible dye rejection. Consequently, the optimal pH value of 4.0 was used in the following studies.

2.2.4. Effect of Deposition Time. Subsequently, the effect of deposition time on the separation performance was discussed with other conditions being fixed (viz., CS concentration of 1.4 wt %, GA concentration of 0.10 wt %, solution pH of 4.0, and heating time of 1 h), and the results are summarized in Figure 7b. With increasing the deposition time from 1 to 2 h, the permeance gradually decreased from 30.2 to 14.0 L h⁻¹ m⁻² bar⁻¹ while the rejection increased from 91.0 to 97.2% for CR. It is likely that with the extension of deposition time, the selective layer becomes thicker and denser, which increased the mass transfer resistance of water, resulting in low permeance but high retention for dye.55 However, when the deposition time was prolonged over 2 h, both permeance and CR rejection were almost constant at around 14.0 L h⁻¹ m⁻² bar⁻¹ and 97.2%, respectively.

2.2.5. Effect of Heating Time. The heating temperature was fixed at 50 °C. The elevated temperature (>60 °C) resulted in a very dense membrane with negligible water flux because of the shrinkage of PS substrate and the selective layer.56 However, the low heating temperature (30 °C) seemed to have no effect on the separation performance. The effect of heating time on the membrane separation performance was
also investigated with other conditions being fixed (viz., CS concentration of 1.4 wt %, GA concentration of 0.10 wt %, solution pH of 4.0, and a deposition time of 4 h). As shown in Figure 8a, with the increase of heating time from 0.5 to 2 h, the permeance gradually decreased from 28.6 to 7.3 L h⁻¹ m⁻² bar⁻¹, whereas the rejection of CR increased from 91.0 to 97.1% for CR. Obviously, with the increase of heating time, the porosity inside the PS substrate may slightly shrink, and GA-g-CS conjugates became denser. Both factors led to a decreased permeance but an enhanced rejection.55

### 2.2.6. Separation Performance toward other Dyes.

Based on the investigations above, it can be seen that our designed GA-g-CS/PS composite membranes exhibited a satisfying separation performance for CR/water mixture. Then, the composite membranes fabricated under the optimal conditions (e.g., CS concentration of 1.4 wt %, GA concentration of 0.10 wt %, solution pH of 4.0, deposition time of 4 h, and heating time of 1 h) were also used to separate other dye/water solutions, and the results are summarized in Figure 8b. Because Alcian blue 8GX (AB) was positively charged at the pH of 7 (Table S1), adsorption was found at the initial time point. Nevertheless, the adsorption equilibrium was achieved before the investigation of membrane behavior. As shown in Figure 8b, the membranes exhibited a total permeance of 14.0, 12.9, 11.9, and 10.9 L h⁻¹ m⁻² bar⁻¹, along with the rejection of 97.2, 97.3, 97.6, and 98%, for CR/water, Evan blue (EB)/water, Acid red 94 (AR)/water, and AB/water solutions, respectively. It is noted that the rejection of dye was highly dependent on the molecular weight, which showed a following trend: 98% (Mw(AB) = 1298.9 Da) > 97.6% (Mw(AK) = 1017.6 Da) > 97.3% (Mw(EB) = 960.8 Da) > 97.2% (Mw(CR) = 696.7 Da). The phenomena could be explained by the steric hindrance effect and the Donnan effect.26 Dyes with large molecule weights (AB and AR) would suffer from greater steric hindrance in comparison with small dyes (EB and CR) when passing through the membrane, leading to lower permeance.57

In addition, the composite membrane showed a high water flux, which may be related to the hydrophilicity of the membrane. The water contact angles of the composite membrane and PS substrate are displayed in Figure S2, from which we can see that the composite membrane has a hydrophilic surface, being conducive to the transportation of water molecules. In addition, the separation performance of our prepared membranes was compared with other reported nanofiltration membranes in the literature.30,55,58–63 As shown in Table 1, our obtained GA-g-CS/PS composite membranes had higher water permeance than most nanofiltration membranes while maintained high rejections toward organic dyes.

### 3. CONCLUSIONS

In summary, we have developed a novel free-radical graft copolymerization method to prepare GA-g-CS/PS composite membranes for dye/water separation. The GA-g-CS conjugates were tightly adhered to the PS ultrafiltration substrate (average pore size of 17 nm) because of a strong electrostatic interaction. The formation of a thin and defect-free selective layer was demonstrated by a variety of characterization techniques, including SEM, AFM, UV–vis, FTIR, XPS, and so forth. The effects of preparation conditions such as the concentrations of CS and GA, pH of GA-g-CS mixed solution, deposition time, and heating time on membrane performance were investigated in detail. The optimal GA-g-CS/PS membrane exhibited a high permeance of 14.0 L h⁻¹ m⁻² bar⁻¹ with a high rejection of 97.2% for CR/water separation under the following preparation conditions: CS concentration of 1.4 wt %, GA concentration of 0.10 wt %, solution pH of 4.0, deposition time of 4 h, and heating time of 1 h. In addition, the composite membranes also have good rejections toward other organic dyes such as EB (97.3%), AR (97.6%), and AB (98%), which was comparable or even better than most conventional nanofiltration membranes prepared via IP. Therefore, we believe that the as-designed composite membranes with high reproducibility are suitable for waste-water treatment in practical applications.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials.

Commercially available fibrous PS, polyethylene glycol (PEG 4,000), pluronic F-127, and N,N-dimethylacetamide (DMAc) were purchased from Shanghai Macklin Biochemical Co., Ltd. to prepare dope solutions for PS substrates. CS (Sinopharm Chemical Reagent Co., Ltd.), GA (Shanghai Macklin Biochemical Co., Ltd.), ascorbic acid (Vc, Shanghai Macklin Biochemical Co., Ltd.), and hydrogen peroxide (Sinopharm Chemical Reagent Co., Ltd.) were acquired to prepare solutions for the fabrication of selective layers. Polyethylene glycols with two different molecular weights (Mw) of 70,000 and 100,000 g/mol (i.e., PEG 70,000 and PEG 100,000) purchased from Shanghai Macklin Biochemical Co., Ltd. were used to prepare filtration solutions for the measurement of pore size of PS substrates. Acetic acid, hydrochloric acid, and sodium hydroxide were obtained from Sinopharm Chemical Reagent Co., Ltd. Meanwhile, various organic dyes including Congo red (CR, CI no. 22120, Direct red 28), Evan blue (EB, CI no. 23860, Direct blue 53), Acid red 94 (AR, CI no. 45440), and Alcian blue 8GX (AB, CI no. 74240, Ingrain blue 1) purchased from the commercial suppliers were employed as model dyes in nanofiltration tests. Detailed information of the dyes (e.g., chemical structures, molecular weight, and charge) is illustrated in Table S1.
All tested membranes were home-made dead-ended permeation cells at 1 bar and 25 °C. Separation followed by immersing in DI water for the following 1 h. The membrane was heated in an oven at 50 °C for 0.5 h to reach a steady state. The flux (F, L h⁻¹ m⁻²) and permeance (P, L h⁻₁ m⁻² bar⁻¹) were calculated using eqs 1 and 2, respectively.

\[ F = \frac{\Delta V}{A \times \Delta t} \]  
\[ P = \frac{\Delta V}{A \times \Delta t \times \Delta P} \]  

where \( \Delta V \) represents the volume of the collected permeate (L), \( \Delta t \) represents the interval time (h), \( A \) represents the effective membrane area (m², 3.462 × 10⁻⁴ herein), and \( \Delta P \) represents the transmembrane pressure (bar).

The solute rejection (R, %) was calculated using eq 3.

\[ R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \]  

In the above formula, \( C_f \) and \( C_p \) represent the solute concentrations in the feed and permeate, respectively.

4.2. Fabrication of PS Substrates. Porous PS substrates were prepared via a nonsolvent induced phase inversion process. Herein, five types of PS substrates were prepared based on different compositions of the casting solution containing PS, PEG 4000, Pluronic F-127, and DMAc (see Table S2). Among them, PEG 4000 and Pluronic F-127 were used as membrane surface modifiers as well as pore-forming agents. First, a homogeneous polymer dope was prepared in DMAc solution and stirred at 80 °C for about 24 h. The solution was then degassed for 5 h at room temperature. Then, the polymer dope was poured onto a glass plate and casted slowly (800 mm/min) by a casting knife with a gap of 200 μm. The glass plate together with the nascent polymer solution was then degassed for 5 h at room temperature. Then, the solution was removed, and the obtained membrane was heated in an oven at 50 °C for 18 h under atmospheric air. The pH values were adjusted in the range of 2.0–5.0 by the addition of HCl (0.1 M) and NaOH (0.1 M). Afterward, the PS substrate was immersed in a water coagulation bath (DI water) immediately immersed in a water coagulation bath (DI water) at ambient temperature to complete the phase inversion. Subsequently, the formed membranes were peeled from the glass plate and washed thoroughly with DI water again to remove the residual solvent. The as-prepared membranes had a thickness of 200 μm in the wet state and were stored in DI water until they were tested.

4.3. Fabrication of GA-g-CS/PS Composite Membranes. The GA-g-CS conjugates were synthesized according to a modified method. Briefly, a certain amount of CS was dissolved in 100 mL of water solution containing 2 mL of acetic acid. Then, 2 mL of H₂O₂ (1.0 mol/L) and 0.108 g of Vc were added into the CS solution, and the mixture was further stirred for 60 min. Next, a certain amount of GA was added into the above mixture, and the reaction was carried out at 25 °C for 18 h under atmospheric air. The pH values were adjusted in the range of 2.0–5.0 by the addition of HCl (0.1 M) and NaOH (0.1 M). Afterward, the PS substrate was immersed in the above GA-g-CS mixed solution at 25 °C for 1–4 h. Finally, the solution was removed, and the obtained membrane was heated in an oven at 50 °C for 0.5–2 h followed by immersing in DI water for the following characterization and nanofiltration tests.

4.4. Membrane Performance toward Dye/Water Separation. The nanofiltration test was conducted by using home-made dead-ended permeation cells at 1 bar and 25 °C. All tested membranes were first prepressurized at 2 bar for 30 min to reach a steady state. The flux (F, L h⁻¹ m⁻²) and permeance (P, L h⁻¹ m⁻² bar⁻¹) were calculated using eqs 1 and 2, respectively.

SEM (ZEISS, EVO18) was used to observe the surface and cross-section morphologies of the membranes. AFM (Bruker, MultiMode 8) was used to observe the roughness of the membrane surface. FTIR (Thermo, Nicolet iS50) under the attenuated total reflectance mode and XPS (Thermo, ESCALAB 250XI) were employed to analyze the chemical properties of the membranes. A contact angle goniometer (Shanghai, JC2000D3, POWEREACH) was used to study the hydrophilicity of the membranes. In addition, the zeta potential analyzer (Bruker, Nano Brook Omnil) was used to measure the zeta potentials of GA, CS, and GA-g-CS solutions.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01013. Properties of organic dyes used in this study, compositions of dope solutions for the preparation of the PS substrates, zeta potential of different solution samples, absorption band assignments in ATR-FTIR spectra of PS, CS/PS, and GA-CS/PS membranes, atomic elemental composition, and element ratio on the membrane surface as determined by XPS, pore size distribution of the PS UF substrate, and water contact angle on the membrane surface (PDF).

AUTHOR INFORMATION
Corresponding Authors
Xin Yang − College of Chemical Engineering, Integrated Nanocatalysts Institute (INCI), Huaqiao University, Xiamen, Fujian 361021, P. R. China; Email: yangxin@hqu.edu.cn
Dan Hua − College of Chemical Engineering, Integrated Nanocatalysts Institute (INCI), Huaqiao University, Xiamen, Fujian 361021, P. R. China; Email: hudan@hqu.edu.cn
Guowu Zhan − College of Chemical Engineering, Integrated Nanocatalysts Institute (INCI), Huaqiao University, Xiamen, Fujian 361021, P. R. China; Email: gwzhan@hqu.edu.cn

Authors
Jie Wang − College of Chemical Engineering, Integrated Nanocatalysts Institute (INCI), Huaqiao University, Xiamen, Fujian 361021, P. R. China
Dayuan Zheng − College of Chemical Engineering, Integrated Nanocatalysts Institute (INCI), Huaqiao University, Xiamen, Fujian 361021, P. R. China
Ayan Yao — College of Chemical Engineering, Integrated Nanocatalysts Institute (INCI), Huqiao University, Xiamen, Fujian 361021, P. R. China
Vijayan Srinivasapriyan — College of Chemical Engineering, Integrated Nanocatalysts Institute (INCI), Huqiao University, Xiamen, Fujian 361021, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01013

Notes
The authors declare no competing financial interest.

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