

# Electrospinning Oriented Self-Cleaning Porous Crosslinking Polymer for Efficient Dyes Removal

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The separation of harmful substances by supramolecular crosslinking polymers is the focus of current research. As far as it is known, supramolecular crosslinking systems based on electrospun nanofibers are rarely reported. However, electrospun nanofibers should be promising candidates for interfacial crosslinking substrates because of their adjustable morphology and can be doped with different functional nanoparticles. In this study,  $\beta$ -cyclodextrin and acyl chloride compounds are interfacially polymerized on polyacrylonitrile electrospun nanofibrous substrates with different morphologies. The diameter and orientation of electrospun nanofibrous substrates affect the dye-filtration efficiency, with a porous membrane composed of aligned nanofibers giving the highest efficiency. Cationic dyes can be selectively filtered from mixtures of cationic and anionic dyes, and the porous supramolecular crosslinking polymers are also suitable for mixtures of various cationic dyes. When TiO<sub>2</sub> is present in the nanofibrous substrate, UV irradiation of the used porous composite membranes efficiently in situ degrade the absorbed dye, making the membranes self-cleaning and thus reusable.

The separation of pollutants by supramolecular crosslinking polymers is the focus of current research, because macrocyclic compounds can encapsulate compounds by means of host-guest interactions.<sup>[1-3]</sup> For example, Dichtel and coworkers reported that a high-surface-area polymer prepared by crosslinking  $\beta$ -cyclodextrin with compounds bearing rigid aromatic groups effectively adsorbs various pollutants, including simple aromatic compounds, pharmaceuticals, pesticides, plastic components, and volatile organic compounds.<sup>[4-6]</sup> In addition, Liu and co-workers reported a crosslinked pillar[5] arene polymer that efficiently removes various anionic organic dyes from aqueous solution upon irradiation at 450 nm in the air.<sup>[7]</sup> There are also some reports on the selective separation of pollutants by the membranes prepared from supramolecular polymers. Generally, macrocyclic compounds and crosslinkers are polymerized at the interface of commercially available membranes, and the resulting composite membranes can be

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D The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/admi.202001050.

DOI: 10.1002/admi.202001050

used to selectively separate molecules on the basis of their electrical properties or shapes.<sup>[8-10]</sup> The topological morphology of the interfacial polymerization substrate is very important for the construction of supramolecular crosslinking polymers. We believe that the combination of interfacial polymerization<sup>[11,12]</sup> and electrospinning technology<sup>[13]</sup> could be a good universal method for preparing composite nanofiltration membranes, the structures and properties of which can be controlled by means of surface modification,<sup>[14]</sup> adjustment of the electrospinning parameters,<sup>[15]</sup> and the addition of functional nanoparticles to the spinning solution.

Membrane separation technology is now widely used in pollutant treatment.<sup>[16–18]</sup> However, contamination of porous membrane surfaces is a bottleneck that prevents even wider use of this technology.<sup>[19–22]</sup> After dye-containing wastewater is filtered, membranes are generally

recycled by washing with organic solvents, but this process generates dye-containing organic solvent waste. If this new waste is not handled properly, the dissolved dyes can re-enter the environment and cause secondary pollution. Therefore, the development of innovative methods for controlling membranes surface structure and preparing self-cleaning membranes would be highly valuable.<sup>[23,24]</sup> Self-cleaning membranes responding to environmental stimuli such as magnetic fields,<sup>[25]</sup> temperature fluctuations,<sup>[26]</sup> and light<sup>[27,28]</sup> can cause changes in water flux and surface characteristics. Among the various stimulusresponsive materials, photocatalytic materials have attracted considerable attention;<sup>[29–31]</sup> and TiO<sub>2</sub> is of particular interest because of its high catalytic activity, good chemical stability, low cost, and low toxicity.<sup>[32,33]</sup>

In the current study, we interfacially polymerized  $\beta$ -cyclodextrin and four crosslinking agents on polyacrylonitrile (PAN) electrospun nanofibrous substrates with different morphologies (depending on the PAN concentration and the spinning orientation), and we investigated the utility of the resulting composite membranes for dye removal from aqueous solution. If TiO<sub>2</sub> was incorporated in the PAN electrospun nanofibrous substrate, UV irradiation of the used composite membranes efficiently degraded the adsorbed dye, rendering the composite membranes self-cleaning and thus reusable (Scheme 1).

First, electrospinning technology was used to fabricate nanofibrous PAN and PAN/TiO<sub>2</sub> membranes with controlled fiber diameter and morphology. Then,  $\beta$ -cyclodextrin and







Scheme 1. Schematic illustration of a) the preparation of self-cleaning composite membranes with four acyl chloride crosslinkers: terephthaloyl chloride, 1,3,5-benzotriacyl chloride, naphthaline-2,6-dicarbonic acid dichloranhydride, and 4,4'-biphenyl diacetyl chloride, and b) the dye filtration process.

terephthaloyl chloride were interfacially crosslinked on the nanofibrous membranes. The obtained compacted composite membranes are designated pTC- $\beta$ -CD/PAN and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub>, respectively.

Scanning electron microscopy (SEM) showed that the nanofibers were uniformly distributed in the PAN and PAN/TiO<sub>2</sub> membranes (**Figure 1**a,b). The average diameters of the nanofibers in the PAN and PAN/TiO<sub>2</sub> membranes were  $\approx$ 220 and 210 nm, respectively. Notably, there were large holes among the fibers of both membranes. SEM indicated that the overall thicknesses of pTC- $\beta$ -CD/PAN and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes were about 83 and 26 µm, respectively, and the crosslinking layers of pTC- $\beta$ -CD/PAN and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes had thicknesses of about 1.92 and 1.32 µm, respectively (Figure 1d,f).

To investigate the thermal stability of the membranes, we conducted thermogravimetric analysis (TGA) (**Figure 2**a). The TGA curve of the PAN membrane showed a multistage weight loss; the initial weight loss below 300 °C was attributed to solvent evaporation, and the solvent was DMF derived from the electrospinning process. It is reported that the weight loss of PAN started from 300 °C.<sup>[34]</sup> For PAN membrane, the weight

loss before 300 °C can only be the solvent DMF. The weight loss was more before 200 °C and relatively stable between 200 °C and 300 °C. TGA showed that all four membranes were basically stable below 300 °C, indicating that they had good thermal stability. PAN decomposition occurred mainly in three temperature ranges: 300, 300-500, and >500 °C. Previous work showed that these three stages correspond to three chemical reactions: cyclization, carbonization, and thermal oxidation.<sup>[35]</sup> Solvent evaporation accounted for ≈10% of the weight loss; and cyclization, carbonization, and thermal oxidation accounted for ≈30%, 10%, and at most about 50% of the remaining weight loss, respectively. Compared with the PAN membrane, the other three membranes showed less weight loss due to cyclization, which proves that these three membranes contained other components besides PAN. Because the PAN/TiO2 and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes contained TiO<sub>2</sub>, they could not be completely decomposed at temperatures below 800 °C; the residual weight was about 30%, which is consistent with the amount of TiO<sub>2</sub> added in the electrospinning process.

In the Fourier transform IR spectra of the membranes (Figure 2b), absorption peaks characteristic of the cyano group (-CN) were observed at 2242 cm<sup>-1</sup>, indicating the formation of







**Figure 1.** SEM images of the a) PAN (top view) and b) PAN/TiO<sub>2</sub> (top view) membranes, and the c,d) pTC- $\beta$ -CD/PAN and e,f) pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> composite membranes prepared by interfacially crosslinking  $\beta$ -cyclodextrin and terephthaloyl chloride on the PAN and PAN/TiO<sub>2</sub> membranes. The insets in panels (a) and (b) show the average diameters of the nanofibers in the PAN and PAN/TiO<sub>2</sub> membranes, and the insets in panels (d) and (f) show the thicknesses of the pTC- $\beta$ -CD/PAN and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes, as calculated with the Nano Measurer software.

PAN nanofibers. The peaks at 2929, 1447, and 1227 cm<sup>-1</sup> were assigned to stretching vibration,  $-CH_2$  bending vibration, and left-right swing vibration of -CH, respectively. In the spectrum of the PAN/TiO<sub>2</sub> membrane, a broad peak at 500 cm<sup>-1</sup> assigned to TiO<sub>2</sub> was observed, confirming the formation of PAN/TiO<sub>2</sub> nanofibers. In the pTC- $\beta$ -CD/PAN spectrum, the -OH peak at 3309 cm<sup>-1</sup>, the C=O peak at 1715 cm<sup>-1</sup>, and the  $-COO^-$  peaks at 1555 and 1386 cm<sup>-1</sup>, as well as the aromatic ring peaks at 1500–1700 cm<sup>-1</sup>, indicated successful crosslinking on the interface of the electrospun membrane. The characteristic peak of TiO<sub>2</sub> at around 500 cm<sup>-1</sup> was also observed in the pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> spectrum.

The X-ray diffraction pattern of the PAN membrane had a strong diffraction peak at  $2\theta = 17^{\circ}$  arising from the (100) crystal plane diffraction and a characteristic diffraction peak at  $2\theta = 29^{\circ}$  that was assigned to the (110) crystal plane of the cyano group (Figure S1, Supporting Information). The PAN/TiO<sub>2</sub> and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes showed characteristic diffraction peaks for TiO<sub>2</sub> at  $2\theta = 25^{\circ}$ , 38°, 48°, 55°, and 63°.

To investigate the hydrophilicity of the four membranes, we determined their water contact angles: the angles for the PAN, PAN/TiO<sub>2</sub>, pTC- $\beta$ -CD/PAN, and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub>

membranes were 9.8°, 9.5°, 24.3°, and 14.5°, respectively (Figure S2, Supporting Information), indicating that all the membranes were hydrophilic, a property that facilitates the spreading and permeation of water and makes these membranes suitable for dye filtration. Measurement of the nitrogen adsorption isotherms indicated that the Brunauer–Emmett–Teller surface areas of the PAN, PAN/TiO<sub>2</sub>, pTC- $\beta$ -CD/PAN, and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes were 11.147, 12.524, 14.883, and 9.142 m<sup>2</sup> g<sup>-1</sup>, respectively (Figure S3, Supporting Information). It can be seen from the SEM images that in the composite membranes, the proportion of electrospinning matrix is larger than that of crosslinking layer. Therefore, the Brunauer–Emmett–Teller surface areas of the composite membranes and the electrospinning membranes should be similar, all about 10 m<sup>2</sup> g<sup>-1</sup>.

X-ray photoelectron spectroscopy (XPS) measurements were used to investigate the chemical compositions of the membrane surfaces (Figure 2c–f; Figure S4, Supporting Information). The XPS spectrum of the PAN membrane showed peaks at 284 and 397 eV, which are characteristic of C and N, respectively. Similarly, the spectrum of PAN/TiO<sub>2</sub> showed peaks assignable to C (284 eV), N (397 eV), Ti (456 eV), and O (528 eV);







Figure 2. Characterization of the membranes: a) TGA curves, b) FT-IR spectra, and c-f) XPS C1s spectra.

pTC- $\beta$ -CD/PAN showed peaks assignable to C (284 eV), N (397 eV), O (528 eV), and Na (1069 eV); and pTC-β-CD/PAN/ TiO<sub>2</sub> showed peaks assignable to C (284 eV), N (397 eV), O (528 eV), Na (1069 eV), and Ti (456 eV). The sodium present on the surfaces of the two composite membranes was due to the use of NaOH in the interfacial polymerization of  $\beta$ -cyclodextrin and terephthaloyl chloride on these membranes. The C1s spectra are shown in Figure 2c-f. For the PAN and PAN/TiO<sub>2</sub> membranes, curve-fitting of the C1s signal was consistent with two peaks, at binding energies of about 284.6 and 285.7 eV, which were attributed to C-C/C-H/C=C and  $C\equiv N$  species, respectively (Figure 2c,d). The pTC- $\beta$ -CD/PAN and pTC- $\beta$ -CD/ PAN/TiO<sub>2</sub> membranes also showed peaks for these two species (Figure 2e,f). In addition, the spectra of the latter two membranes showed the characteristic C-O peak at about 286.5 eV and the characteristic O=C-O peak at about 288.5 eV. Collectively, these results strongly suggest that the nanofibrous PAN and PAN/TiO2 membranes had successfully been coated with the polymer generated by crosslinking  $\beta$ -cyclodextrin and terephthaloyl chloride. By weighing the washed PAN, PAN/ $\beta$ -CD, and pTC- $\beta$ -CD/PAN membranes, the contents of  $\beta$ -CD and terephthaloyl chloride in the pTC- $\beta$ -CD/PAN membrane were obtained. After dividing by the amount of feed, the calculated reaction conversion of  $\beta$ -CD and terephthaloyl chloride were about 5.3% and 10%, respectively.

Cyclodextrins are known to selectively bind various guest molecules by means of host-guest interactions. To evaluate the dye-filtration efficiencies of our cyclodextrin-containing membranes, we selected 12 dyes (8 cationic and 4 anionic) for vacuum filtration experiments. The concentration of each aqueous dye solution was fixed at  $10^{-5}$  mol L<sup>-1</sup>. The solutions were filtered through the PAN, PAN/TiO<sub>2</sub>, pTC- $\beta$ -CD/PAN, and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes at room temperature, and filtration efficiencies were determined by means of UVvis absorption spectroscopy (Figure 3a,b; Figures S5 and S7, Supporting Information). These experiments revealed that the pTC-β-CD/PAN and pTC-β-CD/PAN/TiO<sub>2</sub> membranes efficiently removed the cationic dyes (G4, ethyl violet, thioflavin T, rhodamine B, crystal violet, pararosaniline hydrochloride, bright green, and malachite green). In contrast, the PAN and PAN/TiO2 membranes showed poor filtration efficiency toward these dyes. The poor performance of these latter membranes may have been due to leakage of the dyes through the many large holes among the fibers of these two membranes. The compacted structure of the pTC- $\beta$ -CD/PAN composite membrane prevented dye leakage. In addition, the







**Figure 3.** UV–vis absorption spectra of a) G4 and b) ethyl violet dye solutions before and after filtration through the four membranes. c) With G4 as a model dye, the pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membrane was regenerated four times by UV irradiation. Inset: Photos of the pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membrane before and after irradiation. d) UV–vis absorption spectra of a solution of ethyl violet and tropaeolin O before and after filtration through the pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membrane before and after irradiation. d) UV–vis absorption spectra of a solution of ethyl violet and tropaeolin O before and after filtration through the pTC- $\beta$ -CD/PAN membrane. Inset: Photos of the solution before and after filtration. The dye concentration for the experiments was 1 × 10<sup>-5</sup> mol L<sup>-1</sup>. (The spectrum of ethyl violet alone is in (b), and the spectrum of tropaeolin O alone is in Figure S7c in the Supporting Information).

 $\beta$ -cyclodextrin encapsulated some of the dye molecules via host–guest interactions.

Significantly, the presence of TiO<sub>2</sub> in the pTC- $\beta$ -CD/PAN/ TiO<sub>2</sub> permitted regeneration of the membrane by means of TiO<sub>2</sub>-catalyzed photodegradation of the absorbed dye. Using G4 as a model dye, we regenerated the membrane four consecutive times and observed no decrease in filtration efficiency (>98%, Figure 3c). After dye adsorption, the flow rate slowed down slightly, and then the flow rate basically returned to the initial state after the used composite membrane was regenerated by UV irradiation. We also evaluated the effect of UV irradiation time on the color of the used pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> and pTC- $\beta$ -CD/PAN membranes (Figure S6, Supporting Information). After irradiation for 1 h, the used pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes were colorless, whereas the pTC- $\beta$ -CD/PAN membranes remained colorful.

Furthermore, these membranes did not hinder the permeation of negatively charge molecules (Figure S7, Supporting Information). The efficiency with which pTC- $\beta$ -CD/PAN removed the anionic dyes tropaeolin 1, brilliant crimson red, tropaeolin O, and indigo carmine was poor. This result indicates that the chargeability of nanofiltration membranes is one of its most important characteristics. Typically, nanofiltration membranes are negatively charged under neutral and alkaline conditions and positively charged under acidic conditions. The composite membranes reported herein were synthesized under alkaline conditions, and their IR and XPS spectra indicate that they contained  $-COO^-$  groups and were thus negatively charged. Therefore, cationic dyes were trapped by means of electrostatic interactions, whereas anionic dyes could pass through the membranes.

To explore the behavior of our membranes with differently charged dyes, we prepared solutions containing the cationic dye ethyl violet and one of each of the four anionic dyes, and we filtered the four resulting solutions through the pTC- $\beta$ -CD/PAN membrane. As shown in Figure 3d, ethyl violet and tropaeolin O could be effectively separated by the pTC- $\beta$ -CD/PAN membrane; that is, the anionic dye (tropaeolin O) passed through the membrane, whereas the cationic dye (ethyl violet) was completely removed. Similar results were observed for the other dye pairs (Figure S8, Supporting Information).

We also evaluated the dependence of the dye-filtration efficiency of the membranes on dye concentration by using ethyl violet as a model dye (**Figure 4**a–c). When the ethyl violet concentration was  $10^{-5}$  mol L<sup>-1</sup>, the filtration efficiencies of all four membranes were close to 100%. As the dye concentration was increased, the efficiencies of the pTC- $\beta$ -CD/PAN or pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes remained close to 100%, whereas those of PAN or PAN/TiO<sub>2</sub> clearly decreased.

It was also important to investigate the removal efficiency of the membranes with dye mixtures, which are more representative of real-world conditions in wastewater treatment contexts. Therefore, we determined the filtration efficiencies of the pTC- $\beta$ -CD/PAN and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes via UV-vis spectroscopy by using solutions containing various concentrations of the eight cationic dyes (G4, thioflavin T, rhodamine B,







**Figure 4.** UV–vis absorption spectra of solutions of ethyl violet at various concentrations before and after filtration through the four membranes: a)  $10^{-5}$  mol L<sup>-1</sup> ethyl violet, b)  $10^{-4}$  mol L<sup>-1</sup> ethyl violet (10-fold dilution before measuring UV absorption spectrum), and c)  $5 \times 10^{-4}$  mol L<sup>-1</sup> ethyl violet (50-fold dilution). UV–vis absorption spectra of solutions containing a mixture of eight cationic dyes at various concentrations before and after filtration through the pTC- $\beta$ -CD/PAN and pTC- $\beta$ -CD/PAN/TiO<sub>2</sub> membranes: d)  $10^{-5}$  mol L<sup>-1</sup> mixed dyes, e)  $10^{-4}$  mol L<sup>-1</sup> mixed dyes (2-fold dilution). The eight dyes were G4, thioflavin T, rhodamine B, ethyl violet, crystal violet, pararosaniline hydrochloride, bright green, and malachite green.

ethyl violet, crystal violet, pararosaniline hydrochloride, bright green, and malachite green). These experiments showed that the filtration efficiencies of both membranes were >95% for solutions that were 10<sup>-5</sup> mol L<sup>-1</sup>. When the concentration of the dye mixture was increased to 10<sup>-4</sup> or 10<sup>-3</sup> mol L<sup>-1</sup>, the filtration efficiencies decreased slightly, to >90% and ≈60%, respectively (Figure 4d–f).

Because substrate morphology is believed to affect interfacial polymerization, we investigated the effects of carrying out the interfacial polymerization of  $\beta$ -cyclodextrin and terephthalyl chloride on PAN electrospun membranes with different morphologies. The PAN concentration used in all the experiments mentioned above was 12% (w/v), so we prepared 8% and 15% PAN solutions for comparison, leaving the other electrospinning parameters unchanged. When the PAN concentration was 12%, a membrane composed of aligned PAN nanofibers could be obtained by increasing the rotation speed of the collector from 400 to 2800 rpm as indicated in the Experimental Section in the Supporting Information. The fibers density of the electrospun membrane is very important for dye filtration. As shown in Figure 5, for electrospun membranes, the smaller the PAN concentration, the smaller the fiber diameter and the greater the fiber density. For the crosslinking composite membranes, the density of the crosslinking layer is greater than that of the electrospinning matrix. SEM images of PAN membranes obtained at three different concentrations are shown in Figure 5a. As the PAN concentration was increased, the diameter of the nanofibers increased gradually. At a concentration of 8%, the membranes contained a large number of beads, whereas at concentrations of 12% and 15%, smooth and uniform nanofibers were obtained. Most of fibers in the 12% aligned PAN fibrous membrane are oriented. When  $\beta$ -cyclodextrin and terephthaloyl chloride were interfacially polymerized on these three different PAN membranes, composite membranes with the micromorphologies shown in Figure 5b,c were obtained. Dense polymer membranes formed on the surfaces of the 8% PAN membrane and the 12% aligned PAN membrane, but there were some cracks in the polymer membrane formed on 15% PAN, which may be due to the large pore size of the 15% PAN substrate.

Then, we evaluated the performance of the pTC- $\beta$ -CD/8% PAN, pTC- $\beta$ -CD/12% PAN, pTC- $\beta$ -CD/12% aligned PAN, and pTC- $\beta$ -CD/15% PAN membranes with ethyl violet at three different concentrations (**Figure 6**). At concentrations of 10<sup>-5</sup> and 10<sup>-4</sup> mol L<sup>-1</sup>, the filtration efficiencies of all the membranes were nearly 100%. At a dye concentration of 5 × 10<sup>-4</sup> mol L<sup>-1</sup>, the filtration efficiencies of the pTC- $\beta$ -CD/8% PAN, pTC- $\beta$ -CD/12% PAN, and pTC- $\beta$ -CD/12% aligned PAN membranes were still >98%, whereas that of pTC- $\beta$ -CD/15% PAN was slightly lower (95%). When these membranes were tested on the solution of eight cationic dyes mentioned above at a concentration of 10<sup>-3</sup> mol L<sup>-1</sup>, the filtration efficiencies of the pTC- $\beta$ -CD/8% PAN and pTC- $\beta$ -CD/12% aligned PAN membranes were as high as 95%; the efficiency of pTC- $\beta$ -CD/12% PAN was  $\approx$ 60%; and that of pTC- $\beta$ -CD/15% PAN was  $\approx$ 45%.

We also evaluated the water permeances of the PAN, PAN/TiO<sub>2</sub>, pTC- $\beta$ -CD/12%PAN, pTC- $\beta$ -CD/12%PAN/TiO<sub>2</sub>, pTC- $\beta$ -CD/8%PAN, pTC- $\beta$ -CD/12% aligned PAN, and







**Figure 5.** SEM images of a) PAN membranes obtained at PAN concentrations of 8%, 12%, and 15% (the designation "12% aligned PAN" indicates a membrane with aligned PAN fibers at a concentration of 12%), and b) top views and c) side views of composite membranes obtained by interfacial crosslinking of  $\beta$ -cyclodextrin and terephthaloyl chloride on the three membranes shown in panel (a).



**Figure 6.** UV–vis absorption spectra of ethyl violet solutions before and after filtration through the pTC- $\beta$ -CD/8%PAN, pTC- $\beta$ -CD/12%PAN, pTC- $\beta$ -CD/12% aligned PAN, and pTC- $\beta$ -CD/15%PAN membranes: a) 10<sup>-5</sup> mol L<sup>-1</sup> ethyl violet, b) 10<sup>-4</sup> mol L<sup>-1</sup> ethyl violet (10-fold dilution before measuring UV absorption spectrum), and c) 5 × 10<sup>-4</sup> mol L<sup>-1</sup> ethyl violet (50-fold dilution). d) UV–vis absorption spectra of a solution of 10<sup>-3</sup> mol L<sup>-1</sup> ethyl violet (20-fold dilution) before and after filtration through the pTC- $\beta$ -CD/12%PAN, pTC- $\beta$ -CD/12%PAN, pTC- $\beta$ -CD/12%PAN, and pTC- $\beta$ -CD/15%PAN membranes. The eight cationic mixed dyes were G4, thioflavin T, rhodamine B, ethyl violet, crystal violet, pararosaniline hydrochloride, bright green, and malachite green.





**Figure 7.** SEM images of composite membranes prepared by interfacial crosslinking of  $\beta$ -cyclodextrin and a) 1,3,5-benzotriacyl chloride, b) 4,4'-biphenyl diacetyl chloride, and c) naphthaline-2,6-dicarbonic acid dichloranhydride on a 12% PAN electrospun membrane. UV–vis absorption spectra of a 5 × 10<sup>-4</sup> mol L<sup>-1</sup> ethyl violet solution (50-fold dilution before measuring UV absorption spectrum) before and after filtration through composite membranes prepared from  $\beta$ -cyclodextrin and d) 1,3,5-benzotriacyl chloride, e) 4,4'-biphenyl diacetyl chloride, and f) naphthaline-2,6-dicarbonic acid on a 12% PAN membrane.

pTC-β-CD/15%PAN composite membranes; the respective permeances were calculated to be 6910.83, 24 401.27, 101.91, 103.82, 1.72, 10.83, and 176.27 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> (Figure S9, Supporting Information). The SEM images in Figure 1 show that the PAN and PAN/TiO<sub>2</sub> electrospun membranes had large pores, which is consistent with their high water permeance. The permeances of the five tested composite membranes were far lower than those of the electrospun membranes, confirming that the composite membranes had relatively dense structures. However, the permeances of the composite membranes reported in this work were almost the same as or greater than those of nanofiltration membranes reported in the literature.<sup>[8,9]</sup> The high permeances of these composite membranes can be attributed to the hydroxyl groups on the exterior of the  $\beta$ -cyclodextrin cavities; these groups make the spaces between the  $\beta$ -cyclodextrins relatively hydrophilic, giving them a high affinity for water. Moreover, the porosity of the electrospun membranes that served as the substrates for the composite membranes also favored the passage of water, because such porous substrates show good molecular accessibility, a variety of pore sizes, and a high pore volume, all of which facilitate mass transport through the matrix.<sup>[36]</sup> Herein, the high pore volume may be resulted from the pores of electrospinning, the cavities of  $\beta$ -CD, and the monomer wash off during the washing process.

To determine whether the PAN membrane could be used as a universal substrate for the interfacial polymerization of  $\beta$ -cyclodextrins with linkers other than terephthaloyl chloride, we carried out interfacial polymerization of  $\beta$ -cyclodextrin and three different acyl chlorides on PAN membranes. SEM images of the composite membranes obtained by interfacial crosslinking between  $\beta$ -cyclodextrin and 1,3,5-benzotriacyl chloride, 4,4'-biphenyl diacetyl chloride, or naphthaline-2,6-dicarbonic acid dichloranhydride on a 12% PAN membrane are shown in **Figure 7**a–c. Dense polymer films were formed by interfacial crosslinking between  $\beta$ -cyclodextrin and 1,3,5-benzotriacyl chloride or naphthaline-2,6-dicarbonic acid dichloranhydride but not between  $\beta$ -cyclodextrin and 4,4'-biphenyl diacetyl chloride.

The performances of the three composite membranes for the filtration of ethyl violet solutions and mixed dye solutions were evaluated (Figure 7d-f; Figures S10-S12, Supporting Information). UV-vis absorption spectra obtained before and after filtration showed that the membranes prepared with 1,3,5-benzotriacyl chloride or naphthaline-2,6-dicarbonic acid dichloranhydride almost completely removed the ethyl violet regardless of its concentration. In addition, these membranes performed well with the mixed dye solution (Figure 7d,f; Figures S10 and S12, Supporting Information). In contrast, although the filtration efficiency of the membrane prepared with 4,4'-biphenyl diacetyl chloride was ≈100% at an ethyl violet concentration of 10<sup>-5</sup> mol L<sup>-1</sup>, the efficiency dropped sharply as the dye concentration was increased. When the concentration was  $5 \times 10^{-4}$  mol L<sup>-1</sup>, the efficiency was only about 67% (Figure 7e; Figure S11, Supporting Information). A large amount of tetrahydrofuran was used to dissolve the 4,4'-biphenyl diacetyl chloride during the synthesis of the crosslinked membrane, and this solvent is not conducive to interfacial polymerization.

In summary, composite membranes composed of PAN, TiO<sub>2</sub>,  $\beta$ -cyclodextrin, and terephthaloyl chloride were prepared by means of a method involving electrospinning and subsequent interfacial crosslinking. A pTC-β-CD/12%PAN/ TiO<sub>2</sub> composite membrane showed excellent dye-filtration efficiency when tested on eight individual cationic dyes, as well as a mixture of all the dyes. After use, the dye adsorbed on the membranes could be degraded by UV irradiation, making the membranes suitable for reuse. In addition, because the membranes were negatively charged, they could be used to separate cationic and anionic dyes on the basis of electrostatic interactions. By adjustment of the electrospinning solution concentration and the spinning orientation, electrospun membranes with different morphologies could be obtained, and composite membranes prepared by interfacial polymerization of  $\beta$ -cyclodextrin on these substrates showed different dye-filtration efficiencies. Composite membranes prepared with an electrospun membrane containing 8% PAN beads and with one containing 12% ADVANCED SCIENCE NEWS \_\_\_\_\_



aligned PAN fibers showed the best filtration performances. In addition to membranes prepared with terephthaloyl chloride, membranes prepared with 1,3,5-benzotriacyl chloride or naphthaline-2,6-dicarbonic acid dichloranhydride also showed nearly 100% filtration efficiency toward cationic dyes. The above-described results demonstrate that PAN electrospun membranes are ideal candidate substrates for interfacial polymerization to construct a variety of self-cleaning composite membranes with useful functions.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

### Acknowledgements

The authors thank National Natural Science Foundation of China (NSFC) for financial support (grant nos. 21672113, 21772099, 21971127, and 21861132001).

## **Conflict of Interest**

The authors declare no conflict of interest.

#### **Keywords**

aligned nanofibers, dye removal, electrospinning, self-cleaning crosslinking polymers,  $\beta$ -cyclodextrin

Received: June 12, 2020 Revised: August 8, 2020 Published online:

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