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Mesoporous phenolics filled in macroporous membranes for
tunable tight-ultrafiltration

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Abstract

Separation of colloidal nanoparticulates requires tight ultrafiltration (TUF) membranes. Phenolic polymers with well-defined sub-10 nm mesopores are promising candidates for such membranes, but suffer from intrinsic fragility. Herein, robust mesoporous phenolic membranes with flexibly adjustable TUF functions are realized through a new pore-filling strategy. Phenolic prepolymer with tunable fluidity are spontaneously filled into macroporous substrates with precisely controllable filling depths. Subsequent thermopolymerization fully cures the prepolymer and acid soaking removes the templating pluronic copolymers, producing composite TUF membranes with mesoporous phenolics embedded in flexible substrates. The membranes exhibit widely adjustable molecular-weight-cut-offs (MWCOs) (2.6 to 41 kg/mol) depending on the filling depth of phenolics while maintain otherwise unattainable high permeabilities. We further investigate the separation of CdTe and carbon quantum dots dispersed in water and toluene by these membranes, and they show excellent concentration and fractionation effect. This work enables efficient separation of ultra-small colloids by robust TUF membranes.

Keywords: tight ultrafiltration; mesoporous membranes; phenolic; chemical stability; pore filling
1. Introduction

Membrane separation has attracted a growing interest in many industrial processes such as water purification, seawater desalination, gas permeation and biomedicine due to its synergetic advantages including energy efficiency, easy operation and low possibilities of pollution (Basu et al., 2010; Elimelech and Phillip, 2011; Shannon et al., 2008). However, separations of biomolecules, colloids with sizes smaller than 10 nm such as proteins, DNA and other water-borne fine particles, are frequently frustrated with poor permeability and/or selectivity using commonly nanofiltration (NF) and ultrafiltration (UF) membranes (Bai et al., 2010; Lin et al., 2016). Recently, tight ultrafiltration (TUF) membranes with pore sizes approximately in the range from 2 to 10 nm have emerged as a solution to this issue (Lin et al., 2015). Here TUF membranes are defined as UF membranes with typical molecular-weight-cut-offs (MWCOs) of ~ 1k-10k g/mol (Winter et al., 2017), although there is still no clear consensus about its definition (Kramer et al., 2015; Shang et al., 2014).

Compared to the extensive researches on traditional NF or UF membranes, studies on TUF membranes are much sparser. A number of inorganic and polymeric materials usually used for conventional UF and NF membranes have also been explored for the preparation of TUF membranes by carefully adjusting the membrane-forming parameters to narrow the pore sizes. In this regard, titanium dioxide (TiO$_2$) (Kramer et al., 2015; Lee and Cho, 2004; Shang
et al., 2014b), regenerated cellulose (RC), polyamide (PA) and polyethersulfone (PES) (Park et al., 2007) are typically used. Additionally, some new materials with unique morphologies and physicochemical properties, which are not traditional starting materials for membranes, have been recently developed to produce membranes delivering TUF functions. For example, Liu et al. (2015) prepared zwitterionic chitosan (ZICS)-silica-polyvinyl alcohol (PVA) hybrid membranes with a typical asymmetric structure by linking ZICS with PVA using tetraethyl orthosilicate as a bridge. The membranes were utilized for the separation of bovine serum albumin (BSA) and lysozyme and separation factors up to ~ 20 were achieved. Liu et al. (2017) synthesized carboxylated cardo poly(arylene ether ketones) (PAEK-COOH), and used this polymer to prepare TUF membranes by the nonsolvent induced phase inversion (NIPS) process. The membranes exhibited a MWCO as low as 9.3 kg/mol while maintained an appreciable water permeability of 29.9 L/(m²·h·bar). However, only very limited number of materials have been exploited to prepare TUF membranes, and many of the previously reported TUF membranes are still far from mature and frequently suffering from high costs and/or tedious and cumbersome preparative processes. Therefore, it is highly desired to explore new methods to develop TUF membranes, and it remains a challenge to develop TUF membranes through controllable and efficient strategies using affordable starting materials.

Recently, mesoporous phenolics were synthesized with affordable phenol
and formaldehyde as starting materials and amphiphilic block copolymers (pluronics) micelles as the sacrificial templates (Kimura et al., 2013; Liang et al., 2013; Liu et al., 2013). The mesoporous phenolics which have pores sizes exactly in the range of 2-10 nm are expected to deliver superior TUF performances (Meng et al., 2005; Song et al., 2010; Tanaka et al., 2005). Also importantly, the intrinsic chemical and thermal stability of phenolics enables the applications of the TUF membranes in harsh conditions, e.g. in aggressive solvents and/or at high temperatures, which are often encountered in the purification of fine chemicals, synthesis of polypeptides, pharmaceuticals, and concentration of base/consumer chemicals, etc (Marchetti et al., 2014; McKeown, 2016). However, because of the fragile nature of phenolic polymers which are highly crosslinked as well as the difficulty in the degradation of the pluronics templates, only very few efforts have been successful to make mesoporous phenolics as membranes for pressure-driven separations. Li et al. (2017) tried to synthesize dense phenolic membranes without removal of the pluronics templates to ensure mechanical stability. The membranes showed good separation capability for multivalent anions, however their permeability was considerably low because of the low porosity. Previously, we prepared robust mesoporous phenolic TUF membranes by infiltrating solutions of phenolic precursor into macropores of polyvinylidene fluoride (PVDF) membranes followed by thermopolymerization and template removal by acid soaking (Lan et al., 2017). Because of the flexible nature of PVDF membranes,
the obtained membranes showed good mechanical stability and could be directly applied for TUF under pressures up to 23 bar. However, filling with precursor solutions took place very fast and involved the evaporation of the solvent in the pores, which was not only hard to control the filling depth of phenolics in the pores, but also was prone to form defects. Moreover, their TUF properties can only be tuned in a relatively narrow range, limiting their applications in many fields in which larger MWCOs and higher permeabilities are necessary.

Inspired by the observation that the dried films of resol (the precursor of phenolic) and pluronic exhibit certain fluidities depending on the degree of thermopolymerization before fully cured, we report on a new pore-filling strategy herein to prepare mesoporous phenolics interlaced in macroporous PVDF substrates with flexibly tunable TUF performances. In this method, the solutions of resol and pluronic were evaporated and thermally treated to prepare partially solidified prepolymer films with certain fluidities. PVDF substrates were attached on the prepolymer films to allow the spontaneous filling of the prepolymer into the macropores in the PVDF substrates. The filling depths of the prepolymer were readily tuned by using prepolymer films with different fluidities, enabling the preparation of mesoporous phenolic@PVDF membranes with flexibly tunable TUF properties. Thus-produced TUF membranes showed much better separation performances compared to membranes prepared by other methods, and they exhibited excellent effect in
the concentration/fractionation of quantum dots (QDs) with sizes of a few nanometers dispersed either in water or in organic solvents.

2. Materials and methods

2.1. Materials

Pluronic F127 (poly (ethylene oxide)-block-poly (propylene oxide)-block-poly (ethylene oxide), abbreviated as PEO$_{106}$-b-PPO$_{70}$-b-PEO$_{106}$, $M_w = 12.6$ kg/mol), lysozyme from chicken egg white ($M_w = 14.3$ kg/mol, lyophilized powder, ≥ 98.0%, SDS-PAGE), and polyethylene glycols (PEGs, $M_w = 1.5$, 4, 10, 100 kg/mol) were purchased from Sigma-Aldrich. Ethanol (≥ 99.8%) and rhodamine B were supplied by Aladdin. PVDF microfiltration membranes (nominal pore diameter ~ 0.22 μm, porosity ~ 70%) in the form of round coupons with the diameter of 2.5 cm were provided by Merck Millipore. Phenol (≥ 99.0%), HCl (36.0-38.0%) and H$_2$SO$_4$ (95.0-98.0%), formaldehyde aqueous solution (37.0-40.0%), and NaOH (≥ 96.0%) were obtained from local suppliers. The aqueous solution of cadmium telluride (CdTe) QDs and toluene solution of carbon QDs with a concentration of 10 g/L were purchased from Janus New-Materials Co., Ltd. All chemicals were used as received without further purification. Deionized water with a conductivity of ~ 50 μs/cm was in-house prepared and used throughout the tests.

2.2. Preparation of resol/F127 solution
Resols were synthesized by a base-catalyzed polymerization reaction that was described in our previous work (Lan et al., 2017). Briefly, 0.61 g of phenol was mixed with 0.13 g of 20 wt% NaOH and 1.05 g of 37 wt% formaldehyde and then stirred at 75 ºC for 1 h to generate a claret solution. The solution was titrated to pH 7.0 with 0.6 mol/L HCl. The neutralized solution was further vacuum-dried at 45 ºC for 15 h to produce resols. Resols were redissolved in 20 mL ethanol to remove NaCl precipitates with 0.2 μm syringe filters, followed by the addition of 1.49 g F127. After stirring at room temperature for 30 min, a homogeneously faint yellow resol/F127 solution was obtained, in which the mass ratio of phenol/F127/ethanol was 0.38/0.95/10.

2.3. Fabrication of mesoporous phenolic@PVDF membranes

The synthesis of mesoporous phenolic@PVDF membranes is shown in Figure 1. Firstly 9.0 g resol/F127 solutions were evaporated at room temperature for 12 h in a polycarbonate petri dish, and then prepolymerized for various durations up to 4 h at 100 ºC to produce partially solidified phenolic prepolymer films. Macroporous PVDF membranes were then gently attached, with the top side down, onto the phenolic prepolymer films, and the thermopolymerization was continued at 100 ºC for 12 h (the duration of prepolymerization was included) to convert phenolic prepolymer to fully cured, completely solidified phenolic polymers. The phenolic films remaining on the surface of the PVDF substrates could be easily peeled off, thus producing
phenolic@PVDF composite films. Mesoporous phenolic@PVDF membranes were ultimately fabricated by immersing the composite films in H$_2$SO$_4$ (≈ 48 wt%) at 100 ºC for 12 h. The prepared membranes were washed with deionized water for several times until the washing liquid was neutral and then dried at 60 ºC for 6 h. To clearly observe the filling depths of phenolics in the PVDF substrates, the resol/F127 solution was doped with 40 mg/L rhodamine B for fluorescent detection, and then used to prepare composite films following the procedures described above.

**Figure 1.** Schematic diagram of the synthesis of mesoporous phenolic@PVDF membranes. (a) The resol/F127 solution was dropped in a petri dish and subjected to solvent evaporation at room temperature. (b) Prepolymerization to obtain a phenolic prepolymer film, and attaching macroporous PVDF substrate on the surface of the film. (c) Further thermopolymerization to fully cure the phenolic prepolymer film, and peeling off the film remaining on the surface of PVDF substrate. (d) Degradation of F127 incorporated in the phenolics by H$_2$SO$_4$, producing mesoporous phenolic@PVDF membranes.
2.4. Characterizations

Scanning electron microscopy (SEM, Hitachi S4800) was performed at the voltage of 5 kV. Before SEM characterizations, the samples were sputter-coated with a thin layer of Au/Pd to enhance the conductivity. Fluorescent photographs of the membranes prepared from the dye-doped resol/F127 solutions were obtained with a laser scanning confocal microscope (LSCM TCS/SP2, Leica). Fourier transform infrared spectroscopy (FTIR) was measured on a Nicolet 8700 infrared spectrometer at attenuated total reflection (ATR) mode. Nitrogen adsorption/desorption analysis was performed on a surface area and porosity analyzer (Micromeritics, ASAP-2020) at 77 K. Before measurements, the samples were degassed in vacuum at 150 °C for 12 h. The pore size distributions were calculated from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) theory.

2.5. Separation performances

The pure water permeability and lysozyme rejection rate of mesoporous phenolic@PVDF membranes were tested using a stirred filtration cell (Amicon 8010, Millipore) under the pressure of 1.0 bar. The working volume and effective membrane area were 10 mL and 4.1 cm², respectively. For permeability tests, the cell was linked to a water storage tank to ensure the continuous flow of water. The membranes were pre-pressed at 1.0 bar for 10
min and permeation tests were conducted for another 10 min. For rejection tests lysozyme dissolved in phosphate buffer solution (pH = 7.4) at a concentration of 0.5 g/L was employed. The volumes of feed and collected filtrate solution were 10 mL and 5 mL, respectively. Since the feed solution was progressively concentrated due to permeation throughout filtration tests in the dead-end filtration unit, the initial concentration of feed solution was recorded to calculate the rejection rate. Concentrations of the lysozyme solutions were measured via ultraviolet (UV) absorbance with a UV-vis absorption spectrometer (NanoDrop 2000c, Thermo). Four PEGs with molecular weights of 1.5, 4, 10 and 100 kg/mol were dissolved in water at a concentration of 1.0 g/L for each component, and used to analyze the MWCOs of the mesoporous phenolic@PVDF membranes. Concentrations of the PEG solutions were analyzed by gel permeation chromatography (GPC, Waters 1515). The durability and acid resistance of mesoporous phenolic@PVDF membranes were tested by immersing the membranes in 1 mol/L HCl solutions for 30 days. The treated samples were then washed with copious water and tested again to determine their water permeability and lysozyme rejection rate.

2.6. Filtration of quantum dots

The mesoporous phenolic@PVDF membranes were housed in detachable polypropylene filter holders for filtrations (Figure S1). The holders were composed of a needle tubing with a working volume of 5 mL and a detachable
filter with an effective membrane area of 4.1 cm². Mesoporous phenolic@PVDF membranes were fixed in the middle of the filter. 5 mL of solutions to be separated were sucked into the holder and then 2.5 mL of solutions were permeated through the membrane by manually pushing the piston. Aqueous solutions of CdTe QDs and toluene solutions of carbon QDs were diluted to a concentration of 0.5 g/L and then used as feed solutions for the filtration tests. Photoluminescence (PL) fluorescent spectra of feed and filtrate were performed with a Varian Cary Eclipse fluorescence spectrophotometer. The excitation wavelength and voltage were 450 nm and 550 V for CdTe QDs, and 420 nm and 630 V for carbon QDs, respectively. JEOL JEM-2100 transmission electron microscope (TEM) was operated at 200 kV to obtain TEM images of the QDs. The particle size distribution of CdTe QDs was determined by dynamic light scattering (Nanoplus, Micromeritics).

3. Results and discussion

3.1. Morphology and chemical composition

Phenolics is widely used a traditional binder and exhibit good fluidity when the curing degree is low before complete solidification in highly cross-linking state (Domínguez et al., 2010). In the prepolymerization stage performed at 100 °C, partially solidified phenolic prepolymer films with viscosity and fluidity depending on the duration of themopolymerization were produced. PVDF membranes partly sank into the phenolic prepolymer films driven by gravity,
enabling the prepolymer to spontaneously fill into PVDF macropores. Further thermopolymerization fully cured phenolics in the PVDF pores. Subsequently, the films remaining outside of the PVDF substrates can be easily peeled off from the surfaces, producing phenolic@PVDF composite films. The pristine PVDF membranes take a milky color. After peeling off the remaining film on the surface, the phenolic@PVDF composite film exhibited a yellowish color on the top surface previously attached by the phenolic films while the bottom surface remained milky (inset in Figure 2a). The discrepancy in appearance between the two surfaces vividly indicates the partial filling of phenolics into the PVDF substrates. As shown in Figure 2a, b, the macropores on the surface of the PVDF substrates are fully occupied by phenolics. Furthermore, a clear boundary between the filled phenolics and the blank PVDF was observed from the cross-section (Figure 2d). As shown in Figure 2d, e, in the filled section of PVDF substrates no gaps along the pore wall could be observed. This complete filling should be attributed to the excessive supply of phenolic prepolymer with a portion remaining on the substrate surface, which may timely provide phenolics to compensate the volume shrinkage of phenolics in the pores as a result of thermopolymerization. Moreover, the filled phenolics exhibited a defect-free, dense and nonporous morphology. The interactions between phenolics and PVDF substrates were considered to come from the physical anchoring effect.

F127 is a commercially available triblock copolymer and is capable to form
micelles in ethanol composed of a hydrophilic shell of PEO and a hydrophobic core of PPO. The hydroxyl groups in resols tend to interact with the ether bonds in PEO chains via hydrogen bonds (*structural schematic in Figure 1*) (Zhang et al., 2005). Solvent evaporation induced self-assembly produces mesophase structures with resols holding the F127 micelles. Because F127 can be degraded in H₂SO₄ while phenolic and PVDF survive (Zhuang et al., 2010), the phenolic@PVDF composite films were finally immersed in hot H₂SO₄ to eliminate F127 and generate pores in the phenolic frameworks, thus producing mesoporous phenolic@PVDF membranes. As shown in *Figure 2c*, f, after degradation of F127, a mesoporous morphology appeared which can be observed both from the surface and cross section. Moreover, the skeleton of the PVDF substrate remained intact. Because PVDF is strongly acid-resistant, acid soaking does not noticeably weak the flexibility and mechanical strength of the PVDF substrate. The seamless filling as well as the intact framework of phenolics and the PVDF substrate is essential for the development of defect-free mesoporous phenolics, which ensures the tight separation performances.
Figure 2. Morphologies of the phenolic@PVDF composite membranes with a prepolymerization duration of 1 h. Surface SEM images (a, b) before and (c) after H$_2$SO$_4$ soaking. The inset photograph in (a) shows the appearance of the top and bottom surfaces of the phenolic@PVDF composite films. Cross-sectional SEM images (d, e) before and (f) after H$_2$SO$_4$ soaking.

FTIR was utilized to analyze the surface compositions of the membranes. As shown in Figure 3a, F127 gives rise to bands at ~ 2870 and 1100 cm$^{-1}$, which are due to the stretching vibrations of C–H and C–O–C, respectively (Huo et al., 2016). The disappearance of these two bands confirms the elimination of F127 after H$_2$SO$_4$ soaking. In contrast, the strong bands of PVDF at ~ 1400, 1180 and 880 cm$^{-1}$ corresponding to the deformation vibration of C–H, the stretching vibration of CF$_2$ and C–C framework remain unchanged (Lang et al., 2007). Meanwhile, the characteristic peaks of phenolics, including the broad phenolic and aliphatic OH band at ~ 3400 cm$^{-1}$, the scissoring vibrations of
–CH$_2$– and C–OH at ~ 1450 and 1240 cm$^{-1}$, also show no significant changes (Yu et al., 2016). These results testify that both PVDF and phenolics survive hot H$_2$SO$_4$. As a result, phenolic@PVDF membranes with well-defined mesopores are obtained. As shown in Figure 3b, nitrogen adsorption/desorption isotherms of the mesoporous phenolic@PVDF membranes depict characteristic type IV curves, further indicating a uniform mesoporous structure of the produced membranes. The formation of uniform mesoporous structure is related to the homogeneous F127 micelles embedded in the phenolics. The pore size distribution curve shows that the mesoporous phenolic@PVDF membranes have a narrowly distributed pore size centered at ~ 6.7 nm, which is in good agreement with literature value (Meng et al., 2005).

**Figure 3.** Characterizations of the phenolic@PVDF composite film before and after H$_2$SO$_4$ soaking. (a) FTIR spectra. The peak located at 1400 cm$^{-1}$ was used to normalize the FTIR spectra. (b) Nitrogen adsorption/desorption isotherms and corresponding pore size distribution curve of the film after H$_2$SO$_4$ soaking.

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We note that the filling depth of phenolics into PVDF can be manipulated simply by controlling the prepolymerization degree of the phenolic prepolymer films since we found that the fluidity and viscosity of the phenolic prepolymer film was progressively decreased with prolonged prepolymerization durations. For the prepolymerization durations ≤ 3 h, the prepolymer films are sticky, allowing conformally attachment of PVDF substrates on their surface. The PVDF substrates spontaneously sink into the phenolic prepolymer films with different depths because of the adequate fluidity of the prepolymers. When the prepolymerization duration is increased to 4 h, the phenolic prepolymer film is not able to fill into the PVDF substrate because of the inadequate fluidity. As shown in Figure 4a-d, f, the phenolic@PVDF composite films fabricated with prepolymerization durations of 0, 1, 2, 3 h exhibit increasingly reduced filling depths of ~ 55, 35, 25, 10 μm, respectively. We also checked the surface morphology of these filled membranes and found that the surface pores were fully occupied by the filled phenolics (Figure S2a-d). However, for the prepolymerization duration of 4 h the prepolymer film hardly penetrated into the PVDF substrate (Figure 4e), and macropores can be clearly seen on the top surface of the PVDF substrate (Figure S2e). We doped trace amount of fluorescent dyes into the phenolic prepolymers, and then filled them into the PVDF substrates. Under the fluorescent microscope, we can vividly observe the progressive filling of phenolics into the substrates to different depths (Figure 4a'-e’). The filled phenolics exhibit uniform fluorescent emission,
confirming the homogeneous filling into the pores.

**Figure 4.** Filling depths of phenolic prepolymers into the macroporous PVDF substrates. Cross-sectional SEM images (a-e) and corresponding fluorescent micrographs (a’-e’) of phenolic@PVDF composite films prepared with various prepolymerization durations: (a, a’) 0 h; (b, b’) 1 h; (c, c’) 2 h; (d, d’) 3 h; (e, e’) 4 h. (f) Filling depths of phenolic@PVDF composite films prepared with various prepolymerization durations statistically according to a-e and a’-e’. (a-e), and (a’-e’) have the same magnifications, and the scale bars are shown in (a) and (a’), respectively.

3.2. Evaluation of the TUF performances
Because of the well-defined pores with diameter smaller than 10 nm, the obtained mesoporous phenolic@PVDF membranes are expected to be outstanding candidates for TUF. We first used lysozyme, which has a molecular weight of ~ 14.3 kg/mol (Alele and Ulbricht, 2016), to evaluate their separation performances. As demonstrated in Figure 5a, the pure water permeability shows an increasing tendency with declined filling depths whereas the lysozyme rejection rate gradually decreases. Membranes with filling depths ≥ 30 μm are very tight as they can completely reject lysozyme although they give relatively low permeabilities in the range of 11 - 41 L/(m²·h·bar). When the filling depth declines to ~ 20 μm, the permeability increases to ~ 83.8 L/(m²·h·bar), while the lysozyme rejection rate decreases to ~ 90.6%. Furthermore, membranes with a filling depth of ~ 10 μm achieve a breakthrough in permeability to ~ 243.7 L/(m²·h·bar). Correspondingly, the rejection rate drops to ~ 65.9%. Here we note that during lysozyme rejection experiments, the membrane permeability is stable. Besides, the lysozyme in the initial feed solution is basically equal to that in the filtrate plus that in the retentate solution. This result indicates a low protein adsorption of the membranes. Figure 5b represents the MWCOs of these membranes, which clearly accordant with the lysozyme rejection rates. To be noted, the membranes with filling depths of ~ 55, 50, 40, 30 μm give rise to MWCOs of ~ 2.6, 3.2, 4.5, 12.0 kg/mol, respectively. According to the relationship between molecular weights of PEGs and their Stokes-Einstein radius (Puhlfurss et al.,
2000), we can estimate that the effective pore sizes of these membranes are 2.6, 2.9, 3.5, and 5.7 nm, respectively. For the membrane with a filling depth of ~ 20 μm, a MWCO of ~ 16.5 kg/mol (effective pore size of 6.6 nm) is determined, suggesting that the membrane can reject 90% of molecules with a molecular weight of 16.5 kg/mol according to the definition of MWCO. Therefore, this membrane is expected to give a rejection rate lower than 90% to lysozyme whose molecular weight is ~ 14.3 kg/mol. However, the tested rejection rate to lysozyme is 90.6%. This small inconsistence should be ascribed to the difference in the molecular shape of lysozyme and PEG. Lysozyme is in the shape of spheroid (Jachimska et al., 2012), and is therefore, more difficult to penetrate through the membrane pores compared to PEG which is in a linear thread-like shape (Prencipe et al., 2009). When the filling depth further decreases to ~ 10 μm, the MWCO extends to ~ 41.0 kg/mol.
Figure 5. The filtration performances of the mesoporous phenolic@PVDF membranes with different filling depths. (a) Pure water permeabilities and lysozyme rejection rates, and (b) MWCOs and effective pore sizes.

The above filtration tests demonstrate that MWCOs of the mesoporous phenolic@PVDF membranes can be adjusted in the range of 2.6 - 41.0 kg/mol with permeabilities correspondingly varied between 11 - 244 L/(m²·h·bar), simply by tuning the filling depths of phenolics. This highly adjustable and controllable filtration properties depending on filling depths facilitate the design and adaptability of the membranes to fit practical applications with specific requirements. Compared to TUF membranes prepared by other methods, the mesoporous phenolic@PVDF membranes prepared in this work exhibit
outstanding filtration performances (Table 1). For example, the phenolic@PVDF membrane with a filling depth of 30 \( \mu \text{m} \) exhibits a similar water permeability (~ 45 L/(m\(^2\)·h·bar)), but a much smaller MWCO of 12.0 kg/mol compared to the polysulfone membrane prepared by the NIPS process, which shows a MWCO of 57.0 kg/mol (Hamid et al., 2011), clearly indicating the much tight selectivity of our phenolic@PVDF membrane. Moreover, compared to a polyethersulfone membrane with a similar rejection rate to lysozyme (~ 60%) also prepared by the NIPS process (Xu and Qusay, 2004), the permeability of our phenolic@PVDF membrane with a filling depth of 10 \( \mu \text{m} \) is at least two times higher.

**Table 1.** Comparison of permeabilities, lysozyme rejection rates and MWCOs among different TUF membranes.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Permeability/ ( \text{L/(m}^2\cdot\text{h} \cdot \text{bar)} )</th>
<th>Rejection rate/%</th>
<th>MWCO/ kg/mol</th>
<th>Reference</th>
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<tr>
<td>Regenerated cellulose</td>
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<tr>
<td>Polyamide</td>
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<tr>
<td>Regenerated cellulose</td>
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<td>10.0</td>
<td></td>
<td>Liu et al., 2017</td>
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<td>(^{a})PAEK-COOH</td>
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<td>9.3</td>
<td>57</td>
<td>Hamid et al., 2011</td>
</tr>
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<td>89.6</td>
<td>57</td>
<td>Hamid et al., 2011</td>
</tr>
<tr>
<td>PVDF-(^{b})PFSA</td>
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<td>91.5</td>
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<tr>
<td></td>
<td>67.9</td>
<td>91.5</td>
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</table>
ethersulfone & 36.7 & 20.0 & 2009 \\
& 11.0 & 100 & 2.6 \\
& 17.3 & 100 & 4.5 \\
Phenolic@PVDF & 41.2 & 99.0 & 12.0 This work \\
& 83.8 & 90.6 & 16.5 \\
& 243.7 & 65.9 & 41.0 \\

\(^a\)PAEK-COOH, carboxylated cardo poly(arylene ether ketones).

\(^b\)PFSA, perfluorosulfonic acid.

3.3. Concentration and fractionation of QDs

The fast permeation and tight size discrimination make the mesoporous phenolic@PVDF membranes particularly promising for the separation of fine nanoparticles. To demonstrate it, the phenolic@PVDF membrane with a phenolic filling depth of ~ 30 μm was used to concentrate CdTe QDs dispersed in water (Figure 6a). The membrane was assembled into a filter holder (Figure S1). The aqueous solution of QDs was sucked into the holder using a needle tubing and then permeated through the membrane by manually pushing the piston. The TEM image clearly shows that the QDs possess a relatively uniform morphology (Figure 6b), and they exhibit a normal size distribution with the average value centered at ~ 3.9 nm (Figure 6c). Moreover, dynamic light scattering recognizes that the CdTe QDs have an average size of ~ 4.2 nm (Figure 6d), which is in good agreement with the TEM results. As shown in Figure 6e, the fluorescent spectrum of CdTe QDs in the feed shows a relatively narrow characteristic peak at the wavelength of ~ 540 nm. However,
the filtrate collected in the downstream of the membrane displays no fluorescent emission at all. Moreover, the fluorescent photograph of the feed (inset in Figure 6e) exhibits a strong viridian fluorescent emission which is characteristic to CdTe QDs in the feed, while totally disappears in the filtrate. These results unambiguously demonstrate the complete interception of CdTe QDs by the membrane and no QDs pass through the membrane. Therefore, the phenolic@PVDF membranes are highly efficient in the concentration of QDs down to ~ 4 nm dispersed in water.

Figure 6. Concentration of CdTe QDs dispersed in water by the mesoporous phenolic@PVDF membrane with a phenolic filling depth of 30 μm. (a) Schematic illustration of the concentration process. (b) TEM image of the CdTe QDs in the feed. (c) Statistical histogram and Gauss fit (the dashed line) of size distribution of the CdTe QDs based on (b). (d) Particle size distribution of CdTe QDs in the feed determined by dynamic light scattering. (e) The fluorescent spectra of CdTe QDs in the feed and filtrate, and their fluorescent photographs
under the irradiation of UV light with the wavelength of 365 nm.

While the mesoporous feature of phenolic@PVDF membranes opens opportunities to access TUF applications in aqueous environments, the membranes are also expected to be used in harsh conditions since both phenolics and PVDF are chemically stable in many organic solvents. By taking advantage of their excellent chemical stability, the mesoporous phenolic@PVDF membranes with a phenolic filling depth of ~ 30 μm was further used to fractionate carbon QDs (particle size ~ 2 nm) dispersed in toluene. Carbon QDs with larger sizes can be blocked while the smaller ones can pass through the membrane. The fluorescent spectrum of the feed carbon QDs solution shows a strong peak at the wavelength of ~ 497 nm. However, the peak of the filtrate was shifted to ~ 489 nm and exhibited a much weaker intensity (Figure 7a). This drop in intensity after filtration indicates a decreased concentration of the QDs in the filtrate compared to the feed, which was also evidenced by a lighter primrose color (inset photographs (1) in Figure 7a). The peak shifted toward the shorter wavelength side indicates a reduced average particle size. The TEM images of the carbon QDs in the feed and filtrate are given in Figure 7c, d. A numerically statistical bar chart with Gauss fit according to the TEM images describes the change of particle sizes before and after filtration (Figure 7b). The average particle size of the carbon QDs is decreased from ~ 2.2 nm in the feed to ~ 1.9 nm in the filtrate. These results
demonstrate the feasibility to fractionate carbon QDs with sizes down to ~ 2 nm. As larger carbon QDs are removed by the membrane, carbon QDs in the filtrate exhibit a stronger fluorescent emission (inset (2), Figure 7a). Moreover, this QD fractionation test also demonstrates that the sharp size-discriminating performance of the mesoporous phenolic@PVDF membrane is maintained even they are used in aggressive organic solvents.

**Figure 7.** Fractionation of carbon QDs dispersed in toluene using the mesoporous phenolic@PVDF membrane with a filling depth of 30 μm. (a) The fluorescent spectra of carbon QDs in the feed and filtrate, and their optical photographs under (1) white light and (2) UV irradiation at 365 nm, respectively. (b) Statistical histograms and Gauss fits (the dashed lines) of carbon QDs particle size distributions based on their TEM images in the (c) feed and (d) filtrate, respectively.
In addition, considering that both phenolics and PVDF substrates are stable in acids, the mesoporous phenolic@PVDF membranes are expected to be acid resistant, which are highly desired in a variety of applications. We immersed the membrane in 1 mol/L HCl for different periods and then checked their water permeability and lysozyme rejection rate. As described in Figure 8, the membranes tested after acid immersion for up to 30 days show no substantial change in both permeability and rejection, confirming their excellent acid resistance. Besides, as the membranes are obtained in hot H$_2$SO$_4$ (Figure 1) and have been used in toluene (Figure 7), they can also tolerate other solvents including H$_2$SO$_4$ and toluene. Therefore, these membranes are expected to find important applications in harsh conditions where aggressive organic solvents or acids are used, for example, in the fields of pharmaceuticals and acid recovery.

![Figure 8](image.png)

**Figure 8.** The permeability and lysozyme rejection rate of mesoporous phenolic@PVDF membrane with a filling depth of 30 $\mu$m immersed in 1 mol/L
HCl for different periods up to 30 days.

4. Conclusions

In conclusion, we demonstrate the fabrication of mesoporous TUF membranes by embedding mesoporous phenolics into macropores of PVDF substrates, and their applications in the separation of ultra-small colloids (quantum dots). Phenolic prepolymerization show varied viscosity and fluidity depending on the prepolymerization duration, and they tend to spontaneously fill into the macroporous substrates with tunable filling depths. Templating pluronic polymer (F127) hydrogen-bonded to phenolics can be degraded by acid soaking, thus generating mesopores in the phenolic framework. The produced mesoporous phenolic@PVDF membranes display widely tunable MWCOs ranging from 2.6 to 41.0 kg/mol while the permeabilities vary from 11 to 244 L/(m²·h·bar). These permeselectivities are much better than TUF membranes prepared by other methods. We investigate the separation of two types of QDs using these membranes. They show excellent concentration effect to CdTe QDs with a diameter of ~ 4 nm dispersed in water. More importantly, they deliver efficient separation performances in organic solvents for they can fractionate 2-nm carbon QDs dispersed in toluene. The membranes exhibit superior resistance to acids as immersion in HCl for one month does not weaken their performances. This work suggests a new pore-filling strategy to prepare robust membranes with widely adjustable TUF
properties, and also demonstrates the potentials of such TUF membranes in the efficient concentration/fractionation of ultra-small colloids dispersed in water or organic solvents.

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Highlights

- Tight ultrafiltration (TUF) membranes are prepared by a new pore-filling strategy
- Fluidizable supramolecular films are filled into macropores of substrates
- Pluronic templates are removed by acid soaking to create mesopores
- TUF capacity is widely tunable by changing the filling depths of supramolecules
- Membranes can separate ultra-small colloids in aggressive solvents