Supporting Information

Enzyme-trigged Coatings of Tea Catechins/Chitosan for Nanofiltration Membranes with High Performance

Wen-Ze Qiu[a,b], Qi-Zhi Zhong[a,b], Yong Du[a,b], Yan Lv[a,b], Zhi-Kang Xu[a,b*]

[a]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: xuzk@zju.edu.cn; Fax/Tel: +86 571-87951773

[b]Key Laboratory of Adsorption and Separation Materials & Technologies of Zhejiang Province, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Experimental Section

Materials: All the chemicals were used as received from commercial sources without any further purification. PSf ultrafiltration membrane molecular weight cut off (MWCO) of around 50K was purchased from Ande Membrane Separation Technology & Engineering Co., Ltd. The water permeation flux of this membrane is about 300 L m^{-2} h^{-1} under 0.6 MPa. All samples were cut into rounds with a diameter of 6 cm. Green tea extract (powder) was purchased from Xing Yuan Chemical Products Co., Ltd. (Henan, China). Chitosan was purchased from Aladdin (China). Laccase (＞0.5 U/mg) was obtained from Sigma-Aldrich. Acetic acid (HAc), sodium acetate (NaAc) and inorganic salts were procured from Sinopharm Chemical Reagent Co. Ltd, China and used as delivered.

Preparation of the TFC NFMs: The preparation procedures are illustrated in Fig. 1 for the studied TFC NFMs. Generally, tea catechins (1 mg/mL), chitosan (0.5 mg/mL) and laccase

(0.1 mg/mL) were dissolved in HAc/NaAc buffer solution (pH = 5.0, 100 mM). PSf ultrafiltration membranes were washed and pre-wetted thoroughly by ethanol for 12 h and then immersed into the freshly prepared reaction solutions. After incubated at 40 ^{o}C for 30 min under mild vibration, the prepared TFC NFMs were rinsed repeatedly with de-ionized water and stored in it for future characterization and performance tests. And in other experiments, each of the experimental conditions including the concentrations of chitosan, laccase and incubation time was varied individually with other parameters remain unchanged.

Charaterization: FT-IR/ATR spectra were measured with an infrared spectrophotometer (Nicolet 6700, USA) equipped with an ATR accessory (ZnSe crystal, 45^{o}). The spectra were obtained in the region of 4000 to 400 cm^{-1} with resolution of 4 cm^{-1} for 64 scans. XPS analyses were performed on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer, USA) with Al Kα radiation ($h\nu$ = 1486.6 eV). Surface morphologies were observed by a field-emitting scanning electron microscope (FESEM, Hitachi S4800, Japan) after sputtered with a 10-20 nm gold layer on the membrane surface. Meanwhile, the surface topographies were also measured by atomic force microscopy (AFM, MultiMode, Vecco, USA) in the tipping mode. And the root mean square (RMS) roughness was calculated by three dimensional AFM images from each membrane surface. Water contact angles (WCA) were determined with a DropMeter A-200 contact angle system (MAIST VisionInspection & Measurement Co. Ltd., China). Zeta potentials were measured by an electrokinetic analyzer using an integrated titration unit for solid surface analysis (Anton Paar, SurPASS, Austria) with KCl (1 mmol/L) solution as electrolyte solution. The size and distribution of aggregates in the reaction solutions was measured using a Malvern Nano ZS90 laser particle size analyzer (Malvern, Nano ZS, U.K.). Temperature was kept at 50 °C during the

whole measurements. The composition of green tea powder was analyzed with a liquid chromatography/mass spectrometer detector (LC-MSD) (Agilent 1100, America). The data was collected at a retention time from 0 min to 15.772 min. And the content of each component was calculated according to its relative peak area.

Nanofiltration performance evaluation: Nanofiltration performance was measured with a laboratory scale cross-flow flat membrane module under the constant pressure of 0.6 MPa at 25 ± 1 °C. The effective area for each membrane is about 7.07 cm^2. Inorganic salts dissolved in DI water (1000 mg/L) were used as the feed solutions with a similar pH of 6.0 ± 0.2. The membrane samples were firstly pre-compacted at 0.7 MPa for about 1 h to reach a stable flux. Then, the operation pressure was lowered to 0.6 MPa and data were recorded after their values reach an equilibrium state. Water flux (J_w, $L/m^2 \cdot h$) and salt rejection (R, %) can be calculated by the following equations:

$$J_w = \frac{V}{A \cdot t} \quad (1)$$

where V, A and t represent the volume of filtrates, the effective membrane area and operation time, respectively.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where C_f and C_p represent the concentrations of solute in the feed and corresponding filtrates. And the concentrations of salt solutions were average values measured with an electrical conductivity meter (METTLER TOLEDO, FE30, China) for three times.

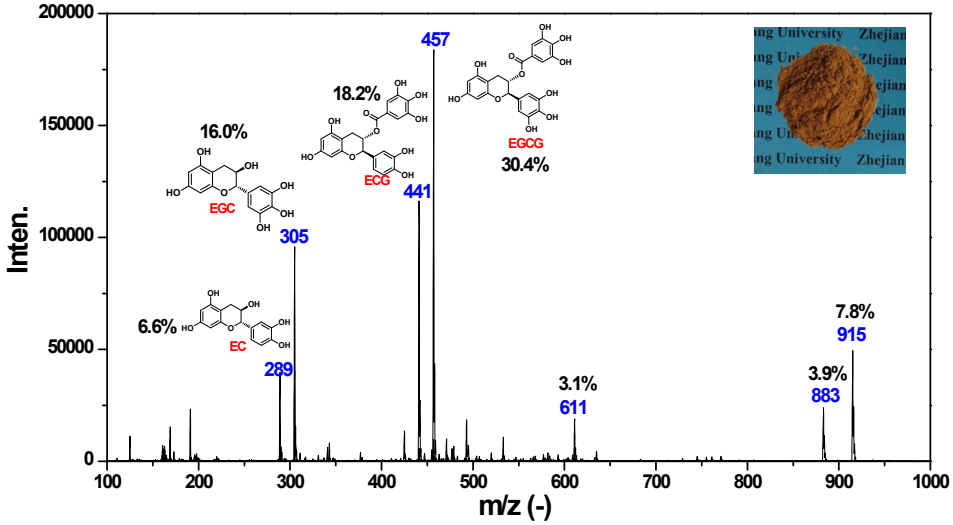

Fig. S1 Ion trap mass spectra of the natural green tea extract.

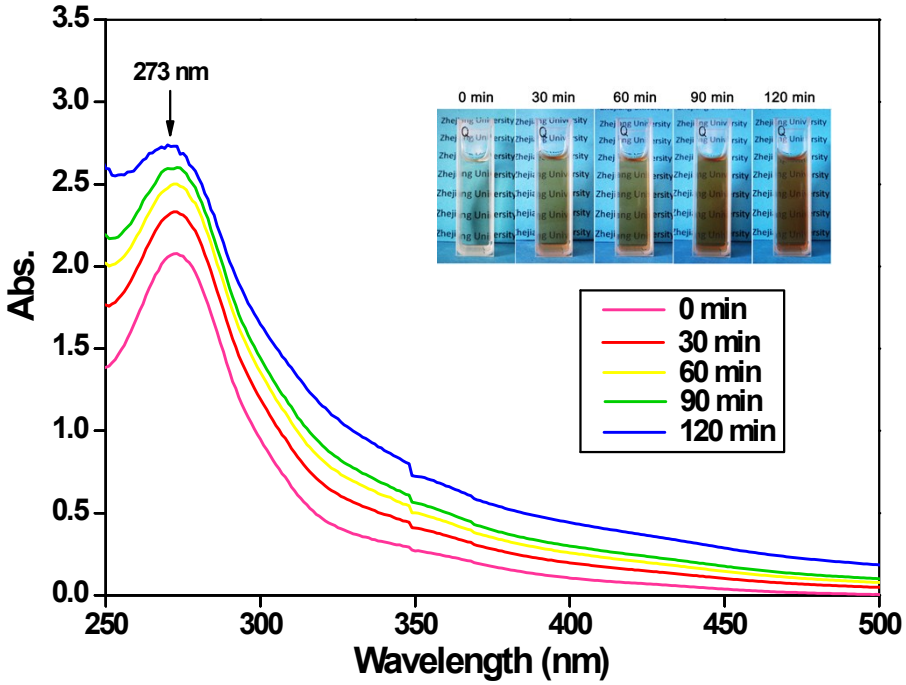

Fig. S2 UV-vis spectra of catechins/chitosan solutions after reaction for 0-120 min.

The UV-vis adsorption >300 nm could be the combination of peaks attributing to the formation of o-quinone and catechin-o-quinone resulting from the oxidation of the catechin and Michael-type or Schiff base adducts between amines and quinones [1-3].

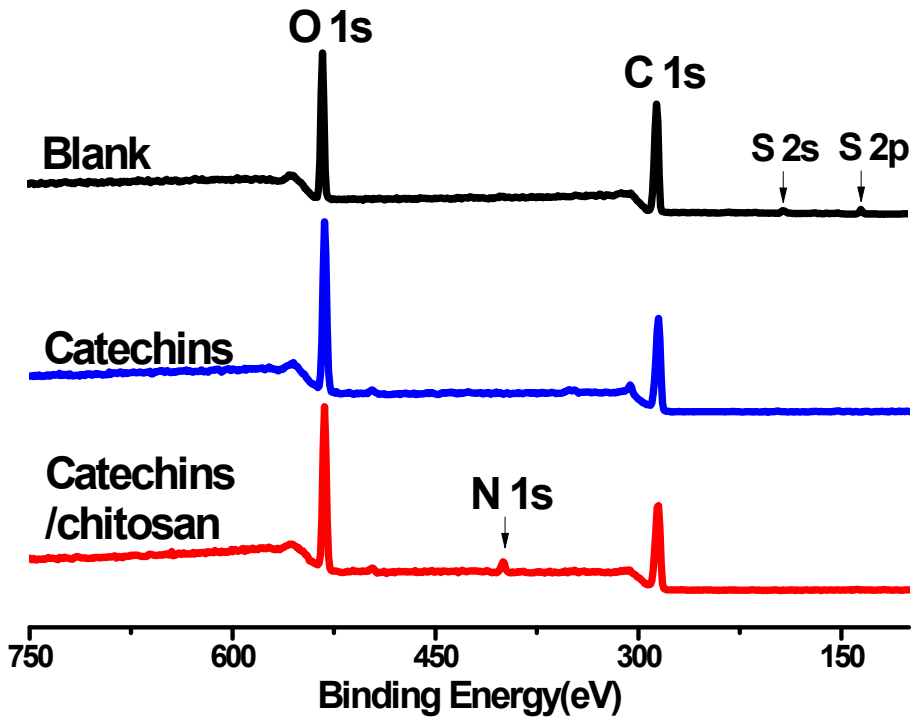

Fig. S3 XPS spectra of the blank PSf substrate, individual catechins deposited and catechins/chitosan co-deposited TFC NFMs.

Table S1 Chemical composition of the blank PSf, individual catechins deposited and catechins/chitosan co-deposited TFC NFMs.

Sample	C 1s (%)	O 1s (%)	N 1s (%)	S 2p (%)
Blank	57.84	40.88	0.98	0.30
Catechins	61.05	38.20	0.67	0.08
Catechins/chitosan	60.41	34.67	4.81	0.11

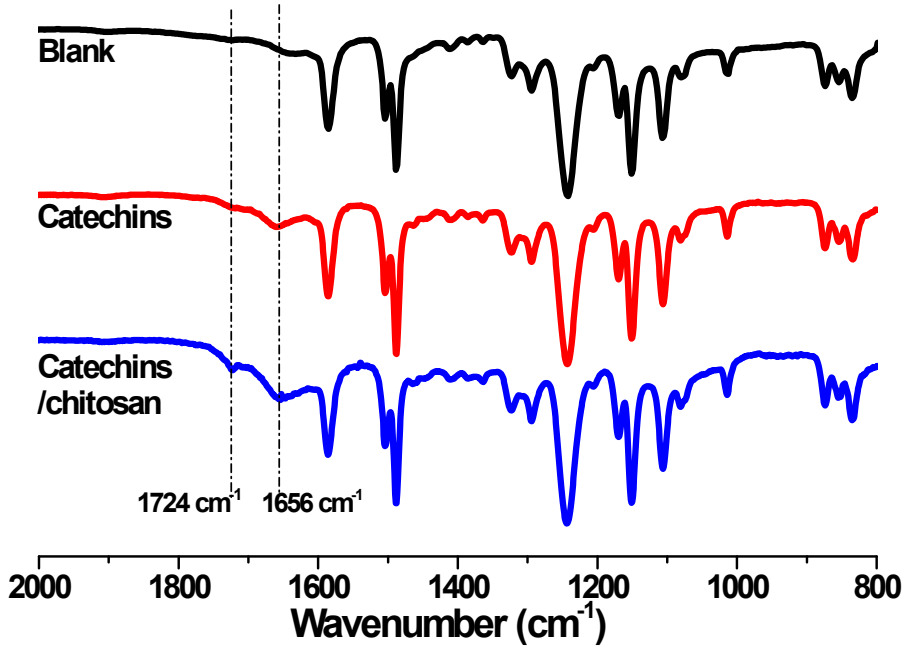

Fig. S4 FT-IR/ATR spectra of the blank PSf substrate, individual catechins deposited and catechins/chitosan co-deposited TFC NFMs.

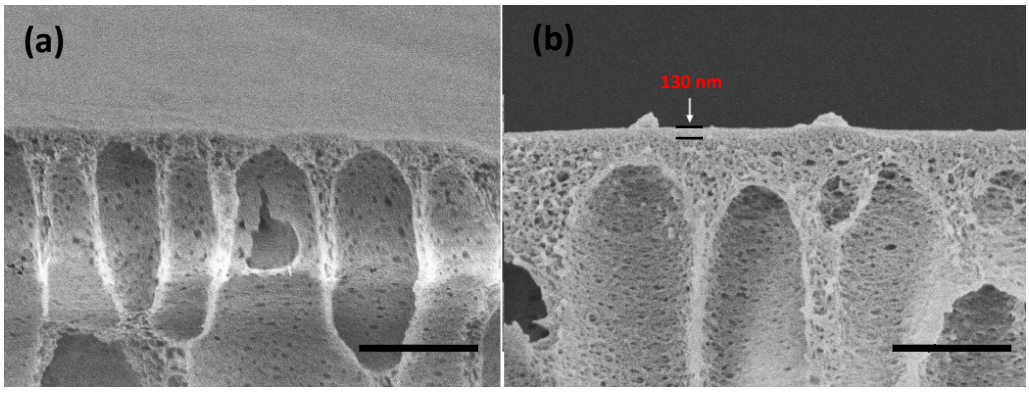

Fig. S5 Cross-section SEM images of the PSf substrate (a) and catechins/chitosan co-deposited TFC NFM (b) after incubation for 30 min. Scale bar = 1 μm.

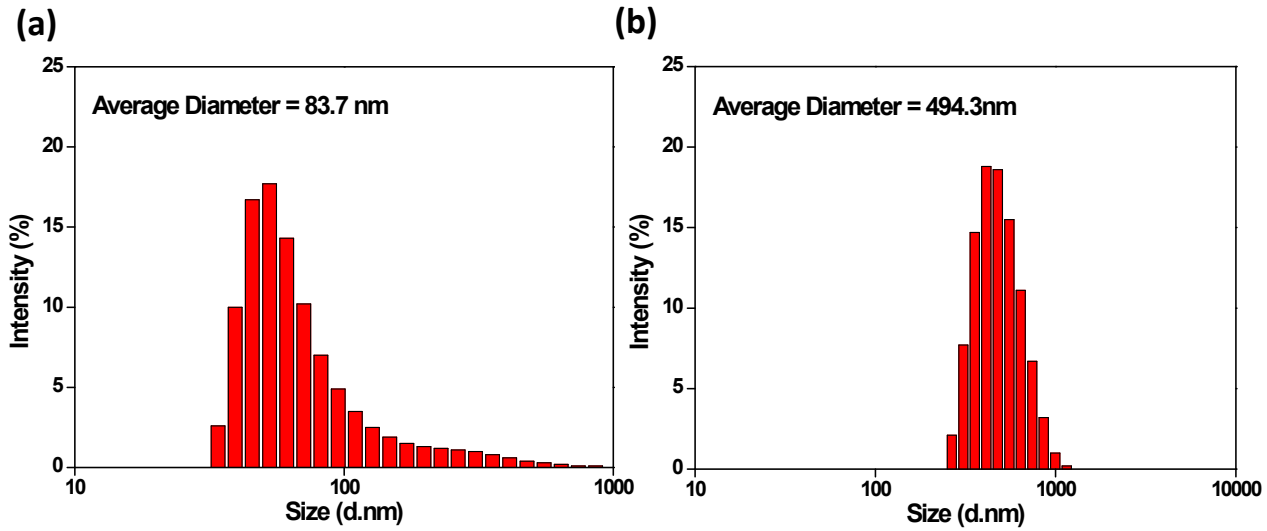

Fig. S6 The size distribution of catechins/chitosan aggregates (a) and individual catechins aggregates (b) in the corresponding solutions after incubation for 30 min.

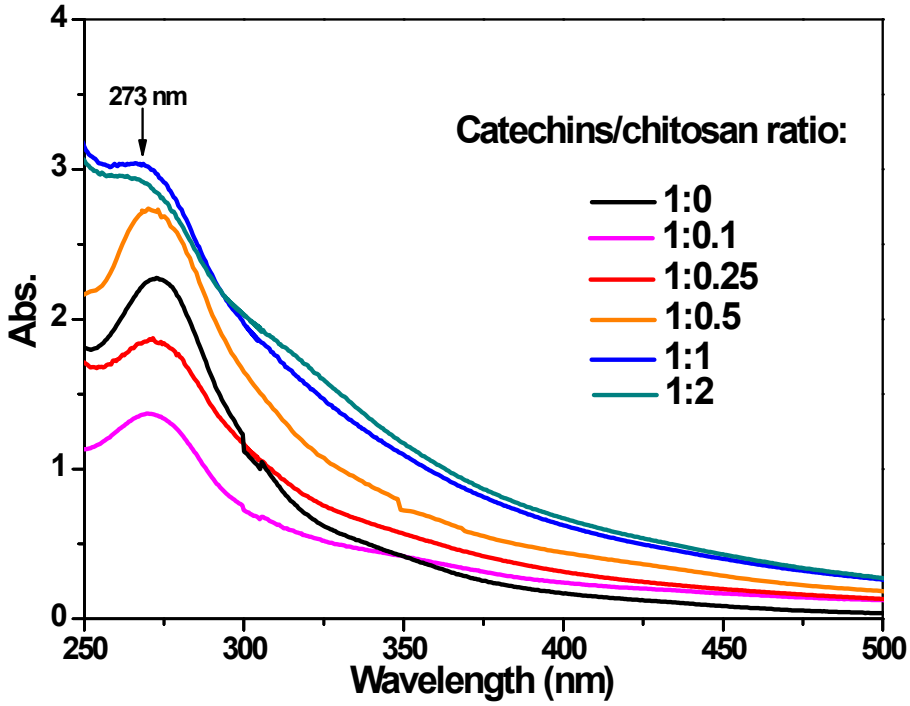

Fig. S7 UV-vis spectra of catechins/chitosan solutions after incubation for 30 min with

different catechns/chitosan ratios.

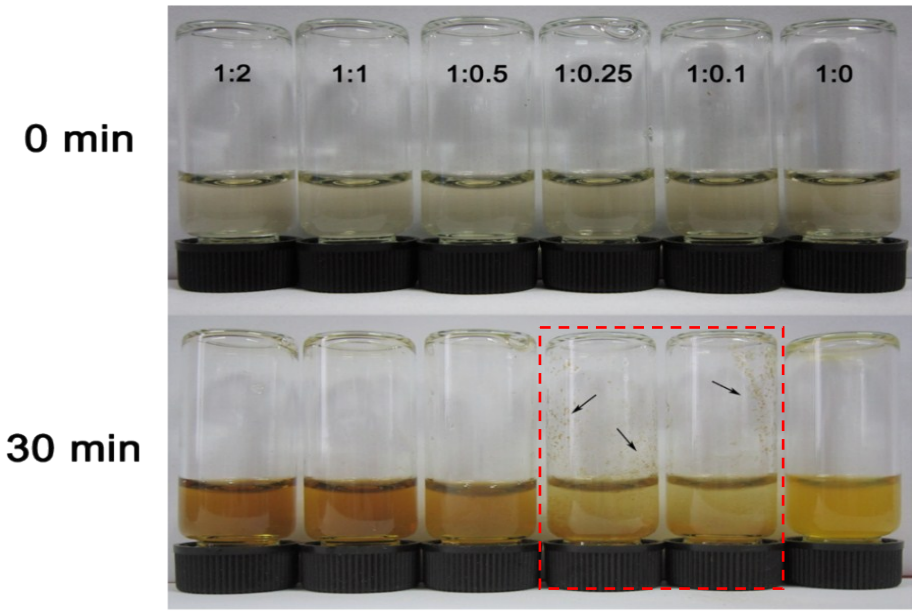

Fig. S8 Digital images of catechins/chitosan solutions after incubation for 30 min with different catechins/chitosan ratios. The black arrows are pointing at large visible catechins/chitosan aggregates.

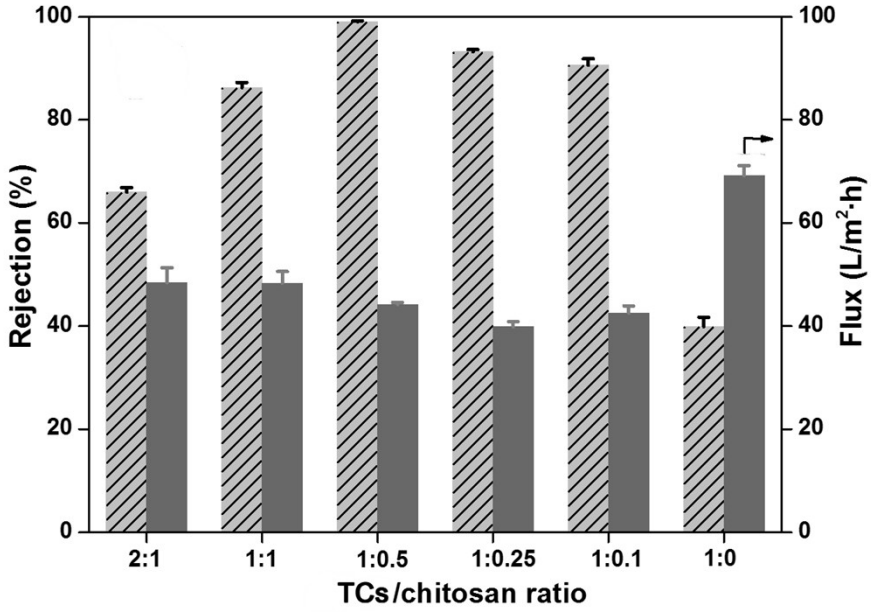

Fig. S9 Influence of catechin/chitosan ratio on nanofiltration performance of TFC membranes after incubation for 30 min. Test conditions: Na_2SO_4 concentration = 1000

mg/L, pH = 6.0±0.1, 25 °C, 0.6 MPa, cross-flow rate = 30 L/h.

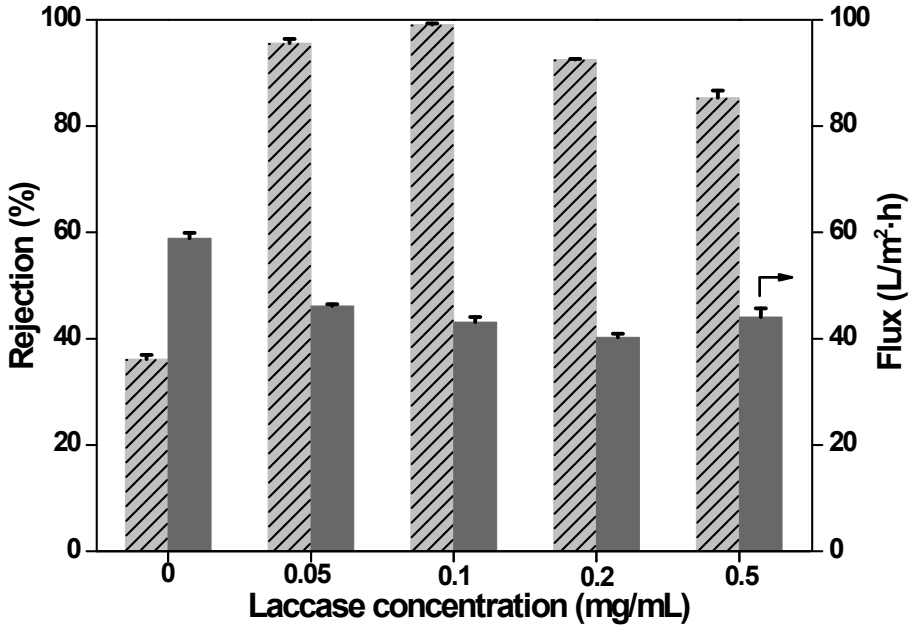

Fig. S10 Influence of laccase concentration on nanofiltration performance of TFC membranes after incubation for 30 min. Test conditions: Na_2SO_4 concentration = 1000 mg/L, pH = 6.0±0.1, 25 °C, 0.6 MPa, cross-flow rate = 30 L/h.

Table S2 Membrane performance information of commercially available TFC NFMs provided by membrane suppliers and other high performance TFC NFMs reported in open literatures.

Membrane type	Permeance range (L m^{-2} h^{-1} bar^{-1})	$MgSO_4$ retention (%)	Na_2SO_4 retention (%)	NaCl retention (%)	$CaCl_2$ retention (%)	Reference
Celgard N30F	2.9–3.6	--	80-95	25-35	--	Summarized in [4]
Desal 5DK	3.1–7.9	98	--	--	--	Summarized in [4]
NTR 7450	5.8-23	--	--	50	--	Summarized in [4]
NF270	8.6–16	>97	--	--	40-60	Summarized in [4]
PIP+BHTTM	13.2	95	99.5	30	--	[5]
DCH+SCHS	7.4	92	98.1	23	--	[6]

This work	7.5	95.2	98.9	40.0	70.3	--

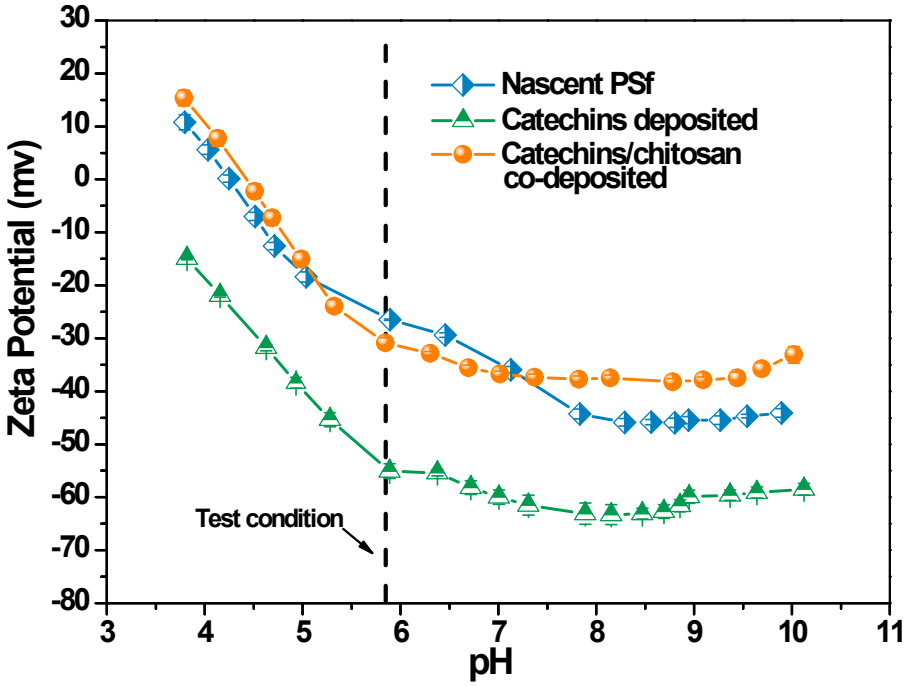

Fig. S11 Zeta potential of the nascent PSf substrate, individual catechins deposited and catechins/chitosan co-deposited TFC NFMs after incubation for 30 min.

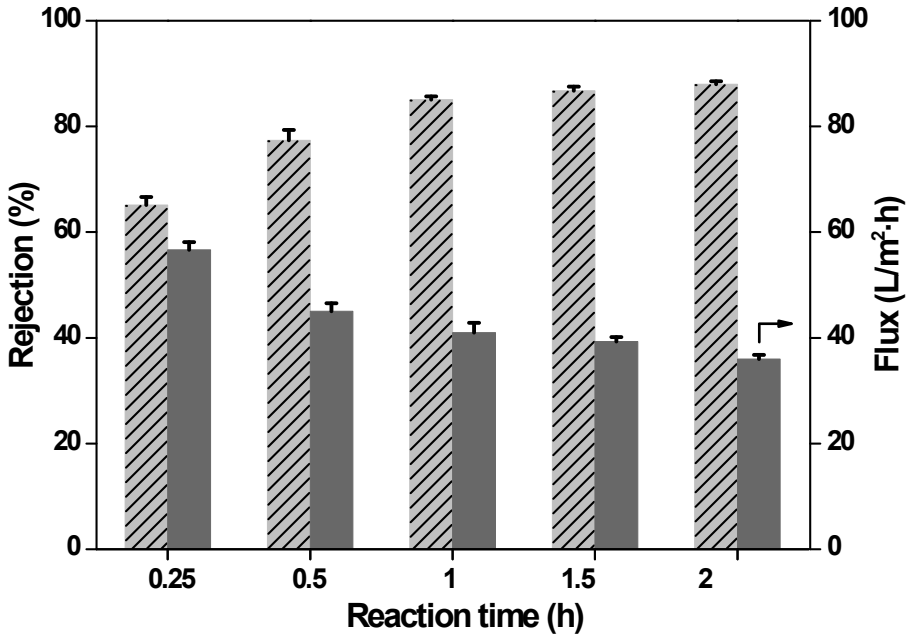

Fig. S12 Influence of co-deposition time on nanofiltration performance of TFC membranes.

Test conditions: $MgCl_2$ concentration = 1000 mg/L, pH = 6.0±0.1, 25 °C, 0.6 MPa, cross-flow rate = 30 L/h.

Table S3 Membrane performance information of TFC NFMs fabricated via PDA or poly-catechol deposition method as reported in open literatures. The listed retention data are the highest rejection values given in each work.

Membrane fabrication method	Permeance ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	Retention (%)	Pressure (bar)	Ref
PDA deposition	14.0	68.7% ($MgCl_2$)	6	[7]
PDA deposition, PEI grafting	7.3	73.7% ($MgCl_2$)	2	[8]
PDA deposition, PEI grafting, cross-linking	5.5	89.3% ($MgCl_2$)	8	[9]
PDA/PEI co-deposition, cross-linking	2.3	92% (Na_2SO_4)	6	[10]
CCh/PEI co-deposition, cross-linking	4.3	91.3% ($MgSO_4$)	6	[11]

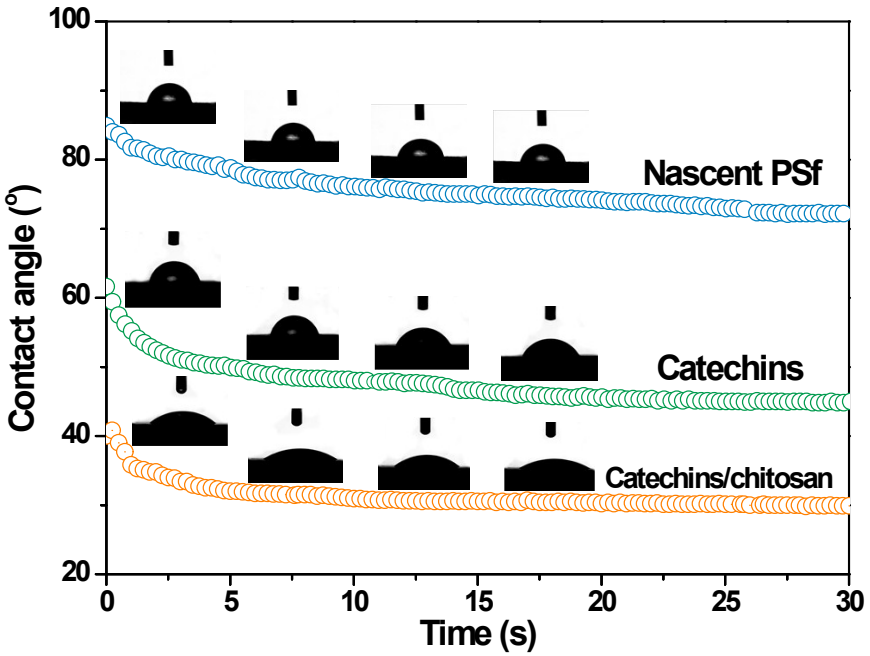

Fig. S13 Water contact angle of the nascent PSf substrate, individual catechins deposited and catechins/chitosan co-deposited TFC NFMs after incubation for 30 min.

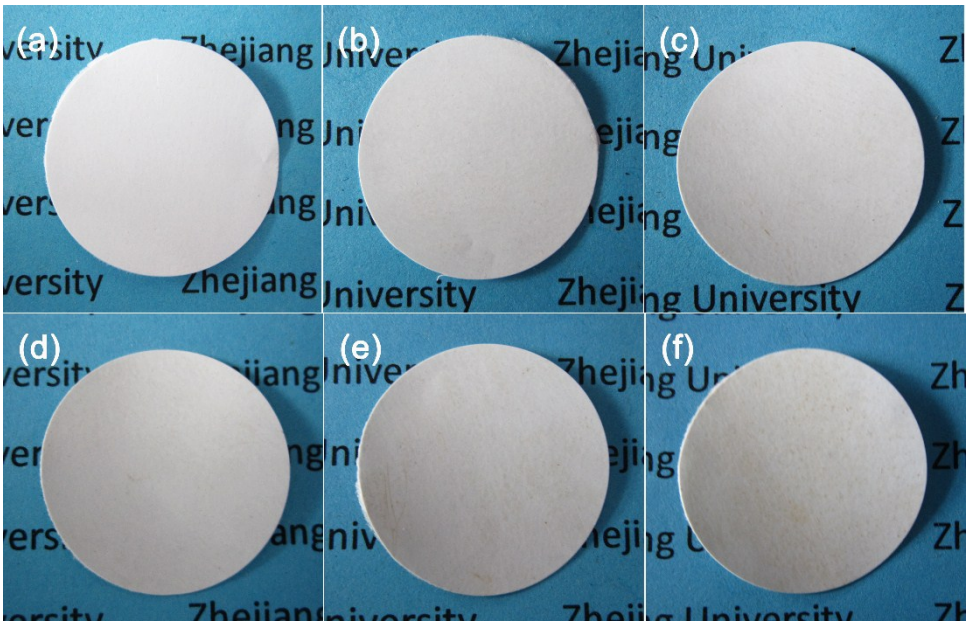

Fig. S14 Digital images of the PSf substrate (a) and TFC NFMs prepared with different co-deposition time: 15 min (b), 30 min (c), 60 min (d), 90 min (e), 120 min (f).

References

1. F. Sousa, G. M. Guebitz and V. Kokol, *Process Biochem.*, 2009, 44, 749-756.
2. L. Q. Wu, M. K. McDermott, C. Zhu, R. Ghodssi and G. F. Payne, *Adv. Funct. Mater.*, 2006, 16, 1967-1974.
3. S. Ryu, Y. Lee, J. W. Hwang, S. Hong, C. Kim, T. G. Park, H. Lee and S. H. Hong, *Adv. Mater.*, 2011, 23, 1971-1975.
4. G. Bargeman, J. B. Westerink, O. Guerra Miguez and M. Wessling, *Sep. Purif. Technol.*, 2014, 134, 46-57.
5. Y.-J. Tang, Z.-L. Xu, S.-M. Xue, Y.-M. Wei and H. Yang, *J. Membr. Sci.*, 2016, 498, 374-384.
6. G.-E. Chen, Y.-J. Liu, Z.-L. Xu, Y.-J. Tang, H.-H. Huang and L. Sun, *RSC Adv.*, 2015, 5, 40742-40752.
7. X.-l. Li, J.-h. Jiang, Z. Yi, B.-k. Zhu and Y.-y. Xu, *Chin. J. Polym. Sci.*, 2012, 30, 152-163.
8. R. Zhang, Y. Su, X. Zhao, Y. Li, J. Zhao and Z. Jiang, *J. Membr. Sci.*, 2014, 470, 9-17.
9. M. Li, J. Xu, C.-Y. Chang, C. Feng, L. Zhang, Y. Tang and C. Gao, *J. Membr. Sci.*, 2014, 459, 62-71.
10. Y. Lv, H.-C. Yang, H.-Q. Liang, L.-S. Wan and Z.-K. Xu, *J. Membr. Sci.*, 2015, 476,

50-58.
11. W.-Z. Qiu, Y. Lv, Y. Du, H.-C. Yang and Z.-K. Xu, *RSC Adv.*, 2016, 6, 34096-34102.