Short Communication

Unprecedented acid-tolerant ultrathin membranes with finely tuned sub-nanopores for energetic-efficient molecular sieving

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The discharge of acidic effluent streams containing multivalent metal ions and toxic dyes from industry poses an ineluctable threat to aquatic ecosystems and public health. Nanofiltration (NF, pore size ranging from 0.5 to 2 nm), featured by the efficient, environmentally friendly and continuous purification way, have been considered as an ideal technology to dispose acidic wastewater [1,2]. However, most polymer membranes suffer from structural instability in acidic media [3]. Consequently, the potential huge markets owing to demanding but rather underdeveloped acid-resistant NF membranes have promoted the urgently intensive research based on material and synthesis innovations.

Polyurethane (PU)-based materials appear promising for acid-resistant NF, as they exhibit desirable solvent tolerance and mechanical and chemical stability, given their relatively inert inherent structure and high hydrogen bond degree per se. PU is typically enabled via interfacial polymerization, which is a step-growth irreversible condensation polymerization process between nucleophile polyols in the aqueous phase and electrophile diisocyanate in the organic phase [4,5]. Nonetheless, the rapid condensation reaction make it difficult to obtain well-tailored nanoporosity and uniform membrane pore size distribution, on the other hand, water-containing system during PU synthesis will trigger the side reactions of isocyanate to produce amines and carbon dioxide resulting in declining membrane structural integrity [6]. To achieve precising sieving PU selective layer, the much longer reaction time and thicker selective layer are inevitable through this approach, and accordingly led to the challenging “trade-off” issue between thickness/pore governed flux and sieving ability that greatly restricted their cost-effective separation applications [7,8].

In this study, nature-inspired phenolic compounds were introduced to replace polyols as rate-limiting nucleophile reactants for kinetically controlled interfacial condensation with diisocyanate (Fig. 1a), while diminishing the side reactions using a minimalist solvent exchange strategy to realize ~10 nm ultrathin acid-tolerant PU membranes with finely tuned sub-nano-sieving pores and improved pore size uniformity. Experiments and density functional theory (DFT) simulation validated the formation mechanism. The resultant nanofiltration membranes exhibited simultaneously increasing flux and sieving ability for diverse dyes and ions that break the traditional “trade-off”. Furthermore, the highly cross-linked structure and unique electron-absorbing ability enable our brand-new membranes to be stable under strong acidic conditions during 500 h of operation, which has great potential for energy-efficient environmental remediation and resource recovery.

The synthesis process for the PU composite membranes with polyimide (PI) porous substrates is shown in Fig. S1 (online). TA coating layer was anchored to the PI substrate through Michael addition and the Schiff base reaction to introduce phenolic hydroxyl groups. The excess water in coating layer was replaced by n-hexane with solvent exchange to reduce side reactions. And then the pre-treated membrane surface was immersed in the organic phase solution of TDI for further reaction. The phenolic hydroxyl in TA coating acts as rate-limiting nucleophile reactants to attack the carbonyl carbon in TDI for the kinetically controlled nucleophilic addition reaction (Fig. 1a), resulting in the ultra-thin and defect-free PU-TA/TDI membranes. Fourier transform infrared (FTIR) spectroscopy results in Fig. S2 (online) showed the stretching vibrations peak of phenolic –OH groups at 3200–3400. For PU-TA/TDI membrane, the flatter peak of –OH groups and the new peaks corresponded to C–N bonds (1534 cm\textsuperscript{-1}), C–O–C stretching vibration (1034 cm\textsuperscript{-1}) and C=O stretching vibration peak (1722 cm\textsuperscript{-1}) indicated that partial phenolic hydroxyl groups

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have reacted with TDI and formed carbamate bonds. The reaction
was further verified by the X-ray photoelectron spectroscopy
(XPS). The increase of N content in PU-TA/TDI membrane surface
compared with the TA coating membrane and the emerged peak
at 285.60 and 287.06 eV associated to N–C=O and coincident peaks
of C–N/C–O in XPS high-resolution scan of C 1s spectra further
demonstrate the cross-linking of TDI and the formation of PU layer
(Figs. S3, S4 and Table S1 online).

Phenolic compounds, as rate-limiting nucleophile reactants, are
key to determining the kinetic process of PU layer construction and
thus tailoring their physicochemical characteristics. As a proof-of-
concept, DFT simulations of the anticipative reaction process
between functional moieties in typical phenolic coatings (i.e., TA,
gallic acid (GA), and dopamine (DA)) and diisocyanate were per-
formed as a simplified model (Fig. 1b). The main reaction sites
were identified according to the structure of phenolic polymers
(Fig. S5 online), where rate-determining step was the one climbing
lower energy barrier to react with isocyanate group. Thus, the reac-
tion activity followed the order DA (0.70 eV) > TA (1.91 eV) > GA
(3.74 eV). The higher cross-linking activity led to a denser effective
pore diameter (PU-DA/TDI: 0.24 nm, PU-TA/TDI: 0.29 nm, PU-GA/
TDI: 0.47 nm) (Fig. 1c). It was because polydopamine (pDA), bear-
ing a myriad of amine functional groups, especially primary amines
in polymeric structure, whose nucleophilic centers with high elec-
tron cloud density show higher reactivity toward isocyanate[9].
While electron-absorbing carboxyl groups in GA molecular struc-
ture not only reduces the activity of phenolic hydroxyl reaction
sites, but also reacts with isocyanates to generate small molecular
gases, thus compromising the compactness of the selective layer
[10]. In contrast, polymerization structure of TA contains a large
number of phenolic hydroxyl groups, in which the ortho or para-
phenolic hydroxyl group has a strong activating effect as an elec-
tron donor group. In addition, the restricted nucleophilic reactivity
of phenolic hydroxyl groups in TA monomer relative to amino
groups in DA monomer enables PU-TA/TDI membranes to exhibit
a more uniform pore size distribution as well as superior sieving
performance than PU-DA/TDI membranes (Fig. 1c and Fig. S6
online).

We further compared the TA coating membranes and PU-TA/
TDI membranes to investigate the role of kinetically controlled
interfacial condensation between the TA coating and TDI. And a
notable result was validated that it is central to transversely
tighten membrane pores contributed to the reduced pore diameter
from 0.68 to 0.29 nm as well as narrower pore size distribution and
thereby increasing selectivity (Figs. S7 and S8 online). However,
according to the scanning electron microscope (SEM) and ellip-
someter test results, the condensation reaction with TDI had
almost no effect on the TA coating layer thickness owing to the
limited reaction rate of TA and TDI and the controlled cross-
linking time of approximately 1 min (Figs. S9 and S10 online).
Transmission electron microscopy (TEM) analysis was conducted
to observe the accurate thickness of PU-TA/TDI layer down to
about 10 nm as shown in Fig. 1d, which is much thinner than those
of the mostly reported polyamide and polyurea based membranes

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**Fig. 1.** (Color online) The preparation and pore characteristics of PU membranes. (a) Schematic illustration of the preparation of PU-TA/TDI NF membrane. TA: tannic acid; TDI: toluene diisocyanate; (b) DFT calculation for the nucleophilic addition reaction between polyphenols and TDI; (c) the pore size distribution of the PU membrane prepared by different phenolic compounds; (d) TEM image of PU-TA/TDI membrane.
Such 10 nm selective layer with finely tuned sieving-pores can simultaneously reduce the mass transport resistance and achieve greatly enhanced sieving ability.

In addition, the water removal plays important roles in circumventing adverse side-reaction during PU membrane synthesis (Fig. S11 online) so as to endow the membrane architecture with more uniform surface, denser pore radius (reduced effective pore size from 0.54 to 0.29 nm), and higher degree of crosslinking (increased 36.7 %) (Figs. S12, S13, and Table S2 online). On the other hand, water removal avoids the formation of by-product amines and polyurea oligomers, which settle in and clog the membrane pores, leading to increased surface roughness and mass transfer resistance (Fig. S14 online). As a result, a 2.7-fold increase in permeation flux and the increased MB rejection (100%) can be simultaneously achieved in synthesized PU-TA/TDI membranes via the screened solvent exchange than the membranes free of water removal. Furthermore, n-hexane solvent exchange can contribute to 541.0 % higher permeation flux in comparison to direct drying at room temperature (Fig. S15 online). This was ascribed to n-hexane presented lower surface tension (γ, n-hexane 18.4 mN m⁻¹; water 72.0 mN m⁻¹) and less Flory-Huggins affinity interaction with membrane polymer than water solvent (χ, n-hexane 16.7; water 1.27) (Table S3 online), that can avoid excessive pore shrinkage owing to capillary pressure (ΔP = 2γ/r) that occur during direct drying process. Most significantly, such solvent exchange is a scalable method to construct PU separation membranes, and enhanced membrane properties were obtained by using chloroform as the exchange solvent (Fig. S16 online). For the choice of fit-for-purpose solvent, the following criteria must be satisfied: due to incomplete exchange solvent remove from the membrane surface, the exchange solvent should preferably be consistent with the subsequent cross-linking solvent and must avoid reacting with isocyanates. Moreover, better affinity with water facilitates accelerated solvent substitution, but decreased affinity with polymer amplifies the hazard of pore shrinkage; selecting solvents of balanced affinity with water and polymer is important, thus we mainly chose n-hexane as the exchange-friendly method. And the final optimized PU-TA/TDI membrane demonstrated the outstanding flux of 169.4 L m⁻² h⁻¹ with excellent rejection (99.9%) of MB (Figs. S17–S20 online).

To evaluate the acid-tolerance performance, PU-TA/TDI membranes were immersed in strongly acidic aqueous solutions at pH 1 for 60 d. As shown in Fig. 2a, PU-TA/TDI membranes showed steady permeation flux and rejection to MB solutions after soaking...
for 60 d. SEM results (Fig. S21 online) illustrated that no microscopic crack or defect were observed and the nanostructured papillae formed by polyphenol self-polymerization remain immobilized on PU-TA/TDI membrane surface after exposure to H2SO4 aqueous solution at pH 1 for 60 d and the roughness remains basically unchanged (Fig. S22 online). Moreover, the consistency of membrane surface ATR-FTIR spectra before and after acid treatment further confirmed the chemical structure stability of PU layer in extreme acid condition (Fig. S23 online). This is because the presence of electron-absorbing structure (∼N-) in carbamate group and abundant benzene rings with conjugation effect and steric hindrance in the PU-TA/TDI membrane will reduce the protonation sensitivity of carbonyl carbon and protect it from nucleophilic attack under acidic conditions (Figs. S24 and S25 online). And the presence of hydrogen bonding in PU-TA/TDI membrane also contributed to a more stable selective layer, which can be verified by the red-shift of absorption peak corresponding to C=O from 1735 to 1722 cm⁻¹ (Fig. S26 online). Therefore, our PU composite membrane exhibited outstanding acid-tolerant performance.

We further explored the separation performance of the PU-TA/TDI membranes for heavy metal ions and dyes in acid wastewater. The PU-TA/TDI membranes exhibited excellent permeation fluxes of more than 142 L m⁻² h⁻¹ and rejection rates greater than 98% for dyes with different molecular weights and charges, whether in neutral or H2SO4 solutions. The permeation flux decreased slightly for dyes with negative charge and vice versa for positively charged dyes owing to the transition of membrane surface charge under the condition of solution at pH 1 (Fig. 2b, Figs. S27 and S28 online). Furthermore, the rejection of PU-TA/TDI membrane for heavy metal ions (1000 ppm) in neutral solution was generally higher than that in acid solution (Fig. 2c). It is because heavy metal ions can coordinate with the unreacted phenolic hydroxyl in neutral solution to reduce membrane pore size [14]. And the PU-TA/TDI membrane demonstrated superior sieving property for heavy metal ions, surpassing that of most of the state-of-the-art nanofiltration membranes (Fig. 2d and Table S4 online), which demonstrated the high competence of the PU-TA/TDI membrane for the industrial wastewater treatment.

The PU-TA/TDI membrane had almost no adsorption of MB compared with the TA coating membrane owing to its denser pore size (0.29 nm) and narrower pore size distribution (Fig. S29 online and Fig. 2e). The acidic condition has no obvious effect on dye adsorption but can significantly reduce metal ion adsorption owing to the restricted coordination chelation and increased repulsion to metal cations (Figs. S30 and S31 online). Furthermore, the relatively hydrophilic PU-TA/TDI membranes showed great flux recovery ratios and low total fouling ratios after three-cycle filtration tests for BSA and HA solution, indicating its excellent anti-fouling behavior (Figs. S32–S34 online). Accordingly, there was almost no discernible degradation of PU-TA/TDI membrane performance during the long-term test up to 500 h with 200 ppm MB acidic solutions (Fig. 2f). These results strongly proved the practical application potential of our PU-TA/TDI composite membranes.

In conclusion, we have demonstrated a de novo kinetically controlled interfacial condensation method for the facile construction of ultrathin and defect-free PU membranes. DFT simulations and complementary experiments clarified that the kinetically controlled nucleophilic addition condensation reaction with TDI played a key role in regulating the selective layer thickness and pore size of the prepared PU membranes. The brand-new PU-TA/TDI membranes showed a remarkable increase in permeance with satisfactory selectivity, breaking the “trade-off” of conventional PU membrane. Such scalable, facile membrane fabrication process potentially enables the large-scale production of durable polyphenol-dominated PU sub-nanoporous membranes for acid wastewater treatment towards the ever-increasing environmental issues.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Author contributions

Fan Yang, Yanqiu Zhang, and Lu Shao conceived the study and designed the experiments. Fan Yang fabricated the membranes and conducted the characterizations with the help of Yanqiu Zhang, Junhui Huang, Gang Gao, Jiaqi Zhu, Jun Ma, and Lu Shao. Fan Yang, Yanqiu Zhang, and Lu Shao analyzed the membrane formation mechanism and characterization results. Fan Yang, Yanqiu Zhang, Junhui Huang, and Lu Shao wrote and edited the manuscript. All authors read and gave final approval to submit the manuscript.

Appendix A. Supplementary materials

Supplementary materials to this short communication can be found online at https://doi.org/10.1016/j.scib.2022.12.021.

References

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