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Cooperative defect tailoring: A promising protocol for exceeding performance limits of state-of-the-art MOF membranes



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Keywords: Metal-organic framework Structural defects Orientation Membrane Gas separation	Preferred orientation control represents an effective method for grain boundary defect elimination at the mesoscopic scale and therefore, performance enhancement of MOF membrane. In contrast, tailoring the separation performance of MOF membrane via structural defect engineering at the microscopic scale remains elusive. In this work, we pioneered the fabrication of (111)-oriented UiO-66 membrane via oriented tertiary growth. The use of ZrS ₂ as metal source during solvothermal synthesis led to higher number of missing linkers within the framework and therefore, preferential adsorption of CO ₂ over N ₂ . In comparison with secondary growth, both CO ₂ /N ₂ selectivity and CO ₂ permeability of obtained UiO-66 membrane after tertiary growth were concurrently increased, thereby transcending both the 2008 Robeson upper bound and the separation performance limits of

state-of-the-art polycrystalline MOF membranes for CO2/N2 gas pair.

1. Introduction

Large-scale energy-efficient separation of CO₂ from flue gas, biogas and natural gas and its green conversion into high value-added fuels and chemicals have become critical to meet the global energy and environmental challenges [1,2]. In comparison with conventional separation technologies, metal-organic framework (MOF) membrane exhibited attractive prospects in the energy-efficient separation of industrially important gas mixtures [3-10]. Recent decades witnessed significant progress made in the preparation of MOF membranes for efficient CO₂ separation. For instance, through heteroepitaxial growth of Co-ZIF-L on Zn-ZIF-L layers, Zhang et al. fabricated well-intergrown Co/Zn-ZIF-L membrane showing attractive CO2/N2 selectivity (17.8) and CO2 permeance (244.9 GPU) [11]; Jiang et al. prepared ZIF-62 glass MOF membrane with superior selectivity towards CO_2/N_2 (34.5) and CO₂/CH₄ (36.6) gas pairs due to the elimination of grain boundary defects [12]; Tokay et al. synthesized Mg-MOF-74/PVAc mixed-matrix membranes (MMMs) by incorporating Mg-MOF-74 crystals into the PVAc matrix with a solvent-casting method. Compared with pure PVAc membranes, both the CO2/CH4 selectivity and CO2 permeability of Mg-MOF-74/PVAc MMMs were improved, owing to the preferential adsorption of CO2 over CH4 in Mg-MOF-74 particles [1]. It is well recognized that defect elimination of MOF membrane represents a

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powerful protocol for improving its separation performance. For instance, preferred orientation control has proven to be effective for eliminating grain boundary defects at the mesoscopic scale and therefore, improving MOF membrane separation performances [13-21]. Nevertheless, this is not always the case regarding to defect tailoring at the microscopic scale. Deliberate tailoring of the missing organic linkers, missing metal clusters, and long-range order within the framework may affect the structure and function of MOF membranes [22-30] and therefore, positively influence their separation performances. For instance, Fischer indicated that metal and/or linker vacancies significantly influenced mass-delivery routes inside the apertures, which was of great value for separation and adsorption processes [23]. Several relevant studies also pointed out that introduction of missing-linker defects within the MOF structure gave rise to dramatically enhanced porosity and therefore, improved performances for gas uptake [31-33]. Although some progress has been made in defect tailoring of MOF powders and membranes [9,34,35], cooperative defect engineering of MOF membranes at different scales, which may jointly contribute to their performance improvement, remains elusive to date.

UiO-66, a representative Zr-MOF possessing chemical composition $Zr_6O_4(OH)_4(BDC)_6$ (BDC represents 1,4-benzene-dicarboxylic acid), has emerged as an encouraging contender for using in membrane-based CO_2 capture, owing to the intrinsic affinity between CO_2 gas molecules and

 $Zr_6O_4(OH)_4$ clusters [36–40]. Previous studies indicated that monocarboxylic acids (i.e., HAc) were capable of yielding defective structures within UiO-66 framework via coordination modulation [26,29,41-45]. Even though the relation between structural defects within the UiO-66 framework and membrane separation performance remains elusive, it is beyond dispute that structural defects located in the framework have a remarkable impact on pore volume, aperture size, and gas uptake behavior. For example, D'Alessandro demonstrated that presence of defects in UiO-66 exerted powerful influences on the adsorption capacity of CO₂ [46]. Zhou found that rational defect introduction in the UiO-66 framework led to a pronounced enhancement in surface area as well as CO₂ uptake [32]. Because separating CO₂ from the flue gas dominantly depends on preferential CO2 adsorption on coordinatively unsaturated sites instead of molecular sieving, increasing the defect concentration within UiO-66 framework may boost the CO2/N2 adsorption selectivity and therefore, enhance its separation performance for the CO_2/N_2 gas pair.

Aside from defect tailoring within the framework, preferred orientation control was expected to improve performance of UiO-66 membranes for CO_2/N_2 separation. Among all possible crystallographic orientations (shown in Fig. 1), adoption of (111)-preferred orientation enabled quasi-perpendicular alignment of 5.7 Å-sized straight apertures, which were profitable for reducing the diffusion path length. However, to date there has not been any report on producing dominantly (111)oriented functional UiO-66 (exclusive of NH₂-UiO-66) membrane.

In the present work, we took an initiative to prepare (111)-oriented UiO-66 membrane possessing higher number of missing linkers within the framework via oriented tertiary growth (Fig. 1). The experimental procedure was described briefly as follow: Firstly, UiO-66 seeds, which

had well-defined octahedral shape, were synthesized according to the procedure reported by Lu [47]; subsequently, close-packed uniform UiO-66 monolayers exhibiting a pronounced preferred orientation with (111) crystal facets lying parallel to substrates were manufactured through turbulent air–liquid interface-assisted self-assembly (ALIAS) procedure; finally, (111)-oriented UiO-66 membranes were fabricated via tertiary growth with ZrS₂ as metal source. The use of ZrS₂ played a vital role during tertiary growth since not only the desirable orientation originated from monolayers was favorably reserved, but also higher content of structural defects (e.g., higher number of missing linkers) within the framework were introduced, which led to much higher CO_2/N_2 IAST selectivity (82.53). Accordingly, prepared membrane manifested better CO_2/N_2 selectivity (35.6) accompanying with a high CO_2 permeance.

2. Experimental section

2.1. Reagents and materials

Zirconium tetrachloride (ZrCl₄, 99.9%, Macklin), zirconium disulfide (ZrS₂, 99.5%, Alfa Aesar), 1,4-benzenedicarboxylic acid (BDC, 99%, Macklin), *N*,*N*-dimethylformamide (DMF, 99.8%, Tianjin Kemiou), acetic acid (HAc, 99.5%, Tianjin Kemiou), polyvinylpyrrolidone (PVP, $M_w = 58,000, 99\%$, Macklin), methanol (CH₄O, 99.5%, Tianjin Kemiou), ethanol (C₂H₆O, 99.7%, Tianjin Kemiou), and triethylamine (TEA, 99%, Sinopharm) were used as received without further purification. Porous α -Al₂O₃ disks with the pore size of 70 nm, diameter of 18 mm, and thickness of 1 mm were purchased from Fraunhofer IKTS, Germany.



Fig. 1. Illustration of (111)-oriented UiO-66 membrane production by tertiary growth. Framework structure is expressed as a single unit cell of UiO-66. C atoms are shown in black, O atoms in red and $Zr_6O_4(OH)_4$ clusters in cyan-blue. H atoms are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2.2. Solvothermal synthesis of UiO-66 seeds using ZrCl₄ as metal source

In a typical synthesis, 0.2 g of BDC and 0.014 g of TEA were dissolved in 140 mL of DMF under stirring for 10 min, and then 20 mL of HAc was added. The above clear solution was heated to 120 °C in an oil bath for 30 min. Subsequently, 0.28 g of ZrCl₄ dissolved in 10 mL of DMF was added in the precursor solution and maintained at 120 °C for 6 h. Obtained white solid powders were centrifuged, washed with DMF and methanol three times, and finally dried in a vacuum oven at 80 °C overnight.

2.3. Solvothermal synthesis of UiO-66 seeds using ZrS₂ as metal source

0.24 g of ZrS_2 and 0.3 g of BDC were dissolved in 60 mL of DMF containing 9 mL of HAc under ultrasonication for 30 min and then placed in an oven preheated to 160 °C for 96 h. Obtained brown solid powders were centrifuged, washed with DMF and methanol three times, and finally dried in a vacuum oven at 80 °C overnight.

2.4. Deposition of UiO-66 seed monolayer

0.05 g of uniform UiO-66 seeds were dispersed in a solution of PVP (0.375 g) in 15 mL of water under stirring for 24 h. Subsequently, PVPmodified UiO-66 seeds were collected by centrifugation, washed five times with water, and mixed with ethanol (5 mL). The seed layer deposition procedure was similar to our previous report [19]. Initially, a water-containing rectangular vessel was connected with a circular pump. Subsequently, an ethanol suspension containing PVP-modified UiO-66 crystals (0.01 g mL⁻¹) was slowly injected to the air-liquid interface with a microsyringe at the speed of 2 μ L·min⁻¹. After 10 min, a compact UiO-66 seed monolayer was formed at the interface. Finally, the UiO-66 seed monolayer was transferred to the porous α -Al₂O₃ substrate by elevating it to the interface.

2.5. Secondary growth of UiO-66 membrane with ZrS₂ as metal source

0.24 g of ZrS₂ and 0.3 g of BDC were dissolved in 60 mL of DMF containing 9 mL of HAc and 0.03 mL of water under ultrasonication for 30 min. Subsequently, the UiO-66 seed monolayer-modified substrate was vertically placed into a 50 mL Teflon-lined autoclave and immersed in the precursor solution. Solvothermal reaction was carried out in a convective oven at 160 °C for 24 h. After solvothermal reaction, prepared UiO-66 membrane was fetched out, soaked in methanol for 15 min, and finally dried overnight at 80 °C under vacuum.

2.6. Tertiary growth of UiO-66 membrane with ZrS_2 as metal source

The detailed procedure for tertiary growth was identical to secondary growth as mentioned above.

2.7. Characterization

The crystal structure, phase purity, and preferred orientation of UiO-66 powders and membranes were measured by Rigaku X-ray SmartLab diffractometer with Cu–K α radiation in the range of 5–50° at a scanning rate of 8°·min⁻¹ at 45 kV and 200 mA. SEM images and EDXS patterns were taken on FlexSEM-1000 instrument (Hitachi). N₂ and CO₂ adsorption isotherms were recorded on Micromeritics ASAP 2020 Plus HD88. The samples were degassed at 120 °C for 15 h prior to analysis. TGA analysis was conducted on a NETZSCH (TG 209) thermal analyzer in air flux from 40 to 900 °C with a ramping rate of 10 °C·min⁻¹. Prepared UiO-66 membrane was put in a membrane module and sealed with Orings on both sides. Mass flow meters were used to maintain both feed and the sweep flow (Helium) rates at 50 mL·min⁻¹, and the differential pressure on the both sides was maintained at 1 bar. The composition of the gas steam was analyzed by using a calibrated gas chromatograph (7890B, Agilent). Separation factor (SF) $\alpha_{A/B}$ was defined as the quotient of the volumetric fractions of components (A, B) in the permeate side divided by the quotient of the volumetric fractions of components (A, B) in the feed side:

$$\alpha_{A/B} = \frac{X_{A,perm} / X_{B,perm}}{X_{A,feed} / X_{B,feed}}$$

The ideal selectivity, i.e., $\alpha_{A/B}$ (ideal), was defined as the single gas permeance ratio of gases A and B:

$$\alpha_{A/B}(\text{ideal}) = \frac{P_A(\text{permeance})}{P_B(\text{permeance})}$$

Permeability (P_i) was defined as the flux of permeate side component per unit area (J_i) scaled on its driving force (the differential pressure (ΔP_i) on the feed side and permeate side) per unit membrane thickness (L) across the membrane:

$$P_i(\text{permeability}) = \frac{J_i \cdot L}{\Delta P_i} = P_i(\text{permeance}) \times L$$

Barrer is the commonly used unit of Permeability (1 Barrer = 3.348 $\times ~10^{-16} \mbox{ mol} \cdot m^{-1} \cdot s^{-1} = 10^{-10} \mbox{ cm}^3$ (STP) $\cdot cm^{-1} \cdot s^{-1} \cdot cmHg^{-1}$).

3. Results and discussion

3.1. Elucidation of structural defects of UiO-66 prepared with ZrS_2 as metal source

The feasibility of solvothermal conversion of ZrS₂ to UiO-66 particles has been demonstrated in previous work [39]. For a comparison, parallel UiO-66 powders were also synthesized from ZrCl₄, which was abbreviated as UiO-66 (ZrCl₄) (Fig. 2a). After solvothermal treatment of ZrS2 with BDC ligands under controlled conditions, newly formed particles displayed an octahedral shape with a broad grain size distribution of 0.4–5.1 µm (Fig. 2b). The XRD pattern of prepared samples indicated the formation of pure UiO-66 phase (Fig. 2c). Fig. 2d showed N₂ adsorption isotherm of powdered UiO-66 synthesized from ZrS₂, abbreviated as UiO-66 (ZrS₂), in the presence of HAc. The BET surface area and pore volume of powdered UiO-66 (ZrS₂) reached 939.8 m²·g⁻¹ and 0.597 cm³·g⁻¹, which were better than those of powdered UiO-66 (ZrCl₄) (866.4 m²·g⁻¹ and 0.441 cm³·g⁻¹). The number of missing linkers of prepared UiO-66 samples was further confirmed by TGA analysis in an air environment (Fig. 2e) by assuming that the final residual after calcination was pure ZrO2 [45]. In theory, the weight loss of defect-free UiO-66 samples was 54.6%. In contrast, prepared UiO-66 (ZrS₂) and UiO-66 (ZrCl₄) showed relative weight losses of 45.7% and 51%, corresponding to missing linker numbers of 1.96 and 0.79 within the framework structure, respectively. This implied that compared with UiO-66 (ZrCl₄), UiO-66 (ZrS₂) possessed higher number of missing linkers. To elucidate the potential influence of missing linker numbers on UiO-66 membrane separation performance, gas adsorption properties of CO2 and N2 on UiO-66 (ZrS2) were evaluated and compared with those of UiO-66 (ZrCl₄). Our results indicated that UiO-66 (ZrS₂) not only exhibited higher CO₂ adsorption capacity (62.29 cm³·g⁻¹ STP) but also higher CO₂/N₂ IAST selectivity (82.53) at 1 bar (Fig. 2f) in comparison with those of UiO-66 (ZrCl₄) (43.15 cm³·g⁻¹ STP and 24.35), relying on preferential adsorption of CO₂ by metal-oxide-like Zr₆ nodes. Therefore, it is reasonable to deduce that the employment of ZrS₂ as metal source during solvothermal synthesis is beneficial for enhancing the UiO-66 membrane performance towards the separation of gas pair CO_2/N_2 .

3.2. Preparation of UiO-66 seeds and (111)-oriented UiO-66 seed monolayer

600 nm-sized UiO-66 seeds exhibiting uniform octahedral shape and



Fig. 2. SEM images of powdered UiO-66 synthesized from (a) $ZrCl_4$ and (b) ZrS_2 . (c) XRD patterns of ZrS_2 powders and corresponding UiO-66 (ZrS_2). (d) N_2 adsorption isotherms of powdered UiO-66 ($ZrCl_4$) and UiO-66 (ZrS_2). (e) TGA curves for UiO-66 (ZrS_2) and UiO-66 ($ZrCl_4$) under air conditions. (f) CO₂ and N_2 adsorption isotherms of powdered UiO-66 ($ZrCl_4$) and UiO-66 (ZrS_2). (e) TGA curves for UiO-66 (ZrS_2) and UiO-66 ($ZrCl_4$) under air conditions. (f) CO₂ and N_2 adsorption isotherms of powdered UiO-66 ($ZrCl_4$) and UiO-66 (ZrS_2). Scale bar: 1 μ m.

narrow size distribution were prepared by following a well-documented procedure (Fig. 2a). Subsequently, (111)-oriented UiO-66 monolayers were deposited on α -Al₂O₃ substrates by turbulent ALIAS method (Fig. 3a–c) [19]. The XRD pattern (Fig. 3g) showed conspicuous peaks (20) at 7.3°, 14.6° and 21.9°, which corresponded to (111), (222) and (333) planes, thereby vividly confirming the dominance of (111)-preferred orientation.

3.3. Fabrication of (111)-oriented UiO-66 membrane via secondary growth $% \mathcal{L}_{\mathrm{S}}^{\mathrm{S}}$

As mentioned above, ZrS_2 was a promising candidate for using as the metal source of UiO-66 membrane since higher number of missing linkers could be introduced within the framework, resulting in preferential adsorption of CO₂ over N₂ as well as higher CO₂ adsorption

capacity; simultaneously, because of its higher stability under solvothermal conditions, employing ZrS_2 as metal source facilitated the production of well-intergrown UiO-66 membrane reserving the preferred orientation originated from the seed monolayer, which was beneficial for eliminating grain boundary defects [20]. As shown in Fig. 3d–f, after secondary growth, well-intergrown 1.2 µm-thick UiO-66 membrane with smooth surface morphology was successfully prepared with ZrS₂ as metal source. The corresponding XRD pattern (Fig. 3g) indicated that only diffraction peaks derived from (111), (222) and (333) planes were present, thereby elucidating the dominance of (111)-preferred orientation.

In the next step, volumetric flow rates of H₂, CO₂, N₂ and CH₄ through prepared UiO-66 membrane were evaluated on a Wicke-Kallenbach apparatus. As shown in Fig. 3h, single gas permeation results indicated the CO₂ permeance (6.77 \times 10⁻⁷ mol·m⁻²·s⁻¹·Pa⁻¹)



Fig. 3. (a–c) SEM images of prepared UiO-66 monolayer. (d–f) SEM images of UiO-66 membrane obtained by secondary growth. (g) XRD characterization of UiO-66 seeds, monolayer, and membrane obtained by secondary growth. (h) Single gas permeation results of UiO-66 membrane. (i) Ideal selectivity and separation factor of equimolar gas pairs of UiO-66 membrane. Detailed experimental data were listed in Table S1. Scale bar: 1 μm.

through the membrane was much higher than that of CH₄, N₂ and H₂, because of its superior affinity interactions between CO₂ and $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters. In addition, permeances of gas molecules were not positively associated with their kinetic diameters since the pore size of UiO-66 (5.7 Å) was much larger than the above gases. The CO₂/N₂, H₂/N₂ and CO₂/CH₄ ideal selectivity achieved 22.48, 7.30 and 6.23, respectively (Fig. 3i), which were much higher than the corresponding Knudsen diffusion coefficients, thereby confirming the presence of very few grain boundary defects.

3.4. Fabrication of (111)-oriented UiO-66 membrane via tertiary growth

Tertiary growth represented a facile, effective, and cost-effective method for repairing grain boundary defects of polycrystalline molecular sieve membranes [48]. Aiming at further eliminating grain boundary defects while maintaining the desired preferred orientation derived from the UiO-66 monolayer, herein tertiary growth was carried out following the procedure identical to secondary growth. After tertiary growth, prepared UiO-66 membrane (Fig. 4a) exhibited larger grain size (2.3 μ m) while maintaining relatively smooth surface morphology. Cross-sectional SEM image indicated that the membrane thickness increased to 2.2 μ m (Fig. 4b). In addition, a clear boundary between the UiO-66 top layer and underlying α -Al₂O₃ substrate could be discerned from the cross-sectional EDXS pattern (Fig. 4c), indicating that prepared membrane did not deeply penetrate into α -Al₂O₃ pores, which was beneficial for reducing gas diffusion barrier. The XRD pattern (shown in

Fig. 4d) further confirmed that prepared UiO-66 membrane remained dominantly (111)-oriented.

Our single-component gas permeation results implied that after tertiary growth, prepared UiO-66 membrane displayed a CO₂ permeance of $4.07\times 10^{\text{-7}}\,\text{mol}\cdot\text{m}^{\text{-2}}\cdot\text{s}^{\text{-1}}\cdot\text{Pa}^{\text{-1}},$ while CO $_2/N_2,$ H $_2/N_2$ and CO $_2/CH_4$ ideal selectivity reached 35.6, 18.35 and 11.64 (Fig. 4e-f), which were close to or even surpassed the 2008 Robeson upper bounds (Fig. 4g-h, S1) [49]. It should be particularly noted that the CO_2/N_2 selectivity was the highest in comparison with other pure MOF membranes tested under similar conditions, resulting in far exceeding of performance limits of state-of-the-art polycrystalline MOF membranes (Fig. 4i); moreover, in comparison with the UiO-66 membrane obtained by secondary growth, not only the CO₂/N₂ selectivity but also the CO₂ permeability of the UiO-66 membrane prepared by tertiary growth were concurrently increased. This was in sharp contrast to the widely used post-synthetic modification (PSM) route [50-52], which led to higher separation selectivity at expense of a moderate decrease in permeability. The simultaneous improvement in selectivity and permeability could possibly be attributed to effective orientation control of UiO-66 membrane during tertiary growth as confirmed by a recent study in which randomly oriented UiO-66 membrane obtained by tertiary growth exhibited higher gas pair selectivity for CO2/N2 but much lower CO2 permeability compared with the one fabricated by secondary growth [39]. To our knowledge, this is the first report of repeated epitaxial growth-induced synergistic enhancement of gas selectivity and permeability in MOF membranes.



Fig. 4. (a, b) SEM images of UiO-66 membrane prepared by tertiary growth. (c) Cross-sectional EDXS mapping of prepared UiO-66 membrane (color code: Zr signal = red; Al signal = green). (d) XRD patterns of simulated UiO-66 powders and UiO-66 membrane prepared by tertiary growth. (e) Single gas permeation results of UiO-66 membrane. (f) Ideal selectivity and separation factor of equimolar gas mixtures of UiO-66 membrane. Comparing UiO-66 membrane separation performances with (g, h) the 2008 Robeson upper-bound and (i) other non-modified pure MOF membranes measured at 1 bar. Detailed experimental data were listed in Tables S2 and S3. Scale bar: 1 µm. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

4. Conclusions

To summarize, we demonstrated that employment of ZrS₂ as metal source of UiO-66 resulted in higher number of missing linkers within the framework and therefore, higher CO2/N2 IAST selectivity as well as CO2 adsorption capacity under ambient conditions. The use of ZrS₂ as metal source during tertiary growth led to the formation of well-intergrown (111)-oriented UiO-66 membrane with higher number of missing linkers. Obtained membrane displayed superior CO₂/N₂ selectivity (35.6) as well as a high CO₂ permeance, which surpassed not only the 2008 Robeson upper bound but also performance limits of state-of-theart pure MOF membranes, thereby confirming effectiveness of cooperative defect tailoring at different scales in performance improvement of non-modified MOF membranes. Moreover, oriented tertiary growth represented a powerful tool for enhancing the gas selectivity of MOF membranes with no compromise in permeability. It was expected that the CO₂/N₂ separation performance could be further enhanced by increasing the number of missing linkers in the UiO-66 membrane on the premise of maintaining the preferred orientation derived from the seed layer. Moreover, UiO-66 membranes were mainly synthesized with the solution-based protocol at present. Alternatively, the solventless high pressure synthesis technique provided with us an opportunity to sustainable preparation of high performance UiO-66 membrane [53]. Simultaneously, we admitted that these UiO-66 membranes were a bit thick. In the future we would seek to develop (111)-oriented ultrathin UiO-66 membrane to overcome the Robeson Trade-off further. In addition, since UiO-66 presented excellent hydrothermal stability, it was anticipated that prepared UiO-66 membrane could be tested and find applications in pervaporation, desalination, and nanofiltration [54,55].

CRediT authorship contribution statement

Jiahui Yan: Completed the main experiments and relevant characterizations, co-wrote the manuscript with contributions from all authors. Yanwei Sun: Assisted in synthesizing UiO-66 membranes. Taotao Ji: Helped with the analysis of experimental data. Liangliang Liu: Assisted in the gas separation test. Mu Zhang: Assisted in related morphological characterization. Yi Liu: Conceived the idea and designed the experiments, co-wrote the manuscript with contributions from all authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2021.119515.

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