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Functionalized Boron Nitride Nanosheet – Thermally Rearranged Polymer Nanocomposite Membrane for Hydrogen Separation

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Abstract: Amino functionalized boron nitride nanosheets (FBN) were incorporated into a crosslinked, thermally rearranged polyimide (XTR) to fabricate FBN-XTR nanocomposite membrane. The FBN-XTR membrane exhibited a small decrease in H₂ permeability but demonstrated a remarkably increased H₂ gas selectivity over other gases, compared with XTR. The XTR membrane heat-treated at 425 °C had a H₂ permeability of 210 Barrers and a H₂/CH₄ separation factor of 24.1, whereas the nanocomposite membrane with 1 wt% FBN exhibited a H₂ permeability of 110 Barrers and H₂/CH₄ separation factor of 275, an order of magnitude greater. At 1 wt% FBN loading, the FBN-XTR membrane showed three times higher tensile strength and 60% higher elongation than pristine XTR membrane. In addition, FBN-XTR was found to be able to be readily processed into thin-film membranes for practical H₂ separation applications.

The hydrogen gas market is developing fast and was valued at \$115 billion USD in 2017.^[1] Much of the hydrogen gas produced in the world, especially for the petrochemical industry, is produced from natural gas, which also contains significant concentrations of methane.^[2–5] However, high purity is a significant requirement for hydrogen energy applications such as polymer electrolyte membrane fuel cells.^[6] Therefore, separation of hydrogen from less desirable gases is industrially important. Conventional hydrogen separation processes such as pressure swing adsorption and cryogenic distillation are energy-intensive.^[7] Membrane separation is an energy-efficient, environmentally- friendly separation technology process which involves no phase change or the use of chemicals. The membrane gas separation performance is characterized by gas permeability and selectivity of the membranes, as denoted by the empirical upper bound summarized by Robeson in 1991 and subsequently revised in 2008.^[8] In the last few decades, there

have been significant efforts to develop gas separation membranes that surpass Robeson's upper bound, by means of (i) design of new polymer backbones, (ii) blending of polymer or copolymers,^[9] (iii) post-treatment of polymers including chemical crosslinking and thermal rearrangement,^[10,11] and (iv) blending of fillers to polymer to produce mixed matrix membranes (MMM).^[12–15]

Thermally rearranged (TR) polymers are a class of microporous polymers that are produced by a thermal conversion from functionalized polyimide to polybenzoxazoles.^[16] This thermal reaction occurs between 350 °C and 450 °C, generating hourglass-shaped cavities inside TR polymers.^[11] The hourglass microporous structures have small and large cavity sizes around 3–4 Å and 8–10 Å that provide unique gas permeability and selectivity as well as high resistance to plasticization.^[17] Currently, reported TR polymer membranes exhibit high separation factor especially for the CO₂/CH₄ gas pair. However, TR membranes exhibit poor toughness after thermal treatment, posing a critical issue in polymer processing and membrane fabrication.^[18] Attempts have been made to improve the mechanical properties of TR membranes including side group modification,^[9,18] blending of polymer or copolymer,^[19] and tuning chain rigidity.^[20] However, There is still a need for a new approach to develop TR membranes with improved mechanical properties.

Recently, 2D graphene analogues (such as graphene oxide^[13] and carbon nitride nanosheets^[14]) have been used as fillers to improve the transport properties of polymer membranes. The 2D fillers could enhance the performance of the polymer membrane via specific adsorption effect from its functional groups^[13] or basal structure,^[21] size sieving effect arising from 2D interlayer nanochannels, and creation of torturous gas diffusion pathways.^[14,22] Boron nitride nanosheets (BN) are a few layers of hexagonal planes constructed by alternating B and N atoms linked to each other via strong B–N covalent (sp²) bonds. This 2D material has unique properties that complements graphene, including wide energy band gap, high electrical insulation, high thermal stability, high resistance to oxidation and excellent chemical inertness.^[23–25] Due to the unique properties of BN, they have been widely studied in many applications including thermal conductive insulating material,^[26–29] hydrogen storage,^[30] waterproof coating,^[31] electrocatalysis,^[32] and water purification.^[33,34]

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Figure 1. (a) Photos of the as-prepared colloidal solutions of 1 wt% functionalized boron nitride (FBN) (left) and 1 wt% FBN-XTR (right) in DMF showing Tyndall effect. (b) SEM image of FBN (c) The chemical structure of FBN. (d) The structure of crosslinkable co-polyimide precursor (HAB50-DAM45-DABA5)-6FDA. (e) Thermal rearrangement (decarboxylation) process. (f) Photo of transparent and flexible 1 wt% FBN-XTR membrane. The membrane thickness is around 40 μm . (g) Schematic illustration of the structure of FBN-XTR membrane and selective gas permeation through the membrane.

In this work we report the use of an amino functionalized boron nitride nanosheets (FBN) as a filler to tailor the gas transport and mechanical properties of a TR polymer membrane. To the best of our knowledge, this work represents the first study on use of a thermally stable filler for thermal rearrangement of TR polymer precursor to enhance its gas transport property. Previously, the use of fillers to improve TR polymer membranes has not been explored because of the limited availability of fillers that can survive the thermal treatment step. Our recent work on the use of GO in making TR membrane demonstrated that 2D fillers can be used as the scaffold to produce ultra-thin TR membrane, but the membrane exhibited limited gas transport enhancement due to the reduction of GO during the heat-treatment step.^[35] In this work, (HAB50-DAM45-DABA5)-6FDA was selected as the crosslinked thermally rearranged polymer (XTR) precursor for its relatively good processability, low cost and low temperature requirement for thermal rearrangement.^[16] BN with functional groups, and importantly, high thermal stability were used as filler. The FBN-XTR membranes exhibit high thermal stability, mechanical property, and remarkable H_2/CH_4

selectivity. After 425°C heat treatment, 1 wt% FBN-XTR achieved 282% higher resistance to tensile stress and one order of magnitude higher H_2/CH_4 selectivity than the pristine TR membrane with only a commensurate decrease in the H_2 permeability, marking the gas separation performance well above the Robeson's upper bound.

The commercial hexagonal boron nitride (h-BN) was exfoliated by ball milling with urea.^[33,36,37] After dialysis to remove the urea, the FBN was dispersed in dimethylformamide (DMF) solution to form a white, stable aqueous dispersion (Fig. 1a). The FBN exhibits 2D morphology with relatively uniform lateral dimensions range from ~100 nm to ~300 nm (Figure 1b) and thickness around 7 nm (Figure S1, Supporting Information). Size reduction and exfoliation were confirmed by the XRD patterns of the products after ball milling, which demonstrates dramatically broadened and less intense (002) diffraction (Figure S2, Supporting Information). The same diffraction peak position (002) of FBN samples indicates that the interlayer spacing of the FBN remains unchanged. The FTIR spectra (Figure S3, Supporting Information) shows that the as-prepared FBN sample

has additional peaks at 3240 cm^{-1} and 3411 cm^{-1} compared to commercial h-BN, which can be ascribed to N-H and O-H stretching vibrations, respectively. The presence of N-H and O-H stretching vibrations indicates that amino and hydroxyl functionalization has occurred, the moieties likely being located at the defect sites and at the edges of BN lamina as mentioned in the previous simulation.^[37] The amount of the attached functional groups was evaluated by thermogravimetric analysis (TGA), which indicates that the content of $-\text{NH}_2$ and $-\text{OH}$ groups in the FBN are ~ 4 wt% (Figure S4, Supporting Information). This TGA curve reveals the excellent thermal stability of FBN up to 500 $^{\circ}\text{C}$, which is over the temperature needed for the thermal treatment of the selected polymer precursor.

The selected polymer matrix is a crosslinked thermally rearranged polybenzoxazole based on (HAB50-DAM45-DABA5)-6FDA, a crosslinkable hydroxyl polyimide precursor (co-HPI), containing $\text{C}=\text{O}$, $-\text{COOH}$ and $-\text{OH}$ groups (Figure 1d; Figure S5, Supporting Information). The pure precursor solution is brownish red and is translucent, while the colour of the solvent gradually becomes less translucent and milky yellow with increasing the loading of FBN (Figure S6, Supporting Information). The Tyndall scattering effect in the as-prepared 1 wt% FBN-co-HPI mixed colloidal solution was observed (Figure 1a), implying the homogeneous FBN distribution in co-HPI solution. The FBN-co-HPI solution was cast on a glass plate to form a film before undergoing thermal rearrangement. During heat-treatment between 300 $^{\circ}\text{C}$ and 425 $^{\circ}\text{C}$, the co-HPI undergoes crosslinking and decarboxylation reactions (Figure 1e),^[38] leading to the TR membrane hourglass-shaped cavities.^[11] The large cavity openings enable relatively non-selective flow while the narrow neck regions enable gas separation properties.^[17] The as-prepared free-standing, flexible FBN embedded XTR membrane appears yellow and translucent, confirming the uniform dispersion of FBN (Figure 1f). The amino groups introduced onto FBN make nanosheets easily dispersed in solvent, which is crucial for forming a stable BN-polymer solution for membrane preparation.^[39,40] In addition, because there exist $-\text{OH}$ and $-\text{COOH}$ groups in the polymer before thermal re-arrangement, good dispersion of FBN in co-HPI should be facilitated by the formation of hydrogen bonds between FBN and co-HPI (Figure 1g).^[26,41,42] After thermal rearrangement, the hydrogen bonding becomes weakened due to loss of functional groups. As shown in the AFM images of membrane surfaces and photos of membranes (Figure S6, Supporting Information), FBN-XTR membranes have rougher surface than XTR membrane. Especially the rough surface of the membrane with 3 wt% FBN can be even seen by naked eyes. These suggest that the incorporation of FBN leads to the formation of FBN-XTR clusters, significantly affecting XTR chain packing.

The permeability of CH_4 of FBN-XTR membrane heat-treated at 425 $^{\circ}\text{C}$ decreases significantly by an order of magnitude compared to that of the pristine XTR membrane with a commensurate decrease in H_2 permeability as the FBN loading increases up to 1 wt% (Figure 2a). The much higher CH_4 permeability decrease suggests that the reduction of the free volume occurs mostly in the range of 3.6–3.8 Å. As FBN loading increases beyond 1 wt%, the improvement on the H_2/CH_4 selectivity gradually diminishes (Figure 2b and Figure S7, Supporting Information). At the loading above 1 wt%, the increase in gas permeability and drop in gas selectivity of the FBN-XTR membrane may be attributed to the high amount of FBN aggregation inside the polymer matrix, as the aggregation

decreases the FBN effective surface area and homogenous dispersity (Figure S6, Supporting Information). On the other hand, at a FBN loading of 1 wt%, the FBN-XTR membrane exhibits significantly higher H_2/CH_4 selectivity with a slight decrease in H_2 permeability compared to that of the pristine XTR membrane (H_2 permeability: 96 Barrers, H_2/CH_4 selectivity: 322, Table S1, Supporting Information). The gas transport performance surpasses the H_2/CH_4 upper bound as shown in

Figure 2c, positioning the result among the best in TR-based polymeric membranes (Table S2, Supporting Information) and most recent MMM (Figure S8; Table S3, Supporting Information). Other industrial important gas separations, including H_2/N_2 , H_2/CO_2 , CO_2/CH_4 and N_2/CH_4 , are shown in Figure S7. Similar to H_2/CH_4 gas pair, the above-mentioned gas pairs achieve the highest selectivity at a different optimal FBN loading, and their separation performance is improved by incorporating FBN. The

Figure 2. (a) Single gas permeability of 1wt%FBN-XTR membrane tested at 25 $^{\circ}\text{C}$ and a transmembrane pressure of 1 bar as a function of the kinetic diameter. (b) Gas permeability and selectivity of the membranes with different FBN loadings for H_2/CH_4 pair at 25 $^{\circ}\text{C}$ and 1 bar. (c) Relationship between H_2 permeability and H_2/CH_4 ideal selectivity of FBN-XTR membranes, compared to other polymer membranes with the 2008 upper bound.^[8,16]

enhanced separation performance of FBN-XTR membrane can

be largely explained by altered diffusion pathways caused by FBN and strong specific affinity between FBN and polar gas molecules.^[13,21,43] Smaller gas molecules can pass through the defective region or around the boundary of 2D lamina,^[44–46] but not through the mainly defect-free FBN. The existence of FBN creates a tortuous pathway for gas transport that leads to decreased gas permeability, especially for larger gas molecules such as CH₄ (Figure 2a). On the other hand, smaller gas molecules such as H₂ are less affected by the pathway and show a faster diffusion rate (Figure 2a, b). Furthermore, the high selectivity may also be attributed to the ionic nature of the B–N bond. In the layered hexagonal BN, B atoms in every BN layer sit exactly above or below the N atoms in the adjacent layers. Such a structure introduces the polarity of B–N bonds, i.e. the partially ionic characteristic of the covalent B–N bonds.^[47] This polarity of BN bonds and the high surface area of h-BN-related nanostructures result in good adsorption properties of various substances such as specific gas molecule.^[34,48] BN have been demonstrated to have high affinity with methane via B–N bonds.^[48] Fillers with polar sites have shown high adsorption rate for polar gas molecules or molecules with polar C–H bond in CH₄.^[48–51] By contrast, to confirm the mechanism, GO-polymer membranes were prepared and compared with BN-polymer membrane (Figure S9, Supporting Information). GO was selected as a comparison of 2D material filler since the oxygen functional groups on GO would be reduced after the thermal treatment, which leads to less polar sites in reduced GO.^[48] Our results indicate that the gas selectivity of BN-polymer membrane was much higher than GO-polymer membrane for all gas pairs, which suggests that the high selectivity of BN-polymer is more likely contributed by the ionic BN nature.

Figure 3. (a) TGA curves of FBN, XTR membrane and 1 wt% FBN-XTR membrane. The yellow region is the TR range. (b) H₂ gas permeability and H₂/CH₄ selectivity of 1 wt% FBN-XTR and pure XTR membranes prepared at different thermal rearrangement temperatures.

Heat-treatment temperature is an important factor in determining the performance of XTR membrane. Below 450°C,

1 wt% FBN-XTR membrane has the similar mass loss to XTR membrane as revealed in TGA curves (Figure 3a). When heated to temperatures above 450 °C (thermal decomposition temperature of XTR membrane), the partial carbonization of the polymer membrane occurs. The incorporation of FBN filler disrupts the polymer packing and crosslinking, which leads to larger polymer mass loss during the carbonization process. Consequently, 1% FBN-XTR membrane underwent more mass loss eventually. Heat-treatments at 500 °C generate a carbonaceous membrane with high gas permeability but low gas selectivity (Figure 3b), while unheated co-HPI membrane and XTR membrane heat treated at 350 °C have limited fractional free volume (FFV) and therefore exhibit relatively low H₂ permeability and H₂/CH₄ selectivity (Figure 3b)^[11]. The similar trend was observed for FBN-XTR membrane, where H₂ permeability and H₂/CH₄ selectivity generally increase with increasing heat treatment temperature up to 425 °C. At 500 °C, the gas transport property resembles that of a carbonaceous membrane. Incorporation of FBN inside the microporous XTR matrix may obstruct the gas transport and thus decrease gas permeability (Figure 3b). 425°C is the optimal heat-treatment temperature for XTR polymer in this work and is consistent with that of other works.^[18,38] These works suggested that co-HPI

membrane heated at around 425°C has a narrow size distribution of cavities, whilst retaining sufficient mechanical properties.

Figure 4. (a) H₂ permeability and (b) H₂/CH₄ selectivity of XTR and 1 wt% FBN-XTR membrane measured with single and mixed gas permeation experiments.

The FBN-XTR also demonstrated good thermal stability up to 500°C (Figure S10, Supporting Information). In all cases, all FBN-XTR membranes showed higher H₂/CH₄ selectivity than pristine XTR membrane regardless of the heat-treatment temperature (Figure 3b). At heat treatment temperature of 425°C, the 1 wt% FBN-XTR membrane shows H₂/CH₄ selectivity one order of magnitude higher than that of the pristine XTR

membrane. Such high enhancement may be attributed to the synergistic effect of both BN laminates and thermal treatment-induced backbone rearrangement that created the narrow hourglass-shaped cavities in size range of 3.6–3.8 Å.^[11]

Mixed gas permeability and selectivity often differ from the single gas permeation results due to competitive permeation of each gas in the gas mixture and plasticization effects of the membrane by the condensable mixed gas stream. Plasticization effects often induce a significant selectivity decline for glassy polymers since considerable amount of carbon dioxide and hydrocarbons sorbed in the polymer increases the mobility of the polymer chains that limits the size-sieving ability.^[17] Previous work has shown that XTR membrane can achieve rigid polymer backbones with sufficient resistance to plasticization and physical aging.^[10,17,20] The same property is consequently demonstrated by the FBN-XTR membrane. The difference in gas permeability and selectivity between single and mixed gas measurements was less than 10% for all gas pairs tested (Figure 4; Table S1, S4, Supporting Information). Apart from enhancement of the gas selectivity, the FBN was also an excellent additive for improving the mechanical properties of the polymer, due to its intrinsic high modulus nature, as well as its strong interaction and superior compatibility with the polymer chains.^[41,42,52–55] At 1 wt% FBN loading, the FBN-XTR membrane shows three times higher tensile strength and 60% higher elongation than pristine XTR membrane (Figure S11, Supporting Information). Owing to the good dispersibility, high modulus FBN enhances the composite modulus. Commercial gas separation membrane is commonly based on thin-film composite (TFC) and has a thin active layer supported on a substrate for high gas flux. To demonstrate the commercial feasibility of FBN-XTR membrane, 1 wt% FBN-XTR doped solution was used to prepare an ultra-thin TR composite membrane by spin-coating on anodic aluminium oxide disk (Figure S12, Supporting Information). Our TFC membranes could achieve thicknesses of around 400–800 nm and high H₂ permeance (1648 GPU) and H₂/CH₄ selectivity (96).

In summary, we have demonstrated the preparation of thermally rearranged polymer-based nanocomposite membrane by incorporating FBN. With increasing the loading of FBN in the membranes, the gas selectivity increases substantially while the H₂ permeability only slightly decreased in comparison with the pure polymer membrane. The as-prepared 1 wt% FBN-XTR membrane prepared under 425°C heat-treatment exhibited an extraordinarily high H₂/CH₄ separation performance, well above the upper bound of state-of-the-art membranes. The system investigated has distinct advantages in terms of facile fabrication and processability of thin-film membrane, thermal stability, enhanced mechanical properties, and gas transport performance, the FBN-modified XTR membrane reported herein offers great potential for practical hydrogen separation.

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Entry for the Table of Contents

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Large improvement in hydrogen selectivity and mechanical properties of thermally rearranged polymer membrane is achieved by incorporating functionalized boron nitride nanosheets. The thin-film nanocomposite membrane can be readily fabricated to achieve ultrahigh hydrogen flux, showing great potential for practical hydrogen separation.

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Page No. – Page No.

**Functionalized Boron Nitride
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