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Surface-etched halloysite nanotubes in mixed matrix membranes for efficient gas separation

Lei Ge¹, Rijia Lin¹, Li Wang¹, Thomas E. Rufford¹, Byron Villacorta¹, Shaomin Liu², Lian X. Liu³, Zhonghua Zhu¹,*

¹ School of Chemical Engineering, the University of Queensland, Brisbane 4072 Australia
² Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia
³ Department of Chemical and Process Engineering, University of Surrey, Guildford, GU2 7XH United Kingdom

Abstract
Possessing the advantages of both polymeric membranes and the specific inorganic nanoparticles or nanotubes, mixed matrix membranes (MMMs) have captured the imagination of researchers for a possible technological breakthrough for efficient gas separation. However, it is still very challenging to achieve defect-free interface between fillers and polymer matrix. In this study, the naturally abundant and low cost halloysite nanotubes (HNTs) were applied as fillers for MMMs synthesis. To improve the filler dispersion and filler-matrix interface affinity, the raw HNTs were modified by either alkali etching or (3-Aminopropyl) triethoxysilane grafting. After surface etching, the defect holes were formed on the surfaces of etched-HNTs, resulting in the rougher HNT walls and significant increment of surface area and CO₂ adsorption capacity. The filler/polymer interfacial voids and filler dispersion were quantitatively assessed by tomographic focused ion beam scanning electron microscopy. HNTs surface etching significantly improved the HNTs/polymer interfacial affinity (void%=0.06% for Raw-HNTs MMM, 0.02% for Etched HNTs MMMs) and filler dispersion, while grafted-HNTs mainly contribute to the filler dispersion. Compared to the pure polymer membrane and MMMs with untreated HNTs,
MMMs containing 10 wt.% etched HNTs filler exhibited both increased CO\textsubscript{2} permeability (807 Barrer) and higher CO\textsubscript{2} selectivity (CO\textsubscript{2}/CH\textsubscript{4} selectivity of 28) on the well-known limit of Robeson upper bound. In contrast, grafting HNTs only increased the membrane permeability without enhancing CO\textsubscript{2} selectivity. The results suggest that surface etching can be an effective route in filler modification to improve interfacial morphology and membrane separation performance.

**Keywords:** mixed matrix membranes, surface modification, interfacial defects, halloysite nanotubes

1. Introduction

To target an energy-efficient and environmentally friendly separation process, most polymer membranes are limited by a trade-off between mass transport rates and separation efficiency, and thus extensive industrial-scale applications of membranes have not occurred yet [1, 2]. Mixed matrix membranes (MMMs) derived from embedding filler materials (e.g. carbon nanotubes, metal-organic frameworks, zeolites, silica, metal oxides and graphitic nanosheets) in polymer matrix is a hybrid system synergistically combining the processing versatility of polymers and the separation characteristics of fillers, showing promising separation performance [3-21]. However, the commercial use of MMMs for gas separation has been constrained by the cost of fillers as the synthesis of these nanoparticles including nanotubes, metal organic frameworks (MOFs), silica, zeolite or graphene is time-consuming and costly. Another factor still impeding the practical application of MMMs is the undesired membrane performance and the instability of fillers (e.g. MOFs). Further enhancements of membrane permeability and selectivity are significantly dependent on the dispersion of fillers, the interface between filler and polymer matrix as well as the chemical and physical properties of filler. Uniform dispersion of fillers within the polymer matrix can greatly increase the fractional free volume in MMMs, bringing in permeability increment [22]. However,
membrane performance deterioration by filler agglomeration exists in all kinds of MMMs, especially at high loading and when using fillers with small particle size, high aspect ratio and large surface area. The characteristics of the interface between filler and polymer matrix are critical to the selective transport of certain gases as they determine the diffusion pattern of the penetrant molecules in disrupted polymer chains and the filler/polymer interface [23]. In addition, defects and non-selective voids can be formed under circumstances of poor interfacial compatibility, resulting in undesired Knudsen flow [24-26]. Therefore, to ensure membrane selectivity and membrane structural integrity, it is mandatory to improve the interaction between fillers and polymer matrix.

Different methods have been applied to enhance filler dispersion and to avoid defects in the filler/polymer interface of MMMs. The first option is to alter the surface chemistry of filler particles or polymer by various surface treatments (e.g. functionalization or applying surfactant). The introduction of functionality also changes the chemical affinity of penetrants in nanocomposite membranes [27-29]. The second method is to reduce filler particle size or use layered nanomaterials [8, 30, 31]. For example, Bae et al. reduced the size of ZIF-90 by nonsolvent-induced crystallization method and fabricated MMMs with the as-synthesized submicrometer-sized ZIF-90 and 6FDA-DAM polyimide. An interfacial void-free MMM with high gas separation performance has been achieved [31]. The last but also important strategy is to eliminate the formation of non-selective interfacial voids via in-situ polymerisation [32-34]. Also, introducing a cross-linkable polymer (e.g. copolyimides) and solidifying it after the cast of MMMs [35, 36] or surface cross-linking the MMMs with a cross-linking agent provides more flexibility to facilitate the filler dispersion and adhesion [37]. One-pot synthesis can also be effective in dispersing nano-fillers and restraining agglomeration [38]. However, it is still a challenge to quantify the filler dispersion and to determine the void volume between the filler and polymer interface for evaluating
effectiveness of any modification.

In this article, we aim to increase the topological roughness (physical heterogeneity) of filler, in order to provide sufficient interaction at the filler/polymer interface without the addition of foreign molecules to the polymer dope. To evaluate the effectiveness of various filler modification routes in the same filler-polymer system, the frequently-used amine functionalization was also carried for comparison. Moreover, rather than using expensive synthetic fillers (e.g. carbon nanotubes, MOFs, graphene and mesoporous silica), the naturally abundant and low cost halloysite nanotubes (HNTs) were selected as the filler for MMMs fabrication. The HNTs were modified through various surface modifications and used to synthesise 6FDA-durene polyimide based MMMs by the same membrane fabrication process. The filler dispersion and filler/polymer adhesi

on were then quantitatively investigated. Through various surface modifications, the dispersion and adhesion of treated HNTs have been enhanced, thereby improving both membrane permeability and selectivity over MMMs prepared with untreated HNTs and pristine polyimide membrane.

2. Experimental

2.1. HNT surface modification

Figure 1 illustrates the two procedures used to modify HNTs surface: 1) alkali etching in molten salts to achieve roughened and defective HNTs surfaces (named as Etched-HNTs); 2) (3-Aminopropyl) triethoxysilane (APTES) grafting onto HNTs to introduce surface amine groups (–NH$_2$) (named as Grafted-HNTs). Pristine HNTs without any pretreatment was denoted as “Raw-HNTs”. The detailed information on the materials used and the modification procedures are listed below.

Analytical grade sodium nitrate, sodium carbonate, APTES, 4,4’-(Hexafluoroisopropylidene)diphtalic anhydride (6FDA), 2,3,5,6-Tetramethyl-1,3-phenyldiamine (durene), triethylamine, acetic anhydride, N,N-dimethylformamide (DMF),
N,N-Dimethylacetamide (DMAc) and methanol was supplied by Aldrich. Natural HNTs were collected from Imerys Ceramics Limited, New Zealand, under a product name “Ultrafine”. The detailed sample information is listed in Fig. S1. Two pretreatment procedures were conducted on Raw-HNTs to modify their morphology (surface roughness) or surface chemistry.

The Etched-HNTs were prepared by alkali etching in molten salts, with weak base sodium carbonate as the etchant and sodium nitrate (molten point: 308 ºC) as molten agent [39]. A typical preparation of etched-HNTs included the following steps: (1) 0.6 g of Na$_2$CO$_3$, 10.0 g of NaNO$_3$ and 2.0 g of Raw-HNTs powders were mixed and grinded in mortar; the mixture was then put into a ceramic crucible and heated up to 350 ºC for 1 h in air with a heating rate of 5 ºC/min. (2) After cooling down, the sample was washed with diluted nitric acid and deionised water to remove soluble salts and impurities, and dried overnight in a vacuum oven at 80 ºC.

The Grafted-HNTs were obtained by adding 5 g of Raw-HNTs into a mixture of 4 mL APTES and 150 mL of toluene; and the suspension was continuously stirred and refluxed at 110 ºC for 22 h under N$_2$ atmosphere. After that, the sample was separated by centrifugation and extensively washed with fresh toluene to remove the excess physisorbed APTES, then dried overnight in a vacuum oven at 80 ºC. A monolayer of APTES was attached onto surfaces of grafted-HNTs under the anhydrous conditions.

2.2. Membrane fabrication

The synthesis of 6FDA-durene polyimide was carried out by chemical imidization, the same as in our previous work [40]. Durene sample (1.426 g) was dissolved into 10 mL of DMF. Once the durene was fully dissolved, 3.861 g of 6FDA powder was added, followed by 5 mL of DMAc. The mixture was stirred under N$_2$ at room temperature for 24 h to form polyamic acid. Next, a mixture of triethylamine (3.2 mL) and acetic anhydride (1.2 mL) was added.
The combined mixture was stirred under nitrogen at room temperature for another 24 h. The final polymer was precipitated in methanol, washed several times with methanol, and dried at 180 °C under vacuum for 18 h. The polyimide product is referred here as 6FDA-durene.

For pure 6FDA-durene membrane fabrication, 0.45 g of 6FDA-durene was dissolved in 3 mL DMF at room temperature and stirred until a clear solution was obtained. The resulting solution was cast onto a clean glass substrate, followed by drying at 180 °C for 24 h in a vacuum oven. For the MMMs, the desired amount of raw-HNTs, etched-HNTs or grafted-HNTs was firstly suspended in DMF under sonication, followed by adding 0.45 g 6FDA-durene. The suspension was further stirred for 6 h. The resulting mixture was cast and dried at 180 °C for 24 h under vacuum to form MMMs. The loadings of raw-HNTs, etched-HNTs or grafted-HNTs were fixed as 20 wt.% in this study based on Equation (1).

$$\phi = \frac{m_{\text{Filler}}}{m_{\text{Filler}} + m_{6\text{FDA-durene}}}$$  \hspace{1cm} (1)

where $m_{\text{Filler}}$ and $m_{6\text{FDA-durene}}$ are the mass of HNTs filler and 6FDA-durene in the MMMs, respectively. The membrane thickness of pure 6FDA-durene and MMMs was measured using a micrometer which fell in the range of 20–40 µm. The membranes were stored in a desiccator.

### 2.3. Material characterization

The X-ray diffraction (XRD) data were obtained from a Brucker Advanced X-ray Diffractometer (40 kV, 30 mA) with Cu Kα (λ= 0.15406 nm) radiation at a scanning rate of 1° min$^{-1}$ from 2° to 40°. Fourier transformer infrared spectroscopy (FTIR) was conducted with a PerkinElmer Spectrum 100 FTIR spectrometer by using KBr pellets in transmission mode. The KBr pellets were pressed from mixtures of HNTs (1-2 wt.%) and KBr powder that had been dried overnight at 70 °C in a vacuum oven. X-ray Photoelectron Spectroscopy (XPS) was conducted on a Kratos Axis ULTRA XPS instrument incorporating a 165 mm
hemispherical electron energy analyser. The incident radiation was Monochromatic Al Kα X-rays (1486.6 eV) at 225 W (15 kV, 15 mA). Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 microscope with accelerating voltages of 200 kV. The samples were dispersed by sonication in ethanol, and then deposited on holey carbon copper grids and dried. \( \text{N}_2 \) sorption isotherms of the samples were measured at -196 ºC with a Micromeritics TriStar 3020, after degassing samples for 24 h at 150 ºC. Their corresponding specific surface area \( (S_p) \) was calculated by the Brunauer-Emmett-Teller (BET) equation at relative pressures \( (P/P^0) \) between 0.05 and 0.20. Total pore volume \( (V_p) \) was evaluated from adsorption branches of the isotherms at \( P/P^0 \) close to unity using the Barrett-Joyner-Halenda (BJH) method. The low magnification cross-sectional images of the membranes were obtained with a JEOL JSM7100 scanning electron microscope (SEM) at 8 kV.

Focused ion beam-scanning electron microscopy (FIB-SEM) was performed in a FEI SCIOS FIB/SEM dual beam system to evaluate the distribution of filler in the polymer matrix and the filler/polymer contact. Before milling, the samples were sputtered with a protective layer of Pt (1µm in thickness) using ion beam assisted deposition. Considering image drifting cannot be avoided during image acquisition, the reference marks were created by focused ion beam (FIB) on membrane surface to facilitate precise image alignment. The Ga+ FIB at 30 kV and 1 nA was used to create serial milling of slices. 30nm thin slices were removed from the sample up to a depth of 9 µm and the exposed SEM images of cross-sections were recorded sequentially with an in-lens backscattered electron detector operated at 2 kV. The sizes and spatial resolutions of three membranes are summarized in Table S2. Avizo (FEI Visualization Sciences Group) was used to reconstruct FIB-SEM tomograms, segment different phases (polymer matrix, filler and voids) and quantify the volume fraction and distribution parameters. [8]

2.4. Gas permeation test
A variable feed pressure and constant volume permeation system was used to measure the gas permeation of pure 6FDA-durene and HNT based MMMs, as described previously. [28] The membranes were held under vacuum for approximately 5 min to reach a steady state before exposing to the selected gas. Before switching to another feed gas, the membrane has to be degassed for some time to assure the complete desorption of initial permeate gas. The test was held at 25 °C and 2 atm of feed pressure. Gas permeability values and deviations were calculated from replicated permeation tests from three membranes loaded with each type of HNTs.

The permeability is calculated using the following equation:

\[
P = \frac{273.15 \times 10^{10}}{760\times T} \frac{V \times L}{A} \frac{dp}{dt} \tag{2}
\]

where \( P \) is the permeation coefficient in Barrer (1 Barrer = 1×10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹), \( A \) is the effective area of the membrane (cm²), \( T \) is the absolute temperature (K), \( V \) is the dead-volume of the downstream chamber (cm³), \( L \) is the membrane thickness (cm), \( P_0 \) is the feed pressure (psi), and \( \frac{dp}{dt} \) is the steady rate of pressure increase in the downstream side (mm Hg s⁻¹).

The ideal selectivity for two gases is determined as:

\[
\alpha = \frac{P_A}{P_B} \tag{3}
\]

where \( P_A \) and \( P_B \) are the permeation coefficients of pure gas A and B, respectively.

3. Results and discussions

3.1. Characterization of HNTs

The XRD patterns of pristine, etched and grafted HNTs show that surface treatments do not affect the phase structure of HNTs (Fig. S1). The observed patterns all show typical
diffraction peaks of 7 Å dehydrate halloysite Al$_2$Si$_2$O$_5$(OH)$_4$ with Joint Committee on Powder Diffraction Standards (JCPDS) card number of 29-1487. The FTIR spectra of three HNT samples are shown in Fig. S2. Compared to the spectrum of Raw-HNTs, the spectrum of etched-HNTs shows a decrease in the intensity of O-H stretching vibration (3696 and 3622 cm$^{-1}$) and bending vibration (914 cm$^{-1}$) bands of inner-surface Al-OH groups. This could be due to the partial removal of inner surface hydroxyl groups during the alkali etching process at elevated temperature of 350 °C [39]. All the other Si-O stretching vibration peaks are weakened to different extents, which can be attributed to the Si-O bond breakage on the surface etching sites. Grafted-HNTs present all the characteristic absorption peaks of HNTs. The successful grafting of APTES onto HNTs is indicated by the peaks at 1700-1450 cm$^{-1}$ (Fig. S2 inset). The new adsorption peaks at 1651, 1605 and 1556 cm$^{-1}$ are ascribed to the deformation vibration of N-H$_2$ in APTES, and the peak at 1492 cm$^{-1}$ is due to the deformation vibration of C-H$_2$ in APTES. XPS was also conducted to reveal the surface composition change after surface modifications, with the spectra shown in Fig. S3. Apart from the O, Si and Al peaks, a weak Na peak was also observed on the etched HNTs, which were from the sodium salts used during the alkali etching treatment. Note that the samples were extensively washed by diluted acid and deionised water to remove the soluble salts. The traces of sodium ions could be strongly bonded to HNTs by ion exchange and are not readily removed. The XPS spectra of Grafted-HNTs exhibit an extra N peak, and the intensity of C peak is significantly enhanced, further confirming that the APTES has been successfully grafted onto the HNTs.

TEM images of the three HNTs samples are displayed in Fig.2. Raw-HNTs present natural open-ended and hollow tubular structures. The size of the nanotubes ranges from tens to hundreds of nanometers in diameter and hundreds of nanometers to several microns in length. It is clear that Raw-HNTs exhibit smooth and flat surfaces (Fig. 2a). After alkali etching, the
The size of HNTs is unchanged and the tubular morphology has been maintained. On the other hand, Fig. 2b shows that defects are formed on the surfaces of etched-HNTs, resulting in the rougher HNT walls. Fig. 2c presents the morphology of grafted-HNTs, showing hollow tubular structure with smooth surfaces that is very similar to Raw-HNTs. Yuan et al. [41] observed less distinguished internal wall after APTES modification, which was attributed to APTES filling into the HNTs lumen completely. In comparison, the grafted-HNTs in this work present clear inner wall with hollow cavity, which indicates that APTES modification mainly occurred on the outer surfaces of HNTs.

The nitrogen adsorption isotherms are depicted in Fig. 3. Raw-HNTs exhibit a type IV isotherm with H3 hysteresis loop. Both etched-HNTs and grafted-HNTs present similar isotherm patterns to raw-HNTs, indicating the tubular pore structure has been maintained after roughness and chemical graft treatment. However, the etched-HNTs show a much higher adsorption amount compared to other two samples. This is because the BET surface area (Sg) and the total pore volume (Vp) of the etched-HNTs are much higher than the other two, which is 98.5 m$^2$/g and 0.188 cm$^3$/g respectively for the etched-HNTs, whereas the Sg and Vp for the raw-HNTs and grafted-HNTs are 25.5 and 23.9 m$^2$/g, 0.108 and 0.107 cm$^3$/g respectively. The significant increase in surface area and pore volume in the Etched-HNTs indicates the introduction of extra surfaces and pores by the roughness treatment. This is in line with the TEM observation, with extra pores and defects observed on the etched-HNTs (Fig. 2b). Grafted-HNTs show a slight decrease in surface area and a similar pore volume compared to Raw-HNTs. This could be due to the fact that APTES is grafted mainly on HNTs external surfaces, leaving the internal lumen unblocked. Fig. 4 presents the gas adsorption isotherms of the untreated and treated HNTs. Compared to the Raw-HNTs, the CO$_2$ adsorption has been significantly enhanced by roughening and grafting surface treatment. At 120 kPa and 298 K, CO$_2$ adsorption capacity of etched-HNTs (6.6 cm$^3$/g (STP)) are much
higher than that of raw-HNTs (1.2 cm³/g (STP)), which can be attributed to the significant
increase in surface area (as can be observed in Fig. 3). The Grafted-HNTs have similar
surface area as the raw HNTs, but they also show exceptionally high CO₂ adsorption capacity
(6.1 cm³/g (STP) at 120 kPa and 298 K). This may be explained by the introduction of amine
groups from the grafting of APTES, which exhibit specific interactions with CO₂. At low
pressure range, the enhancement of CO₂ adsorption by APTES grafting is very significant,
and the trend becomes less significant at high pressure, probably due to the saturation of
amine groups by CO₂ bonding.

3.2. Characterization of mixed matrix membranes
The transport properties of organic-inorganic MMMs are strongly dependent on the
morphology of the membranes. In particular, the elimination of interface voids between
fillers and polymer matrix is crucial to avoid the unselective gas permeation. Fig. 5 compares
the cross section morphology of pure 6FDA-durene membrane and the derived MMMs
incorporated with various HNTs. To further investigate the structure features of MMMs such
as the dispersion of fillers and the existence of interfacial voids, the tomographic focused ion
beam scanning electron microscopy was applied. The spatial distribution of HNTs in the
MMMs and the HNT/polymer interface were evaluated. Fig. S4a depicts the typical low-
magnification SEM images of the carved hole inside the Raw-HNT MMMs. The series of
SEM cross-sectional micrographs were taken on FIB milled thin slices. As can be seen in
Fig.S4a, reference marks (×) are created on membrane surface to assist the latter alignment
process of SEM images. The representative cross-sectional image from backscattered electron
imaging mode is shown in Fig. S4b. The magnified image in Fig. S4c illustrates the different
constituents in MMMs, including bright HNTs, grey polymer matrix and dark HNTs/polymer
interfacial voids.

Tomographic FIB-SEM technique can provide insights of the spatial distribution of fillers,
polymer and void space in MMMs [41]. Figure 6 shows the typical 3D surface-rendered view of the HNTs and void volume in etched-HNTs MMM. The segmentation of the individual phases (e.g. 6FDA-durene, HNTs and voids) was conducted by image thresholding. The 3D images of raw-HNTs MMM and grafted-HNTs MMM are given in Fig. S5 and Fig. S6. Based on the 3D tomographic images (Fig.6, Fig. S5 and Fig. S6), the volume fractions of voids calculated by image analysis are 0.06%, 0.02% and 0.16% for Raw-HNTs, Etched-HNTs and Grafted-HNTs MMMs, respectively. The volume fractions of voids, filler and polymer are summarised in the Table 1. By surface roughening of HNTs, the volume fraction of voids in derived MMMs is reduced to as low as 0.02%. The enhanced compatibility of etched-HNTs with 6FDA-durene can be attributed to the improved interaction at the interface via thermodynamically induced adsorption and physical interlocking of polymer chains on the rough surfaces [11]. On the other hand, filler surface functionalisation does not always facilitate filler/polymer interfacial interaction. It is noteworthy that the increased interfacial voids can be observed by APTES surface grafting on filler, which may be owing to the steric hindrance of APTES long chains.

Fig. 7 displays the HNT volume variation in different depth of HNT based MMMs. Despite the identical HNTs loading content, significant difference of filler dispersion can be observed. The volume fraction of Raw-HNTs fluctuates greatly with membrane depth (Fig.7a), suggesting the poor dispersion of HNT in MMM. Similar phenomenon can also be observed in Grafted-HNTs MMM. However, as seen in Fig. 7b, much less fluctuation of volume distribution suggests that etched-HNTs can uniformly occupy the membrane cross-section at all depth and the effectiveness of surface roughening on filler dispersion. The filler particle volume distributions in these HNT based MMMs are also shown in Fig. 8. Compared to Raw-HNT MMMs, better dispersion and distribution of etched-HNTs can be found due to a predominant small particle size, less aggregation and high uniformity. The enhanced
dispersion of grafted-HNTs in MMMs can be attributed to the extra polar functional groups on the surface of HNTs and improved dispersion in solvent before embedding with polymer. Overall, the surface roughening treatment can be an effective modification method to improve both morphological aspects: filler dispersion and filler/polymer interface.

3.3. Gas permeation of mixed matrix membranes

Figure 9 presents the ideal gas permeability and selectivity of pure 6FDA-durene and MMMs with pristine, roughened and APTES functionalised HNTs. For pure 6FDA-durene membrane, the gas permeability of CO₂, CH₄ and N₂ are 639.3, 27.3 and 31.2 Barrer with CO₂/CH₄ and CO₂/N₂ selectivity of 23.5 and 20.5, respectively. These results are consistent with the published values of 6FDA-durene membrane [42]. Compared to pure 6FDA-durene, the CO₂ permeability increase to 846.3, 807.7 and 913.3 Barrer for raw-HNT, etched-HNT and grafted-HNT MMMs, respectively. The addition of fillers into polymer matrix could affect the polymer chains in two ways: change in free volume or chain rigidification [43-45]. By adding nanofillers into the polymer matrix, disturbed polymer chain packing and increased HNT/polymer interfacial volume can be created, thereby increasing gas diffusivity via introducing more alternative routes to pass through gas molecules [46]. Similar phenomenon was also found in MMMs incorporated with silica nanoparticles and metal-organic frameworks [9,12]. In addition, similar to carbon nanotubes, the tubular structure of natural HNTs may provide smooth diffusion channels for fast gas transportation. On the other hand, literature also showed that the polymer rigidifies near the porous filler surface during formation of mixed matrix membranes [47]. As indicated in Fig. 2b, the etching process introduces extra pores and surface roughness, which stiffens the polymer matrix and enhances the HNTs/polymer adhesion. Therefore, the rigidified polymer region could have lower permeability than the bulk polymer but have the potential to enhance gas selectivity.

With the same filler loading percentage, the ideal selectivity of the MMMs varies with the
surface modification on HNTs. For etched-HNTs MMMs, the carbon dioxide selectivity over methane and nitrogen is 27.8 and 21.5, respectively, higher than carbon dioxide selectivity on pure 6FDA-durene membranes. The improvement of HNT dispersion and HNT/polymer interface (evidenced in Table 1, Fig. 7 and Fig. 8) contributes to the gas/filler interaction and the minimisation of unselective diffusion through interfacial voids. The enhancement of membrane separation can also be attributed to the significant increment of surface area and CO\textsubscript{2} adsorption capacity (Fig. 4) as evidenced by our previous studies [30]. Grafted-HNTs MMMs demonstrate comparable selectivity to that of the pure polymer membrane. Even though the functional groups can improve filler dispersion and membrane permeability in most of MMMs (Fig. 8), in this HNT/6FDA-durene system, the existence of interface void limits further improvement on gas selectivity. Considering the increased permeation by filler introduction, the similar selectivity suggests that the selectivity loss by extra interfacial voids has been compensated by the increased membrane solubility by the amine functional groups on APTES [48]. In contrast, the deterioration of CO\textsubscript{2} selectivity was observed in Raw-HNTs MMMs, which can be attributed to the poor dispersion and adhesion between the Raw-HNTs and polymer. Unselective voids are produced on the interface between Raw-HNTs and the polymer matrix, resulting in an increase in permeability at the expense of decreasing selectivity. Similar observations have been reported previously where the gas selectivity was reduced by incorporating HNTs into polymer matrix [45, 49]. The effectiveness of surface roughing treatment in this study reflects on the superior membrane morphology and separation performance compared to the HNT based MMMs in literature.

Fig. 10 compares the separation performance of our membranes with other MMMs in the literature with respect to the Robeson trade-off line. The Etched-HNT/6FDA-durene exhibits excellent CO\textsubscript{2} permeability and CO\textsubscript{2}/CH\textsubscript{4} selectivity, lying on the Robeson (2008) upper bound line. Compared to the reported HNTs MMMs, the etched-HNTs/6FDA-durene MMMs
show higher permeability and better selectivity, even higher than the MMMs with expensive synthetic fillers (e.g. MOFs, CNTs), indicating its potential for CO$_2$ separation in biogas or field natural gas. It is noteworthy that high filler loading usually deteriorate membrane performance by filler aggregation and interfacial voids, while the higher HNT loading than the referenced HNT MMMs in this study does not compromise the gas separation efficiency. This is because the surface roughening plays a critical role for the improved CO$_2$ separation in the MMMs by providing active sorption sites for the target gas. The increase of filler topological roughness and physical heterogeneity is certainly an effective way for filler surface modification so that adding foreign molecules to MMMs is avoided.

4. Conclusions

Using the low cost HNTs, high-performance MMMs for CO$_2$ separation are successfully fabricated by incorporating surface modified HNTs into 6FDA-durene polyimide polymer matrix. Surface etching and functional group grafting have been applied to modify the HNTs. Filler dispersion and filler-matrix affinity was quantified by tomographic FIB-SEM grafting method. The introduction of HNT fillers into the polymeric membrane increases gas permeability, but the change in gas selectivity depends on the type of surface modifications. The selectivity of MMMs was significantly improved by the etched-HNTs. The superior performance of the etched-HNTs MMMs, on the 2008 Robeson upper bound, can be attributed to the elimination of unselective interfacial voids and the improvement of filler dispersion and uniformity. It is envisaged that the filler surface modification strategy via etching can be used to improve the performance of polymer nanocomposite for possible applications in areas like catalysis and adsorption.

Supporting Information
Physical properties and morphologies of raw-HNTs and treated HNTs, SEM and 3D surface-rendered view of the segmented FIB-SEM tomograms for HNT MMMs and the HNTs dispersion, Comparison of membrane performance with some reported MMMs.

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REFERENCES


[34] S.R. Venna, M. Lartey, T. Li, A. Spore, S. Kumar, H.B. Nulwala, D.R. Luebke, N.L. Rosi,


[42] W.-H. Lin, T.-S. Chung, Gas permeability, diffusivity, solubility, and aging


FIGURE CAPTIONS:

Fig. 1. Schematic diagram of surface modification process to obtain surface etched or APTES grafted HNTs

Fig. 2. TEM images of Raw-HNTs (a), Etched-HNTs (b), and Grafted-HNTs (c)

Fig. 3. Cross-sectional SEM images of Raw-HNTs/6FDA-durene MMMs (a), etched-
HNTs/6FDA-durene MMMs (b), and grafted-HNTs/6FDA-durene MMMs (c) (HNT loading at 20 wt. %).

**Fig. 4.** Typical 3D restructured volume of the portion of etched-HNT MMMs (a), the corresponding surface-rendered view of the segmented FIB-SEM tomograms for HNT MMMs (b), HNTs (c) and voids (d). HNTs appear in green and voids in red. Box size: 8.8 µm× 7.4 µm× 4.7 µm

**Fig. 5.** Evolution of HNT filler volume in MMMs containing (a) raw-HNTs, (b) etched-HNTs and (c) grafted-HNTs

**Fig. 6.** Gas separation performance of HNT/durene MMMs for separating CO\(_2\)/CH\(_4\) gas pairs with respect to Robeson trade-off line, compared with some referenced MMMs in literature. Detailed citations of MMMs are presented in Table S2 in the supplementary Section.

**Table 1** Volume fraction of different phases in HNT-based MMMs as derived from the image analysis of the reconstructed FIB-SEM tomogram

<table>
<thead>
<tr>
<th></th>
<th>HNTs (%)</th>
<th>6FDA-durene (%)</th>
<th>Voids (%)</th>
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</thead>
<tbody>
<tr>
<td>Raw-HNTs MMM</td>
<td>16.1</td>
<td>83.7</td>
<td>0.06</td>
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<tr>
<td>Etched-HNTs MMM</td>
<td>13.5</td>
<td>86.4</td>
<td>0.02</td>
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<tr>
<td>Grafted-HNTs MMM</td>
<td>11.9</td>
<td>87.4</td>
<td>0.16</td>
</tr>
</tbody>
</table>
**Figure 1** Schematic diagram of surface modification process to obtain surface etched or APTES grafted HNTs

**Figure 2.** TEM images of Raw-HNTs (a), Etched-HNTs (b), and Grafted-HNTs (c)
Figure 3. Nitrogen adsorption isotherms of raw-HNTs, etched-HNTs and grafted-HNTs at 77K (Filled symbols: adsorption isotherm; opened symbols: desorption isotherm).
Figure 4. Gas adsorption isotherms on (a) raw-HNTs, (b) etched-HNTs and (c) grafted-HNTs at 25 ºC.
Figure 5. Cross-sectional SEM images of Raw-HNTs/6FDA-durene MMMs (a), etched-HNTs/6FDA-durene MMMs (b), and grafted-HNTs/6FDA-durene MMMs (c) (HNT loading at 20 wt. %).
Figure 6. Typical 3D restructured volume of the portion of etched-HNT MMMs (a), the corresponding surface-rendered view of the segmented FIB-SEM tomograms for HNT MMMs (b), HNTs (c) and voids (d). HNTs appear in green and voids in red. Box size: 8.8 μm × 7.4 μm × 4.7 μm
Figure 7. Evolution of HNT filler volume in MMMs containing (a) raw-HNTs, (b) etched-HNTs and (c) grafted-HNTs
Figure 8. HNT filler particle size distributions as derived from image analysis of the FIB-SEM tomogram: (a) raw-HNT MMM, (b) etched-HNT MMM and (c) grafted-HNT MMM.
Figure 9. Gas permeability (a) and selectivity (b) of the pure 6FDA-durene membrane and HNT based MMMs.
Figure 10. Gas separation performance of HNT/durene MMMs for separating CO$_2$/CH$_4$ gas pairs with respect to Robeson trade-off line, compared with some referenced MMMs in literature. Detailed citations of MMMs are presented in Table S2 in the supplementary Section.
Graphical abstract

Topological roughness on natural halloysite nanotubes was created prior to the fabrication of mixed matrix membranes. The effectiveness of filler modification routes in the same filler-polymer pair was quantified evaluated by FIB-SEM. The surface etching treatment improves the filler/polymer interface and filler dispersion in polymer matrix, exhibiting both increased CO₂ permeability and selectivity over the Robeson upper bound.

Highlights

- Cheap natural halloysite nanotube is applied as the filler for mixed matrix membrane.
- Quantitative evaluation of the filler/polymer interface voids and dispersion is made.
- 3D surface-rendered images of membranes have been provided.
- Surface etching of halloysite is more effective than grafting to enhance the membrane.