SEMARAK ILMU
PUBLISHING
202103268166(003316878-P)

Semarak International Journal of Chemical Process Engineering

Journal homepage:
https://semarakilmu.com.my/journals/index.php/sijcpe/index
ISSN: 3083-8916

Morphological And Chemical Analysis of PAN/a-CNx Composites Membranes For CO_2 Separation

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ARTICLE INFO

Article history:
Received 4 November 2024
Received in revised form 18 November 2024
Accepted 4 December 2024
Available online 20 December 2024

Keywords:
Amorphous carbon nitride; polyacrylonitrile; PECVD; NIPS; CO_2 separation

ABSTRACT

Thin polymeric membranes have attracted significant interest for CO_2 separation due to their high gas permeance and low cost. However, enhancing selectivity often requires an additional selective layer. This study investigates the role of amorphous carbon nitride (a-CNx) thin film deposited via radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD) as a selective layer on polyacrylonitrile (PAN) membrane fabricated through non-solvent induced phase separation (NIPS). Structural and chemical modifications of the membrane due to the introduction of a-CNx thin film were analyzed using Field Emission Scanning Electron Microscopy (FESEM), Brunauer-Emmett-Teller (BET) analysis, and Fourier-Transform Infrared Spectroscopy (FTIR). FESEM shows a textured surface on PAN/a-CNx membrane which confirmed the successful uniform deposition of the a-CNx thin film. BET revealed a slight reduction in BET surface area from 49.84 m^2/g to 48.13 m^2/g after deposition due to partial pore coverage by the a-CNx thin film. The Langmuir surface area increased from 89.94 m^2/g to 97.08 m^2/g, indicating the creation of more uniform adsorption sites. BJH analysis showed an increase in cumulative mesopore volume from 0.0994 cm^3/g to 0.1073 cm^3/g and a significant rise in mesopore width from 8.57 nm to 13.40 nm which implies the merging of smaller pores that led to increase mesoporosity. Both membranes exhibited Type IV isotherms with H3 hysteresis loops that represent characteristic of mesoporous materials, with the PAN/a-CNx membrane displaying a slightly wider hysteresis loop that indicates potential shifts toward slit-like pores. FTIR spectra confirmed the incorporation of a-CNx thin film into the PAN matrix, with characteristic peaks of N-H stretching, C=N stretching, and aromatic C-N stretching. The increase of nitrogen functionalities by the deposition of a-CNx thin film potentially increases CO_2 adsorption through acid-base interactions with nitrogen sites. These findings offer valuable insights for future research on high-performance gas separation membranes.

1. Introduction

Composite membranes are extensively used in industrial gas separation applications, including hydrogen [1-4] production, carbon capture [5-7], natural gas purification [8,9], and many more. The

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https://doi.org/10.37934/sijcpe.1.1.3144

growing efforts on mitigating CO_2 emissions have raised considerable interest in membrane-based technologies due to their energy efficiency and scalability potential. According to a review by Vatanpour *et al.,* [10], polyacrylonitrile (PAN) membrane have been adopted in various separation processes such as pervaporation, ion exchange, membrane distillation, adsorption membrane and water treatment. The diverse applications of PAN membranes in industrial scale were attributed to their excellent thermal and chemical stability in harsh conditions.

Polymeric membranes with high selectivity and permeability, such as cellulose acetate (CA) and polyimide, are the most commonly used materials in large-scale commercial CO_2 separation applications [10,11]. However, these materials are glassy polymers that undergo physical aging, which leads to rigid and brittle behavior over time. Glassy polymers with high free volume prone to degrade and experience faster physical aging when exposed to strong acidic environments [12-16]. This has become a challenge for gas separation performance, particularly in acidic CO_2 separation, as physical aging reduces gas permeability and membrane flux. Therefore, to overcome the issue, PAN membranes offer a promising alternative due to their semicrystalline structure [17-19] which possess higher flexibility and slower physical aging compared to glassy polymers. However, despite their advantageous properties, PAN membranes exhibit low CO_2 selectivity, primarily due to their hydrophilic nature, which is attributed to the -CN groups present in the polymer chains [10,19].

PAN is commonly used as a support layer in composite membranes for CO_2 separation due to its mechanical strength [20-26]. A study carried by Liang *et al.,* [27] developed defect-free PIM composite hollow fiber membranes using PAN as a support layer. The PAN hollow fiber substrates were produced via a dry-wet spinning process, followed by coating with PDMS and PIM-CD via dip coating. The CO_2/N_2 selectivity of pristine PAN membranes and PIM/PDMS/PAN membranes was tested in air separation tests. The study showed an increase in CO_2 selectivity from 0.8 for pristine PAN to 22.5 for PIM/PDMS/PAN composite hollow fiber membranes. However, the CO_2 permeability of the membrane reduced drastically from 50,000 GPU for pristine PAN to 483 GPU for PIM/PDMS/PAN composite hollow fiber membranes due to pore intrusion by the selective layer. Another study by Pohlmann *et al.,* [28] demonstrated the long-term stability of PolyActive™-based composite membranes, with PAN as a support layer, for post-combustion CO_2 capture in a pilot plant. The composite membrane was tested for degradation test in the flue gas for over 740 hours under dynamic conditions. The results showed a CO_2 selectivity of 50–75 mol% and a CO_2 recovery of 42.7%. However, an emergency shutdown led to hydrolysis of the ether groups in the polyethylene oxide (PEO) blocks from the PolyActive™ layer of the membrane material due to acidic condensation from the flue gas containing SO_2, NOx, and CO_2. The CO_2 permeability were dropped from 4.4 m^3(STD)/(m^2 h bar) before the shutdown and 1.4 m^3(STD)/(m^2 h bar) after the shutdown, while selectivity remained stable. While these studies proved the potential of PAN as a support layer, optimizing the selective layer is crucial to achieving a balance between gas permeability, selectivity, and physicochemical stability.

Carbon nitride is a 2D material that has been widely explored in gas separation technologies as an adsorbent and membrane material due to its unique porosity and basicity properties [29-31]. Among the types of carbon nitride, graphitic carbon nitride (g-C_3N_4) is the most used in gas separation applications. Cheng *et al.,* [32] were among the first to discovered and investigate g-C_3N_4 as a building block in gas separation membranes. The study incorporated thermally etched g-C_3N_4 nanosheets into a Pebax matrix and studied its effects on CO_2 and N_2 separation. The composite membrane exhibited enhanced CO_2 selectivity, largely due to the CO_2-philic amine groups present in g-C_3N_4, which increased CO_2 sorption compared to the pristine Pebax membrane. However, the addition of g-C_3N_4 also decreased the diffusion coefficients of the composite membrane, attributed to the molecular sieving effect and transport resistance, influenced by the thickness and porosity of the nanosheets.

Similarly, Li *et al.,* [33] developed mixed matrix membranes (MMMs) by doping g-C_3N_4 nanosheets containing zeolite imidazolate framework-8 (ZIF-8) into a Pebax matrix to further investigate the potential for improved CO_2 permselectivity. The synthesis of g-C_3N_4 is via thermal oxidation etching method and the membrane is characterized for its physical and chemical properties and tested for CO_2 separation performance using mixture of CO_2 and CH_4 gases. The result showed that CO_2 permselectivity of MMMs doped with g-C3N4 nanosheets improved with highest CO_2 permeability of 553 Barrer and CO_2/CH_4 selectivity of 35.5 compared to pristine Pebax by 97.5% and 29.1% increment, respectively. The excellent performance was mainly attributed to the incorporation of g-C_3N_4 with interconnected and nitrogenous (-NH and -NH_2 groups) nanopores that act as selective nanochannels in the MMMs and introduced CO_2 transport freeways in the MMMs.

While incorporating g-C_3N_4 into polymeric membranes has shown significant improvements in CO_2 separation due to the introduction of amine groups, amorphous carbon nitride (a-CNx) offers greater flexibility in terms of functionalization and porosity, providing a broader range of nitrogen functionalities (e.g., pyridinic and pyrrolic nitrogen) [34,35] which potentially further enhance CO_2 separation performance. Additionally, incorporating carbon nitride materials directly into the polymer matrix poses challenges in precisely controlling porosity and nitrogen content, with a risk of damaging the polymer framework. In contrast, coating a polymeric membrane with a thin film of carbon nitride using plasma-enhanced chemical vapor deposition (PECVD) technique simplifies and bypasses the complex fabrication steps of synthesizing and doping. This efficient approach allows better uniformity, tunable thickness, and controlled porosity and nitrogen functionalities by optimizing the deposition parameters for fabrication of CO_2 separation membrane. In this work, a-CNx thin film is introduced onto the PAN membrane using radio frequency plasma-enhanced chemical vapor deposition (rf-PECVD). The effects of a-CNx deposition on morphology, porosity, and surface chemistry are evaluated through Field Emission Scanning Electron Microscopy (FESEM), Brunauer-Emmett-Teller (BET) nitrogen adsorption, and Fourier-Transform Infrared Spectroscopy (FTIR) analysis, respectively. The findings may provide insights into developing composite membranes with wide nitrogen functionalities for enhanced CO_2 separation performance.

2. Experimental Methods

2.1 Sample Preparation

The PAN membranes were fabricated by nonsolvent induced phase separation (NIPS) method as shown schematically in Figure 1. The PAN powder was mixed with dimethyl sulfoxide (DMSO) and stirred continuously for 3 hours until a homogeneous solution formed. The resulting dope solution was cast onto a clean glass plate and evenly spread using the doctor blade casting method. The membrane was allowed to sit at room temperature for 1 minute before being immersed in coagulation bath for 24 hours to complete the solvent exchange. After separating from the glass plate, the membrane was air-dried at room temperature. As demonstrated in Figure 2, the incorporation of a-CNx onto the PAN membrane was carried out using the rf-PECVD technique. A mixture of precursor gases, CH_4 (20 sccm) and N_2 (50 sccm), was used for the deposition process for 45 minutes. The deposition was performed at a fixed RF power of 70 W and a pressure of 1.0 mbar.

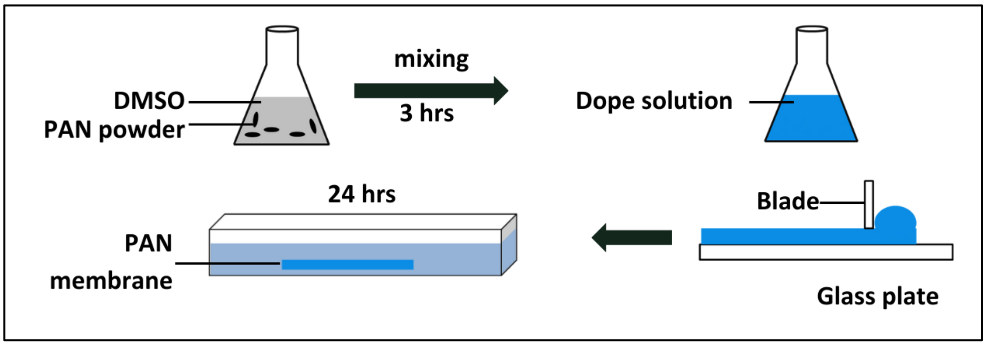


Fig. 1. Schematic diagram of PAN membrane preparation via NIPS method

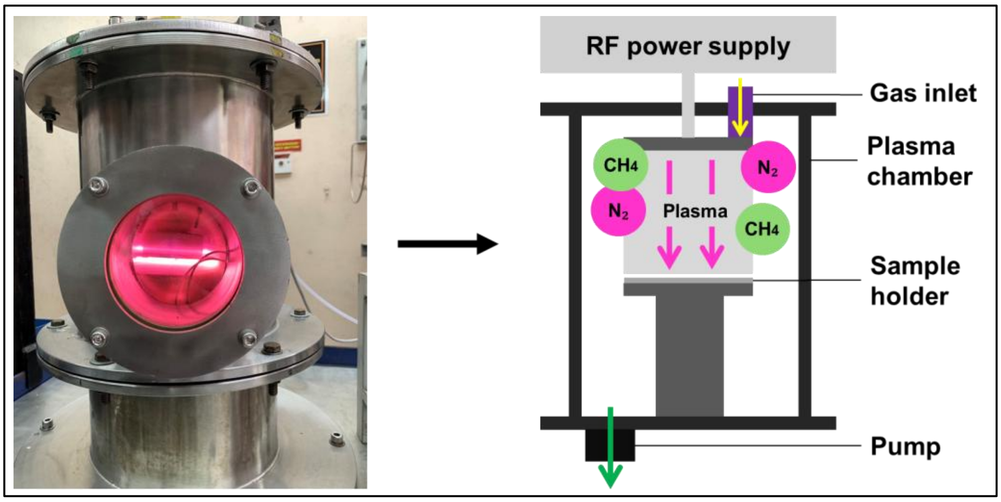


Fig. 2. Schematic diagram of deposition of a-CNx thin film via rf-PECVD method

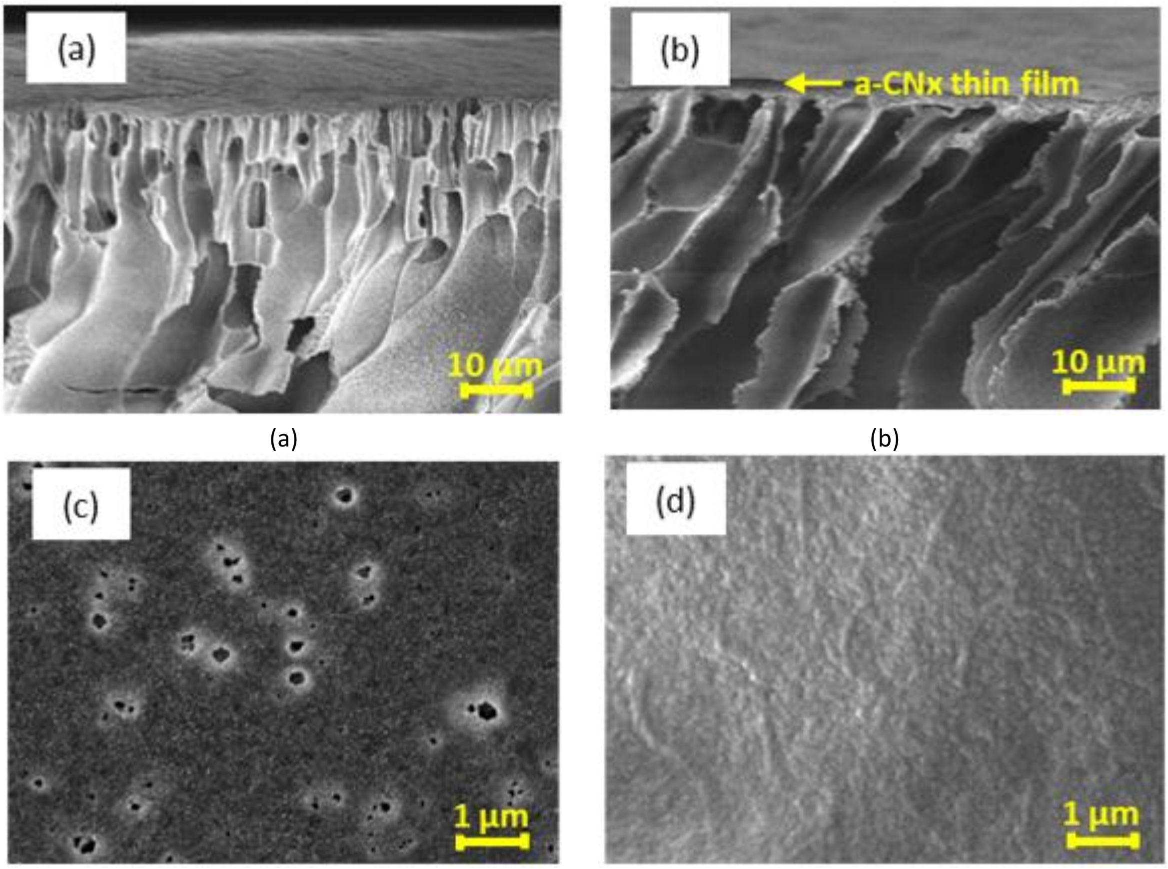
2.2 Characterizations

Field emission scanning electron microscopy (FESEM, Zeiss Merlin, ICRIM, UKM) was used to examine the surface morphology of the PAN and PAN/a-CNx membranes. The membranes were mounted onto stubs using conductive carbon tape, and images were acquired without additional conducting coatings to preserve the surface characteristics. Both top-view and cross-sectional images of the samples were obtained to assess the effect of the a-CNx thin film deposition on the membrane's structure. Brunauer–Emmett–Teller (BET, Micromeritics ASAP 2020, FST, UKM) analysis was conducted to determine the specific surface area, pore volume, and pore size distribution of the PAN and PAN/a-CNx membranes. Nitrogen adsorption-desorption isotherms were measured at 77 K, and the surface area was calculated using the multipoint BET method. The pore size distribution was obtained using the Barrett-Joyner-Halenda (BJH) model based on the adsorption data. The chemical bonds on the PAN and PAN/a-CNx membranes were analyzed using Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum Spotlight 400, ICRIM, UKM). The samples were placed directly on the instrument's stage, and spectra were recorded in the range of 4000–600 cm^{-1}. The measurements were conducted using an attenuated total reflectance (ATR) mode. The spectra provided insights into the functional groups present on the membrane surfaces before and after the deposition of a-CNx.

3. Results And Discussions

3.1 Morphological Analysis

Figure 3 shows FESEM images displaying the surface morphology and cross-sectional structure of both pristine PAN and the PAN/a-CNx membranes. Figures 3(a) and (b) show cross-sectional images of both membranes showing an asymmetric structure characterized by finger-like voids. These voids are formed due to the NIPS process, where rapid solvent-non-solvent exchange occurs. During membrane fabrication, solvent in the dope solution rapidly diffuses into the coagulation bath while non-solvent (water) penetrates the polymer matrix, resulting in the pore gradient where smaller pores are near the surface in contact with the glass plate and larger interconnected pores on the side exposed to the coagulation bath. In Figure 3(b), the darker and denser layer visible on the surface of the PAN/a-CNx membrane corresponds to the selective a-CNx thin film deposited onto the PAN substrate. The presence of a-CNx thin film on the PAN substrate verifies that the deposition method used is capable for surface modification to form a well-integrated composite system. The uneven thickness of this layer is attributed to the irregularity of the porous PAN substrate which influences the uniformity of thin-film deposition.



(a) (b)

(c) (d)

Fig. 3. FESEM images showing the cross-sectional of (a) PAN and (b) PAN/a-CNx membranes, and the morphology of (c) PAN and (d) PAN/a-CNx membranes

The surface morphology of the PAN membrane in Figure 3(c) shows a porous structure with irregularly distributed pores. These pores are formed during the membrane fabrication via NIPS technique [36-38]. The rapid exchange between the dope solution and the deionized water induces phase separation consequently leads to the formation of a porous structure. The resultant pore structure is essential for facilitating gas permeability in membrane applications [39]. After the deposition of a-CNx thin film onto the PAN substrate, the surface morphology of the PAN/a-CNx composite membrane (Figure 3(d)) exhibits obvious changes in surface texture. The surface becomes denser and more compact, with a noticeable reduction in visible pores. The morphological change is an indicative of a successful deposition of the a-CNx thin film, which exhibits a well-distributed cauliflower-like structure consistent with the a-CNx morphology reported by [40]. The high dispersibility of the porous and uneven PAN substrate facilitates strong mechanical anchoring and chemical interaction with the a-CNx thin film, resulting in enhanced adhesion and integration of the film to the PAN matrix.

As noticed in Figure 3(d), the deposition of a-CNx thin film results in the formation of a wrinkled surface which likely caused by the heat generated during the high-power deposition process [41]. The observed wrinkling morphology is attributed to the agglomeration of the a-CNx nanoparticles, which leads to uneven distribution of stresses across the membrane surface, similar to findings reported by Hou *et al.,* [42]. The compact and dense surface of PAN/a-CNx composite membrane suggests that the a-CNx thin film may act as a selective layer to increase its affinity for CO_2 molecules. However, for overall separation performance, a porous and uniform surface morphology is preferable to optimize both permeability and selectivity. Therefore, the stress-induced wrinkling of the a-CNx thin film could potentially be minimized by optimizing the deposition parameters, such as reducing the RF power [43] or extending the deposition duration [44] which would reduce thermal gradients and improve the uniformity of the film.

3.2 N_2 Adsorption-Desorption Analysis

The BET N_2 adsorption analysis was performed to investigate the effect of a-CNx thin film deposition on the surface properties and porosity of the composite membrane. According to N_2 adsorption/desorption isotherms displayed in Figure 4(a), both PAN and PAN/a-CNx membranes exhibited Type IV isotherms with H3-type hysteresis loops, which are characteristics of mesoporous materials according to IUPAC standards [45-48]. Additionally, the higher N_2 uptakes observed from the adsorption isotherm of PAN/a-CNx membrane supported with higher Langmuir surface area of 97.1 m^2/g and 89.9 m^2/g for PAN/a-CNx and PAN membrane, respectively suggests higher adsorption capacity compared to the pristine PAN membrane.

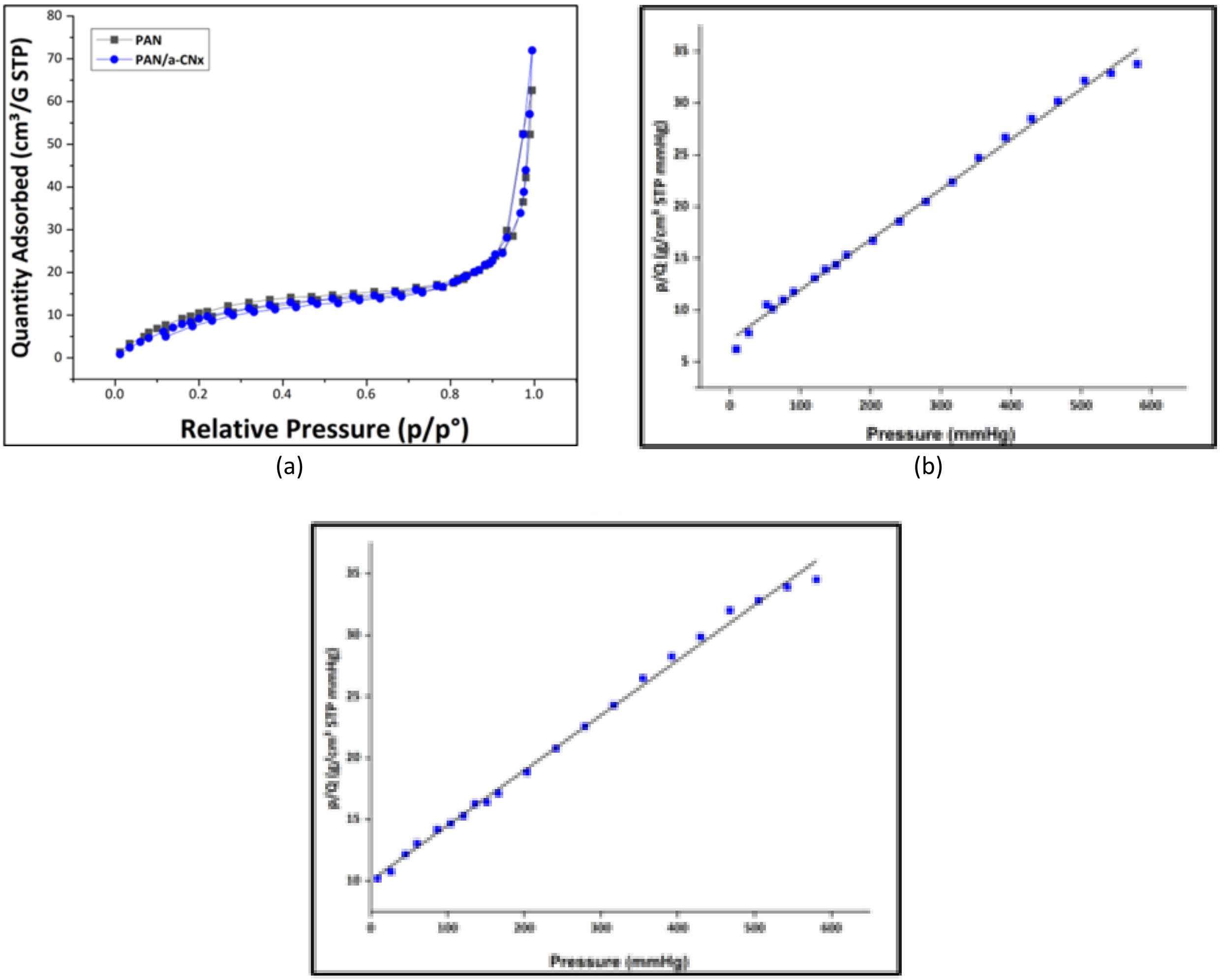
The experimental data were then modelled using Langmuir isotherm. As shown in Figure 4(b) and Figure 4(c), the high regression coefficients ($R^2 = 0.9978$ for PAN and $R^2 = 0.9979$ for PAN/a-CNx) confirms the accuracy and reliability of the model in representing the adsorption behavior. Table 1 provides a quantification summary of the surface area and porosity after the deposition of the a-CNx thin film. After the deposition, Langmuir surface area which reflects the monolayer adsorption capacity increased from 89.94 m^2/g (PAN membrane) to 97.08 m^2/g (PAN a-CNx membrane). The results suggest that the deposition of the a-CNx thin film introduced more active sites for monolayer gas adsorption. Meanwhile, the BET surface area of PAN membrane was measured at 49.84 m^2/g, which slightly decreased to 48.13 m^2/g after the deposition of a-CNx thin film. The reduction indicates the existence of blind pores due to the deposition of the a-CNx thin film, which may have partially covered some of the surface pores of the PAN membrane thereby reducing the surface area accessible for multilayer adsorption [49]. The calculated Langmuir surface area for both membranes has higher values compared to the corresponding BET surface areas mainly due to its assumptions of the entire surface is uniform and all adsorption sites have equal energy [50].

Further analysis using the BJH method revealed an increase in cumulative mesopore volume from 0.0994 cm^3/g to 0.1073 cm^3/g and a significant increase in average mesopore width from 8.57 nm to

13.40 nm after the deposition. This result suggests that the deposition of the a-CNx thin film led to the merging of smaller pores into larger mesopores due to the breakdown of chemical bond on the membrane surface caused by high-energy ion bombardment during the deposition. Additionally, the increase in mesopore volume could be attributed to the introduction of additional mesoporosity on the membrane surface particularly due to the mesoporous structure of the a-CNx itself. The abundance of mesopores could potentially allow higher gas permeability of PAN/a-CNx composite membrane through Knudsen diffusion for more efficient gas separation [51,52].

Table 1
Surface area and porosity characteristics of PAN and PAN/a-CNx membranes

	$S_{langmuir}$ (m^2/g)	S_{BET} (m^2/g)	Mesopore volume (cm^3/g)	Mesopore width (nm)
PAN	89.94	49.84	0.0994	8.57
PAN/a-CNx	97.08	48.13	0.1073	13.40



(a)

(b)

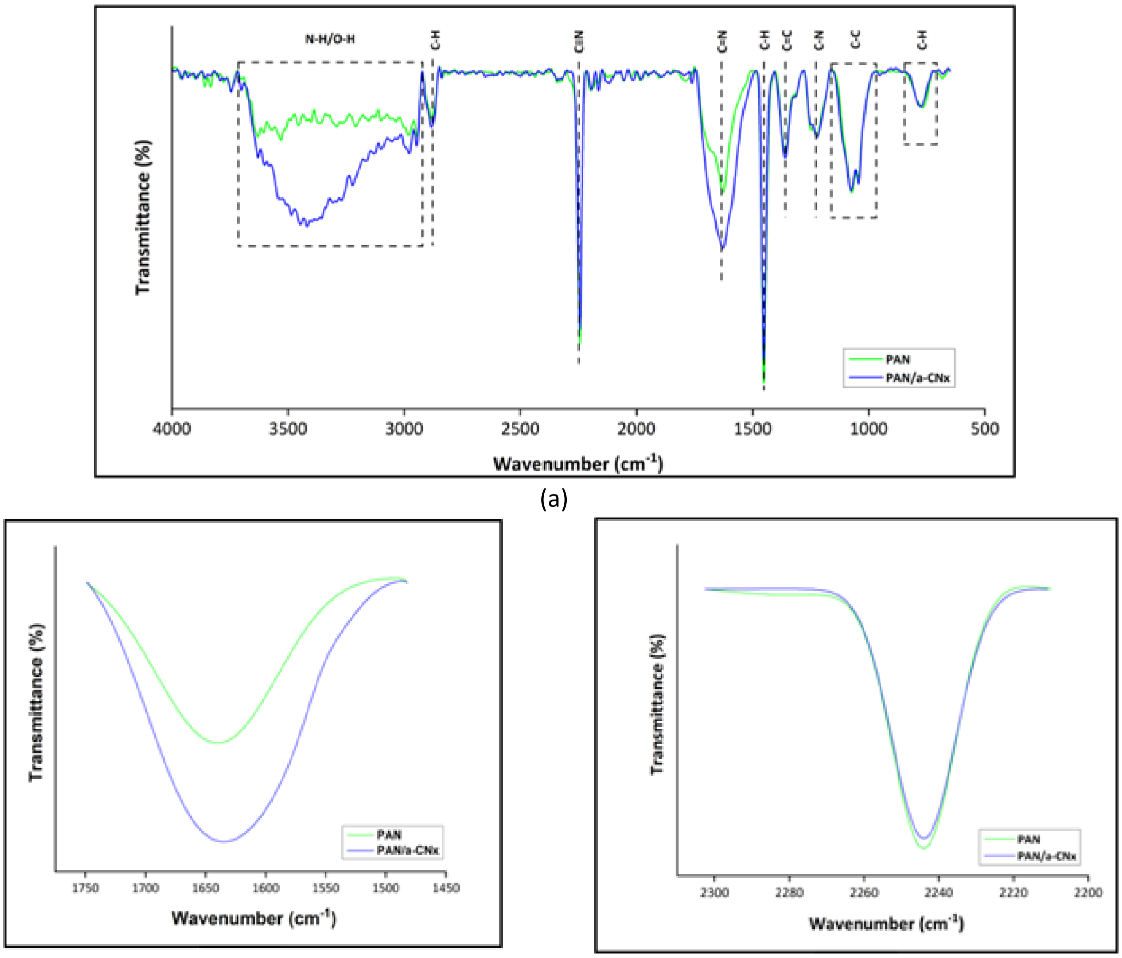
(c)

Fig. 4. (a) N_2 adsorption-desorption isotherm, and Langmuir plot of (b) PAN and (c) PAN/a-CNx membranes

3.3 Chemical Bond Analysis

The surface chemistry and interaction between a-CNx selective layer and PAN matrix was investigated by FTIR spectrometry as shown in Figure 5. As shown in Figure 5(a), the pristine PAN membrane exhibited characteristic peaks corresponding to its chemical properties. A sharp peak at 2243 cm^{-1} corresponds to the C≡N stretching vibration, while the C–H stretching and bending vibrations are observed at 2938 cm^{-1} and 1454 cm^{-1}, respectively. Additionally, the C–H deformation vibration of C=C–H appears at the range of 710-850 cm^{-1}, and the C–C stretching vibration is identified at 1077 cm^{-1}, all consistent with PAN characteristics [53-55]. The OH bonds observed in the 3000-3500 cm^{-1} region may be attributed to residual water molecules within the PAN structure, resulting from the phase separation process during membrane fabrication via the NIPS technique.

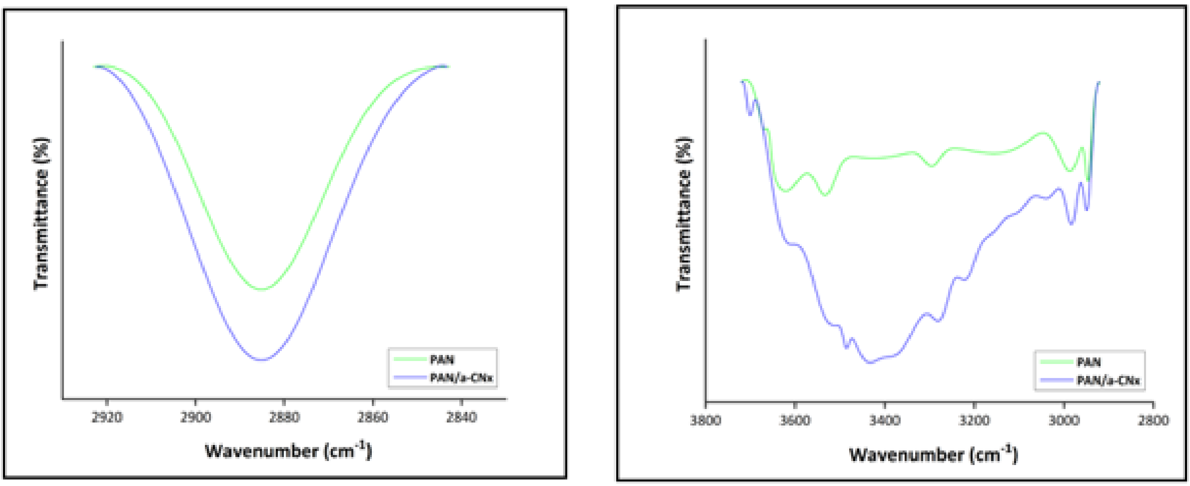
The FTIR spectra of the composite membrane also displayed peaks characteristic of a-CNx, including C-N, C=C, C=N, C-H, and N-H/O-H bonds [56-58], indicating successful deposition and adhesion of the a-CNx selective layer. The deposition of a-CNx selective layer retained the characteristic peaks of the PAN matrix in the composite membrane but with different intensity. Specifically, the PAN/a-CNx composite membrane shows broad bands around 3000–3500 cm^{-1} corresponding to N-H stretching vibrations. Furthermore, the peak observed between 1500 and 1800 cm^{-1} was attributed to C=N stretching, and the significant peak at 1100 cm^{-1} aligns with aromatic C-N stretching. As generally observed from the FTIR spectra, both C=N and N-H peaks were less pronounced in the pristine PAN membrane and confirms that the a-CNx deposition increases the presence of nitrogen-containing functional groups on the membrane surface.



(a)

(b)

(c)



(d) (e)

Fig. 5. FTIR Spectral showing: (a) Characteristic peaks of pristine PAN and PAN/a-CNx membrane, (b) enhanced C=N Bond Intensity, (c) reduced C≡N bond intensity, (d) strengthened C–H stretching, and (e) increased N–H Bond intensity of the composite membrane

Figure 5(b) shows an increased intensity of C=N bond which could be attributed to the breakdown and decomposition of C≡N bonds in the membrane matrix caused by the high-power deposition of a-CNx. The reduced intensity of the C≡N bond shown in Figure 5(c) influenced by the elevated temperature from the a-CNx deposition further supports the breakdown and partial conversion of acrylonitrile groups into imino (C=NH) groups in the PAN/a-CNx composite [54,55]. The intensification of the C-H stretching peak as depicted in Figure 5(d), is likely due to the increased bond strength caused by the deposition of a-CNx, which leads to a corresponding decrease in the intensity of the C-H bending peak at 1454 cm^{-1}. Moreover, the ruptured C≡N may also contribute to formation of N-H bonds. Figure 5(e) shows that the intensity of the N-H peak was significantly stronger after the incorporation of a-CNx due to the hydrogen bonding between N-H groups in the a-CNx layer and the -OH groups in the PAN matrix. The hydrogen bonding facilitates the interaction between PAN and the a-CNx selective layer and promotes the adhesion of a-CNx to the PAN matrix [53]. The N-H and O-H groups play important roles in increasing surface activity and effectively interacting with CO_2 molecules which potentially increase CO_2 permeability [37]. The increase in nitrogen functionalities observed in the composite membrane modifies the membrane's surface chemistry and functionality for CO_2 separation. The presence and intensified primary amine (NH) and imine (C=N) groups increase the basicity of the membrane surface and strongly interact with acidic CO_2 molecules through Lewis interactions between CO_2 molecules and nitrogen sites [59-62]. However, this study is limited to structural and chemical characterizations as a proof-of-concept to demonstrate the potential of the rf-PECVD method for introducing carbon nitride material in fabrication of CO_2 separation membranes. Future studies are required with focus on quantifying CO_2 permeability and selectivity to directly evaluate the separation performance of these modified membranes.

4. Conclusions

This study confirmed the successful and uniform deposition of a-CNx thin film onto PAN membrane using RF-PECVD technique. FESEM images showed a textured surface indicating a layer of a-CNx on the PAN membrane. The integration of the a-CNx thin film led to structural and chemical modifications in the PAN membrane. The Langmuir surface area increased (from 89.94 m^2/g to 97.08

m^2/g), suggesting the creation of more uniform adsorption sites. The BET analysis showed a slight reduction in the BET surface area (from 49.84 m^2/g to 48.13 m^2/g) due to partial pore coverage by the a-CNx thin film. BJH analysis revealed an increase in cumulative mesopore volume (from 0.0994 cm^3/g to 0.1073 cm^3/g) and a significant rise in average mesopore width (from 8.57 nm to 13.40 nm). These changes indicate the merging of smaller pores into larger mesopores, resulting in increased mesoporosity which could enhance gas diffusion through the membrane. FTIR spectra confirmed the incorporation of a-CNx into the PAN matrix increases nitrogen functionalities (e.g., N-H, C=N, and aromatic C-N stretching). This study demonstrates that a-CNx deposition on PAN membranes introduces variety of nitrogen functionalities that are theoretically favorable for CO_2 separation. While promising, further research is necessary to validate these findings through direct CO_2 separation testing, including permeability and selectivity measurements. Future studies will address these aspects, completing the evaluation of a-CNx/PAN membranes for CO_2 capture applications.

Acknowledgement

This work was supported by the Malaysia Ministry of Higher Education under the Fundamental Research Grant Scheme (FRGS/1/2021/STG05/UKM/02/3). We would also like to express our gratitude to UKM for the funding provided (TAP-K012608) and extend our thanks to the Research Management and Instrumentation Centre, UKM, for the facilities provided.

References

[1] Hu, Yaoxin, Yueqin Wu, Citsabehsan Devendran, Jing Wei, Yan Liang, Masahiko Matsukata, Wei Shen, Adrian Neild, Han Huang, and Huanting Wang. "Preparation of nanoporous graphene oxide by nanocrystal-masked etching: toward a nacre-mimetic metal–organic framework molecular sieving membrane." Journal of Materials Chemistry A 5, no. 31 (2017): 16255-16262. https://doi.org/10.1039/C7TA00927E

[2] Li, Wei, Yanhong Li, Jürgen Caro, and Aisheng Huang. "Fabrication of a flexible hydrogen-bonded organic framework based mixed matrix membrane for hydrogen separation." *Journal of Membrane Science* 643 (2022): 120021. https://doi.org/10.1016/j.memsci.2021.120021

[3] Qiao, Lu, Zixi Kang, Zhelun Li, Yang Feng, and Daofeng Sun. "Crystalline porous material based membranes for hydrogen separation." *Fuel* 359 (2024): 130477. https://doi.org/10.1016/j.fuel.2023.130477

[4] Singla, Shelly, Nagaraj P. Shetti, Soumen Basu, Kunal Mondal, and Tejraj M. Aminabhavi. "Hydrogen production technologies-Membrane based separation, storage and challenges." *Journal of environmental management* 302 (2022):113963. https://doi.org/10.1016/j.jenvman.2021.113963

[5] He, Guangwei, Shiqi Huang, Luis Francisco Villalobos, Jing Zhao, Mounir Mensi, Emad Oveisi, Mojtaba Rezaei, and Kumar Varoon Agrawal. "High-permeance polymer-functionalized single-layer graphene membranes that surpass the postcombustion carbon capture target." *Energy & Environmental Science* 12, no. 11 (2019): 3305-3312. https://doi.org/10.1039/C9EE01238A

[6] He, Guangwei, Shiqi Huang, Luis Francisco Villalobos, Jing Zhao, Mounir Mensi, Emad Oveisi, Mojtaba Rezaei, and Kumar Varoon Agrawal. "High-permeance polymer-functionalized single-layer graphene membranes that surpass the postcombustion carbon capture target." *Energy & Environmental Science* 12, no. 11 (2019): 3305-3312. https://doi.org/10.1039/C9EE01238A

[7] Chen, Danlin, Kaifang Wang, Ziyi Yuan, Zhihong Lin, Manman Zhang, Yang Li, Jiali Tang et al. "Boosting membranes for CO2 capture toward industrial decarbonization." *Carbon Capture Science & Technology* 7 (2023): 100117. https://doi.org/10.1016/j.ccst.2023.100117

[8] Li, Panyuan, Zhi Wang, Yanni Liu, Song Zhao, Jixiao Wang, and Shichang Wang. "A synergistic strategy via the combination of multiple functional groups into membranes towards superior CO2 separation performances." *Journal of membrane science* 476 (2015): 243-255. https://doi.org/10.1016/j.memsci.2014.11.050

[9] Harrigan, Daniel J., John A. Lawrence III, Harrison W. Reid, Jason B. Rivers, Jeremy T. O'Brien, Seth A. Sharber, and Benjamin J. Sundell. "Tunable sour gas separations: Simultaneous H2S and CO2 removal from natural gas via crosslinked telechelic poly (ethylene glycol) membranes." *Journal of Membrane Science* 602 (2020): 117947. https://doi.org/10.1016/j.memsci.2020.117947

[10] Vatanpour, Vahid, Mehmet Emin Pasaoglu, Borte Kose-Mutlu, and Ismail Koyuncu. "Polyacrylonitrile in the preparation of separation membranes: A review." *Industrial & Engineering Chemistry Research* 62, no. 17 (2023): 6537-6558. https://doi.org/10.1021/acs.iecr.3c00057

[11] Valappil, Riya Sidhikku Kandath, Nayef Ghasem, and Mohamed Al-Marzouqi. "Current and future trends in polymer membrane-based gas separation technology: A comprehensive review." *Journal of Industrial and Engineering Chemistry* 98 (2021): 103-129. https://doi.org/10.1016/j.jiec.2021.03.030

[12] Regula, Camille, Emilie Carretier, Yvan Wyart, Geneviève Gésan-Guiziou, A. Vincent, D. Boudot, and Philippe Moulin. "Chemical cleaning/disinfection and ageing of organic UF membranes: A review." *Water research* 56 (2014): 325-365. https://doi.org/10.1016/j.watres.2014.02.050

[13] Low, Ze-Xian, Peter M. Budd, Neil B. McKeown, and Darrell A. Patterson. "Gas permeation properties, physical aging, and its mitigation in high free volume glassy polymers." *Chemical reviews* 118, no. 12 (2018): 5871-5911. https://doi.org/10.1021/acs.chemrev.7b00629

[14] Kelman, Scott D., Brandon W. Rowe, Christopher W. Bielawski, Steven J. Pas, Anita J. Hill, D. R. Paul, and B. D. Freeman. "Crosslinking poly [1-(trimethylsilyl)-1-propyne] and its effect on physical stability." *Journal of membrane science* 320, no. 1-2 (2008): 123-134. https://doi.org/10.1016/j.memsci.2008.03.064

[15] Yavari, Milad, Sajjad Maruf, Yifu Ding, and Haiqing Lin. "Physical aging of glassy perfluoropolymers in thin film composite membranes. Part II. Glass transition temperature and the free volume model." *Journal of membrane science* 525 (2017): 399-408. https://doi.org/10.1016/j.memsci.2016.08.033

[16] Bernardo, P., Fabio Bazzarelli, F. Tasselli, Gabriele Clarizia, C. R. Mason, Louise Maynard-Atem, P. M. Budd et al. "Effect of physical aging on the gas transport and sorption in PIM-1 membranes." *Polymer* 113 (2017): 283-294. https://doi.org/10.1016/j.polymer.2016.10.040

[17] He, Chunfeng, Jiuqing Liu, Jinqiang Cui, Jie Li, and Xiufeng Wu. "A gel polymer electrolyte based on Polyacrylonitrile/organic montmorillonite membrane exhibiting dense structure for lithium ion battery." *Solid State Ionics* 315 (2018): 102-110. https://doi.org/10.1016/j.ssi.2017.12.014

[18] Adegbola, T. A., O. Agboola, and O. S. I. Fayomi. "Review of polyacrylonitrile blends and application in manufacturing technology: recycling and environmental impact." *Results in Engineering* 7 (2020): 100144. https://doi.org/10.1016/j.rineng.2020.100144

[19] Whba, Rawdah, Mohd Sukor Su'ait, Fathyah Whba, and Azizan Ahmad. "Research progress on polyacrylonitrile-based polymer electrolytes for electrochemical devices: Insight into electrochemical performance." *Journal of Power Sources* 606 (2024): 234539. https://doi.org/10.1016/j.jpowsour.2024.234539

[20] Zhao, Qian, Rui Xie, Feng Luo, Yousef Faraj, Zhuang Liu, Xiao-Jie Ju, Wei Wang, and Liang-Yin Chu. "Preparation of high strength poly (vinylidene fluoride) porous membranes with cellular structure via vapor-induced phase separation." *Journal of Membrane Science* 549 (2018): 151-164. https://doi.org/10.1016/j.memsci.2017.10.068

[21] Bhavsar, Rupesh S., Tamoghna Mitra, Dave J. Adams, Andrew I. Cooper, and Peter M. Budd. "Ultrahigh-permeance PIM-1 based thin film nanocomposite membranes on PAN supports for CO2 separation." *Journal of Membrane Science* 564 (2018): 878-886. https://doi.org/10.1016/j.memsci.2018.07.089

[22] Guo, Hongfang, Wenqi Xu, Jing Wei, Yulei Ma, Zikang Qin, Zhongde Dai, Jing Deng, and Liyuan Deng. "Effects of Porous Supports in Thin-Film Composite Membranes on CO2 Separation Performances." *Membranes* 13, no. 3 (2023): 359. https://doi.org/10.3390/membranes13030359

[23] Park, Yun Hwan, Mi Song, Chi Hoon Park, and Sang Yong Nam. "Fabrication of Multi-Layer Composite Membranes with Excellent CO2 Permeability and Selectivity for Gas Separation Process." *Journal of Nanoscience and Nanotechnology* 17, no. 10 (2017): 7735-7742. https://doi.org/10.1166/jnn.2017.14785

[24] Karunakaran, Madhavan, Mahendra Kumar, Rahul Shevate, Faheem Hassan Akhtar, and Klaus-Viktor Peinemann. "CO2-philic thin film composite membranes: Synthesis and characterization of PAN-r-PEGMA copolymer." *Polymers* 9, no. 7 (2017): 219. https://doi.org/10.3390/polym9070219

[25] Scofield, Joel MP, Paul A. Gurr, Jinguk Kim, Qiang Fu, Sandra E. Kentish, and Greg G. Qiao. "Development of novel fluorinated additives for high performance CO2 separation thin-film composite membranes." *Journal of Membrane Science* 499 (2016): 191-200. https://doi.org/10.1016/j.memsci.2015.10.035

[26] Achalpurkar, Manoj P., Ulhas K. Kharul, Harshada R. Lohokare, and Prasad B. Karadkar. "Gas permeation in amine functionalized silicon rubber membranes." *Separation and Purification Technology* 57, no. 2 (2007): 304-313. https://doi.org/10.1016/j.seppur.2007.05.002

[27] Liang, Can Zeng, Jiang Tao Liu, Juin-Yih Lai, and Tai-Shung Chung. "High-performance multiple-layer PIM composite hollow fiber membranes for gas separation." *Journal of Membrane Science* 563 (2018): 93-106. https://doi.org/10.1016/j.memsci.2018.05.045

[28] Pohlmann, Jan, Martin Bram, Kai Wilkner, and Torsten Brinkmann. "Pilot scale separation of CO2 from power plant flue gases by membrane technology." *International journal of greenhouse gas control* 53 (2016): 56-64. https://doi.org/10.1016/j.ijggc.2016.07.033

[29] Azmi, A. A., and M. A. A. Aziz. "Mesoporous adsorbent for CO2 capture application under mild condition: a review." *Journal of Environmental Chemical Engineering* 7, no. 2 (2019): 103022. https://doi.org/10.1016/j.jece.2019.103022

[30] Talapaneni, Siddulu Naidu, Gurwinder Singh, In Young Kim, Khalid AlBahily, Ala'A. H. Al-Muhtaseb, Ajay S. Karakoti, Ehsan Tavakkoli, and Ajayan Vinu. "Nanostructured carbon nitrides for CO2 capture and conversion." *Advanced Materials* 32, no. 18 (2020): 1904635. https://doi.org/10.1002/adma.201904635

[31] Gao, Jinhao, Yu Song, Chenyu Jia, Liyue Sun, Yao Wang, Yanxin Wang, Matt J. Kipper, Linjun Huang, and Jianguo Tang. "A comprehensive review of recent developments and challenges for gas separation membranes based on two-dimensional materials." *FlatChem* (2023): 100594. https://doi.org/10.1016/j.flatc.2023.100594

[32] Cheng, Long, Yuyang Song, Huimin Chen, Guozhen Liu, Gongping Liu, and Wanqin Jin. "g-C3N4 nanosheets with tunable affinity and sieving effect endowing polymeric membranes with enhanced CO2 capture property." *Separation and Purification Technology* 250 (2020): 117200. https://doi.org/10.1016/j.seppur.2020.117200

[33] Li, Xueqin, Xia Lv, Siyuan Ding, Lu Huang, and Zhong Wei. "Mixed matrix membranes containing composite nanosheets with three-dimensional nanopores for efficient CO2 separation." *International Journal of Greenhouse Gas Control* 117 (2022): 103658.

[34] Purhanudin, Noorain, and Rozidawati Awang. "Formation of chemical bonds and morphological studies of a-CNx: Effects of PECVD deposition pressure." In *AIP Conference Proceedings*, vol. 1784, no. 1. AIP Publishing, 2016. https://doi.org/10.1063/1.4966804

[35] N Aziz, N. F. H., Richard Ritikos, S. A. A. Kamal, N. I. Azman, and Rozidawati Awang. "Effect of RF Power on the chemical bonding and humidity sensing properties of a-CNx thin films." Advanced Materials Research 1107 (2015): 655-660. https://doi.org/10.4028/www.scientific.net/AMR.1107.655

[36] Choi, Ook, Pravin G. Ingole, and Chul Ho Park. "Precision-aiming tuning of membranes prepared by NIPS and its performance enhancement." *Journal of Cleaner Production* 365 (2022): 132858. https://doi.org/10.1016/j.jclepro.2022.132858

[37] Sherugar, Prajwal, Arnet Maria Antony, Nik Abdul Hadi Md Nordin, Siddappa A. Patil, and Mahesh Padaki. "Tailoring the CH4/CO2/N2 separation performance of ultrapermeable polymeric composite membranes by altering the concentration of Pd/g-C3N4." *Fuel* 361 (2024): 130731. https://doi.org/10.1016/j.fuel.2023.130731

[38] Junoh, Hazlina, Juhana Jaafar, Nik Abdul Hadi M. Nordin, Ahmad F. Ismail, Mohd HD Othman, Mukhlis A. Rahman, Farhana Aziz, Norhaniza Yusof, and Syarifah Noor S. Sayed Daud. "Porous polyether sulfone for direct methanol fuel cell applications: Structural analysis." *International Journal of Energy Research* 45, no. 2 (2021): 2277-2291. https://doi.org/10.1002/er.5921

[39] Yu, Guangli, Yanqin Li, Ziyang Wang, Terence Xiaoteng Liu, Guangshan Zhu, and Xiaoqin Zou. "Mixed matrix membranes derived from nanoscale porous organic frameworks for permeable and selective CO2 separation." *Journal of Membrane Science* 591 (2019): 117343. https://doi.org/10.1016/j.memsci.2019.117343

[40] Awang, Rozidawati, Noorain Purhanudin, and Nur Sakinah Salman. "Effect of radio frequency power on a-CNx film properties and its performance as humidity sensors." *Sains Malaysiana* 47, no. 11 (2018): 2863-2867. https://doi.org/10.17576/jsm-2018-4711-29

[41] De Los Arcos, Teresa, Peter Awakowicz, Marc Böke, Nils Boysen, Ralf Peter Brinkmann, Rainer Dahlmann, Anjana Devi et al. "PECVD and PEALD on polymer substrates (part II): Understanding and tuning of barrier and membrane properties of thin films." *Plasma Processes and Polymers* 21, no. 3 (2024): 2300186. https://doi.org/10.1002/ppap.202300186

[42] Hou, Wen, Jun Cheng, Yingyu Tan, Chen Yang, Xufeng Ren, Jinming Xie, Bangjiao Ye, Hongjun Zhang, and Junhu Zhou. "Simultaneously promoting CO2 permeability and selectivity of polyethylene oxide membranes via introducing CO2-philic KAUST-7." *Fuel* 361 (2024): 130631. https://doi.org/10.1016/j.fuel.2023.130631

[43] Jaritz, Montgomery, Christian Hopmann, Henrik Behm, Dennis Kirchheim, Stefan Wilski, Dario Grochla, Lars Banko et al. "Influence of residual stress on the adhesion and surface morphology of PECVD-coated polypropylene." *Journal of Physics D: Applied Physics* 50, no. 44 (2017): 445301. https://doi.org/10.1088/1361-6463/aa8798

[44] Awang, Rozidawati, Nurul Izzati Azman, and Noorain Purhanudin. "Influence of Deposition Time on Bonding and Morphology of Amorphous Carbon Nitride Thin Films." *In Materials Science Forum*, vol. 846, pp. 657-662. Trans Tech Publications Ltd, 2016. https://doi.org/10.4028/www.scientific.net/MSF.846.657

[45] Hussin, Farihahusnah, and Mohamed Kheireddine Aroua. "Recent trends in the development of adsorption technologies for carbon dioxide capture: A brief literature and patent reviews (2014-2018)." *Journal of Cleaner Production* 253 (2020): 119707. https://doi.org/10.1016/j.jclepro.2019.119707

[46] Rajpure, Manoj M., Rajendra B. Mujmule, Uisik Kim, and Hern Kim. "Fabrication of MgO nanorods blended cellulose acetate-based mixed matrix membranes for selective gas separation of H2/CH4, CO2/CH4 and H2/CO2: Effect of

loading and pressure." *International Journal of Hydrogen Energy* 50 (2024): 615-628. https://doi.org/10.1016/j.ijhydene.2023.09.238

[47] Jedli, Hedi, M. M. Almoneef, Mohamed Mbarek, Abdessalem Jbara, and Khalifa Slimi. "Adsorption of CO2 onto zeolite ZSM-5: Kinetic, equilibrium and thermodynamic studies." *Fuel* 321 (2022): 124097. https://doi.org/10.1016/j.fuel.2022.124097

[48] Patel, Vaishwik, Arun Baskar, Steffi Tiburcius, Brodie Morrison, Bhavya Mod, Pradeep S. Tanwar, Prashant Kumar, Ajay Karakoti, Gurwinder Singh, and Ajayan Vinu. "Mesoporous Carbon Nitrides as Emerging Materials: Nanoarchitectonics and Biosensing Applications." *Advanced Sensor Research* 2, no. 9 (2023): 2300024. https://doi.org/10.1002/adsr.202300024

[49] Ardali, Narges Salehi, Siavash Riahi, Mojgan Abbasi, and Navid Mohammadpour. "Experimental investigation of carbon dioxide adsorption using functionalized MWCNTs with 1, 6-diaminohexane." *Fuel* 338 (2023): 127213. https://doi.org/10.1016/j.fuel.2022.127213

[50] S Yoon, Soong-Seok, Hyun-Kyung Lee, and Se-Ryeong Hong. "CO2/N2 gas separation using Pebax/ZIF-7-PSf composite membranes." *Membranes* 11, no. 9 (2021): 708. https://doi.org/10.3390/membranes11090708

[51] Li, Songwei, Xu Jiang, Hongguang Sun, Shanshan He, Liling Zhang, and Lu Shao. "Mesoporous dendritic fibrous nanosilica (DFNS) stimulating mix matrix membranes towards superior CO2 capture." *Journal of Membrane Science* 586 (2019): 185-191. https://doi.org/10.1016/j.memsci.2019.05.069

[52] Xin, Qingping, Wei Shao, Qiang Ma, Xiaokun Ye, Zhenxuan Huang, Bangyao Li, Shaofei Wang, Hong Li, and Yuzhong Zhang. "Efficient CO2 separation of multi-permselective mixed matrix membranes with a unique interfacial structure regulated by mesoporous nanosheets." *ACS Applied Materials & Interfaces* 12, no. 42 (2020): 48067-48076. https://doi.org/10.1021/acsami.0c10895

[53] Wu, Yongdong, Dan Zhao, Jizhong Ren, Yongtao Qiu, and Maicun Deng. "A novel Pebax-C60 (OH) 24/PAN thin film composite membrane for carbon dioxide capture." *Separation and Purification Technology* 215 (2019): 480-489. https://doi.org/10.1016/j.seppur.2018.12.073

[54] Pérez-Manríquez, Liliana, Jamaliah Aburabi'e, Pradeep Neelakanda, and Klaus-Viktor Peinemann. "Cross-linked PAN-based thin-film composite membranes for non-aqueous nanofiltration." *Reactive and Functional Polymers* 86 (2015): 243-247. https://doi.org/10.1016/j.reactfunctpolym.2014.09.015

[55] Jin, Xin, Lin Li, Ruisong Xu, Qiao Liu, Linghua Ding, Yanqiu Pan, Chunlei Wang, Weisong Hung, Kueirrarn Lee, and Tonghua Wang. "Effects of thermal cross-linking on the structure and property of asymmetric membrane prepared from the polyacrylonitrile." *Polymers* 10, no. 5 (2018): 539. https://doi.org/10.3390/polym10050539

[56] Azman, Nurul Izzati, Rozidawati Awang, and Shafarina Azlinda Ahmad Kamal. "Influence of deposition time on the chemical bonding and composition of amorphous carbon nitride films." In *AIP Conference Proceedings*, vol. 1614, no. 1, pp. 74-77. American Institute of Physics, 2014. https://doi.org/10.1063/1.4895174

[57] Yu, Guo-Qing, Seung-Hoon Lee, and Jung-Joong Lee. "Effects of thermal annealing on amorphous carbon nitride films by rf PECVD." *Diamond and related materials* 11, no. 9 (2002): 1633-1637. https://doi.org/10.1016/S0925-9635(02)00111-5

[58] Abd Aziz, Siti Aisyah, and Rozidawati Awang. "Chemical Bonding Composition and Growth Mechanism of a-CNx Thin Films by Low-Temperature rf-PECVD Technique." *SAINS MALAYSIANA* 49, no. 6 (2020): 1461-1470. https://doi.org/10.17576/jsm-2020-4906-24.

[59] Rehman, Adeela, and Soo-Jin Park. "Facile synthesis of nitrogen-enriched microporous carbons derived from imine and benzimidazole-linked polymeric framework for efficient CO2 adsorption." *Journal of CO2 Utilization* 21 (2017): 503-512. https://doi.org/10.1016/j.jcou.2017.08.016

[60] Chen, Xinwei, Kian Guan Khoo, Min Woo Kim, and Liang Hong. "Deriving a CO2-permselective carbon membrane from a multilayered matrix of polyion complexes." *ACS Applied Materials & Interfaces* 6, no. 13 (2014): 10220-10230. https://doi.org/10.1021/am5015953

[61] Lim, Geunsik, Ki Bong Lee, and Hyung Chul Ham. "Effect of N-containing functional groups on CO2 adsorption of carbonaceous materials: a density functional theory approach." *The Journal of Physical Chemistry C* 120, no. 15 (2016): 8087-8095. https://doi.org/10.1021/acs.jpcc.5b12090

[62] Vorokhta, Maryna, Muhammad Irfan Maulana Kusdhany, Martina Švábová, Masamichi Nishihara, Kazunari Sasaki, and Stephen Matthew Lyth. "Hierarchically porous carbon foams coated with carbon nitride: Insights into adsorbents for pre-combustion and post-combustion CO2 separation." *Separation and Purification Technology* 354 (2025): 129054. https://doi.org/10.1016/j.seppur.2024.129054