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Morphological And Chemical Analysis of PAN/a-CN_x Composites Membranes For CO₂ Separation

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ABSTRACT

Thin polymeric membranes have attracted significant interest for CO₂ 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-CN_x) 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-CN_x 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-CN_x membrane which confirmed the successful uniform deposition of the a-CN_x thin film. BET revealed a slight reduction in BET surface area from 49.84 m²/g to 48.13 m²/g after deposition due to partial pore coverage by the a-CN_x thin film. The Langmuir surface area increased from 89.94 m²/g to 97.08 m²/g, indicating the creation of more uniform adsorption sites. BJH analysis showed an increase in cumulative mesopore volume from 0.0994 cm³/g to 0.1073 cm³/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-CN_x membrane displaying a slightly wider hysteresis loop that indicates potential shifts toward slit-like pores. FTIR spectra confirmed the incorporation of a-CN_x 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-CN_x thin film potentially increases CO₂ 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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growing efforts on mitigating CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂/N₂ selectivity of pristine PAN membranes and PIM/PDMS/PAN membranes was tested in air separation tests. The study showed an increase in CO₂ selectivity from 0.8 for pristine PAN to 22.5 for PIM/PDMS/PAN composite hollow fiber membranes. However, the CO₂ 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 CO₂ 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 CO₂ selectivity of 50–75 mol% and a CO₂ 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 SO₂, NO_x, and CO₂. The CO₂ permeability were dropped from 4.4 m³(STD)/(m² h bar) before the shutdown and 1.4 m³(STD)/(m² 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-C₃N₄) is the most used in gas separation applications. Cheng *et al.*, [32] were among the first to discovered and investigate g-C₃N₄ as a building block in gas separation membranes. The study incorporated thermally etched g-C₃N₄ nanosheets into a Pebax matrix and studied its effects on CO₂ and N₂ separation. The composite membrane exhibited enhanced CO₂ selectivity, largely due to the CO₂-philic amine groups present in g-C₃N₄, which increased CO₂ sorption compared to the pristine Pebax membrane. However, the addition of g-C₃N₄ 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-C₃N₄ nanosheets containing zeolite imidazolate framework-8 (ZIF-8) into a Pebax matrix to further investigate the potential for improved CO₂ permselectivity. The synthesis of g-C₃N₄ is via thermal oxidation etching method and the membrane is characterized for its physical and chemical properties and tested for CO₂ separation performance using mixture of CO₂ and CH₄ gases. The result showed that CO₂ permselectivity of MMMs doped with g-C₃N₄ nanosheets improved with highest CO₂ permeability of 553 Barrer and CO₂/CH₄ 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-C₃N₄ with interconnected and nitrogenous (-NH and -NH₂ groups) nanopores that act as selective nanochannels in the MMMs and introduced CO₂ transport freeways in the MMMs.

While incorporating g-C₃N₄ into polymeric membranes has shown significant improvements in CO₂ separation due to the introduction of amine groups, amorphous carbon nitride (a-CN_x) 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 CO₂ 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 CO₂ separation membrane. In this work, a-CN_x thin film is introduced onto the PAN membrane using radio frequency plasma-enhanced chemical vapor deposition (rf-PECVD). The effects of a-CN_x 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 CO₂ 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-CN_x onto the PAN membrane was carried out using the rf-PECVD technique. A mixture of precursor gases, CH₄ (20 sccm) and N₂ (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.

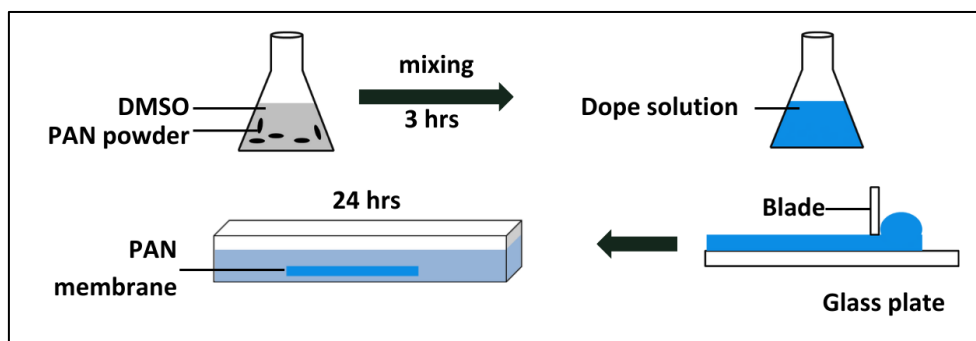


Fig. 1. Schematic diagram of PAN membrane preparation via NIPS method

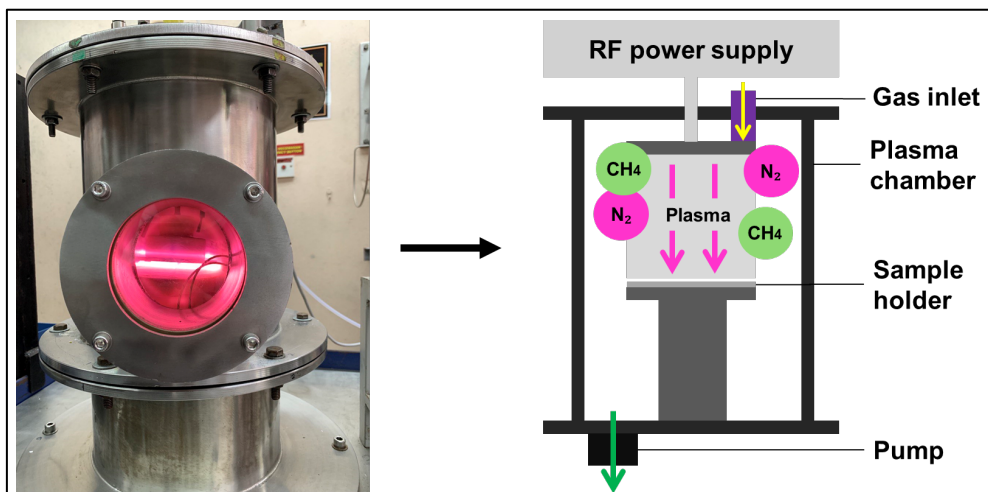


Fig. 2. Schematic diagram of deposition of a-CN_x thin film via rf-PECVD method

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-CN_x 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-CN_x 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-CN_x 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-CN_x 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-CN_x.

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-CN_x 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-CN_x membrane corresponds to the selective a-CN_x thin film deposited onto the PAN substrate. The presence of a-CN_x 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.

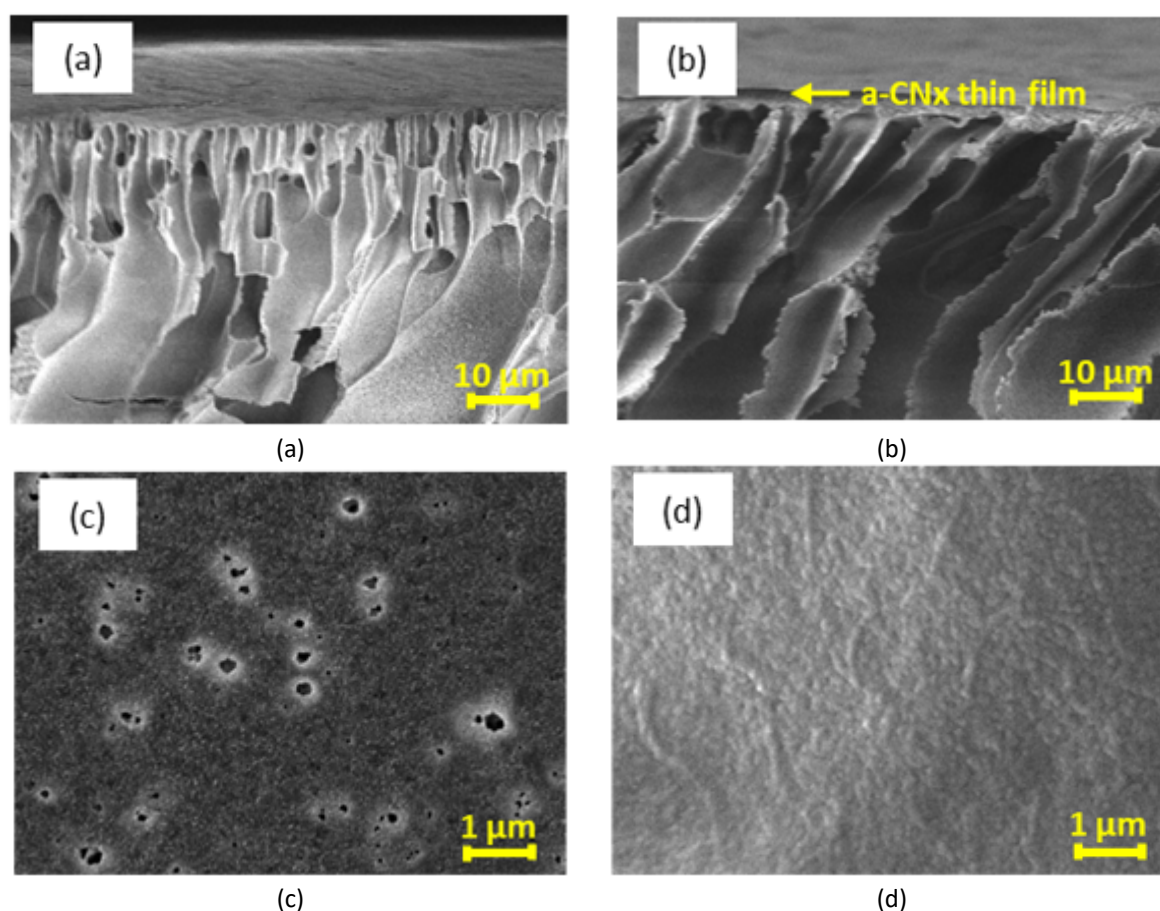


Fig. 3. FESEM images showing the cross-sectional of (a) PAN and (b) PAN/a-CN_x membranes, and the morphology of (c) PAN and (d) PAN/a-CN_x membranes

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-CN_x thin film onto the PAN substrate, the surface morphology of the PAN/a-CN_x 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-CN_x thin film, which exhibits a well-distributed cauliflower-like structure consistent with the a-CN_x morphology reported by [40]. The high dispersibility of the porous and uneven PAN substrate facilitates strong mechanical anchoring and chemical interaction with the a-CN_x 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-CN_x 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-CN_x 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-CN_x composite membrane suggests that the a-CN_x thin film may act as a selective layer to increase its affinity for CO₂ 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-CN_x 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 N₂ Adsorption-Desorption Analysis

The BET N₂ adsorption analysis was performed to investigate the effect of a-CN_x thin film deposition on the surface properties and porosity of the composite membrane. According to N₂ adsorption/desorption isotherms displayed in Figure 4(a), both PAN and PAN/a-CN_x 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 N₂ uptakes observed from the adsorption isotherm of PAN/a-CN_x membrane supported with higher Langmuir surface area of 97.1 m²/g and 89.9 m²/g for PAN/a-CN_x and PAN membrane, respectively suggests higher adsorption capacity compared to the pristine PAN membrane.

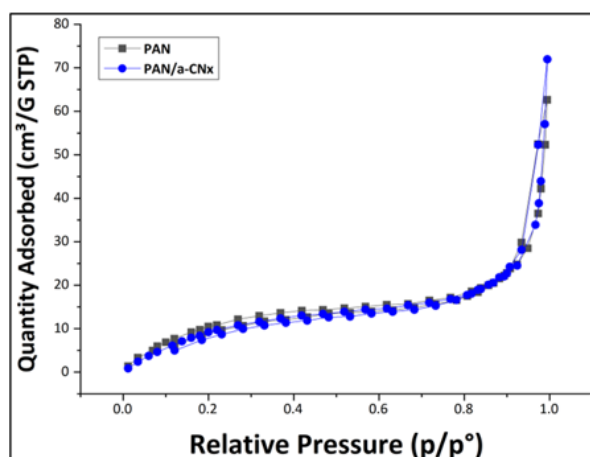
The experimental data were then modelled using Langmuir isotherm. As shown in Figure 4(b) and Figure 4(c), the high regression coefficients ($R^2 = 0.9978$ for PAN and $R^2 = 0.9979$ for PAN/a-CN_x) confirms the accuracy and reliability of the model in representing the adsorption behavior. Table 1 provides a quantification summary of the surface area and porosity after the deposition of the a-CN_x thin film. After the deposition, Langmuir surface area which reflects the monolayer adsorption capacity increased from 89.94 m²/g (PAN membrane) to 97.08 m²/g (PAN a-CN_x membrane). The results suggest that the deposition of the a-CN_x thin film introduced more active sites for monolayer gas adsorption. Meanwhile, the BET surface area of PAN membrane was measured at 49.84 m²/g, which slightly decreased to 48.13 m²/g after the deposition of a-CN_x thin film. The reduction indicates the existence of blind pores due to the deposition of the a-CN_x 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 cm³/g to 0.1073 cm³/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-CN_x 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-CN_x itself. The abundance of mesopores could potentially allow higher gas permeability of PAN/a-CN_x composite membrane through Knudsen diffusion for more efficient gas separation [51,52].

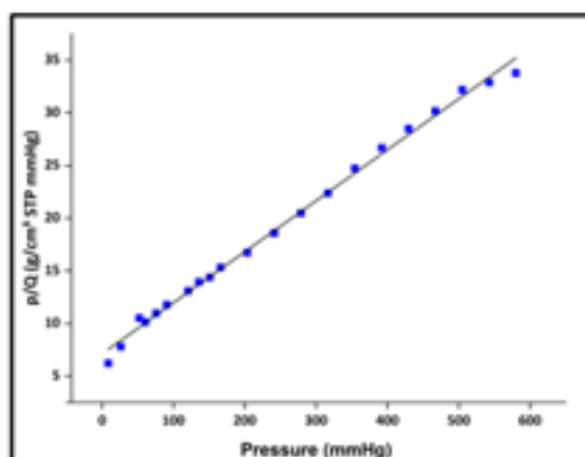
Table 1

Surface area and porosity characteristics of PAN and PAN/a-CN_x membranes

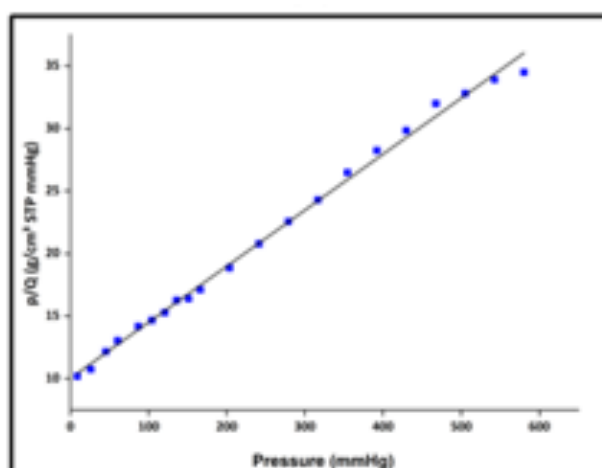
	$S_{Langmuir}$ (m ² /g)	S_{BET} (m ² /g)	Mesopore volume (cm ³ /g)	Mesopore width (nm)
PAN	89.94	49.84	0.0994	8.57
PAN/a-CN _x	97.08	48.13	0.1073	13.40



(a)



(b)



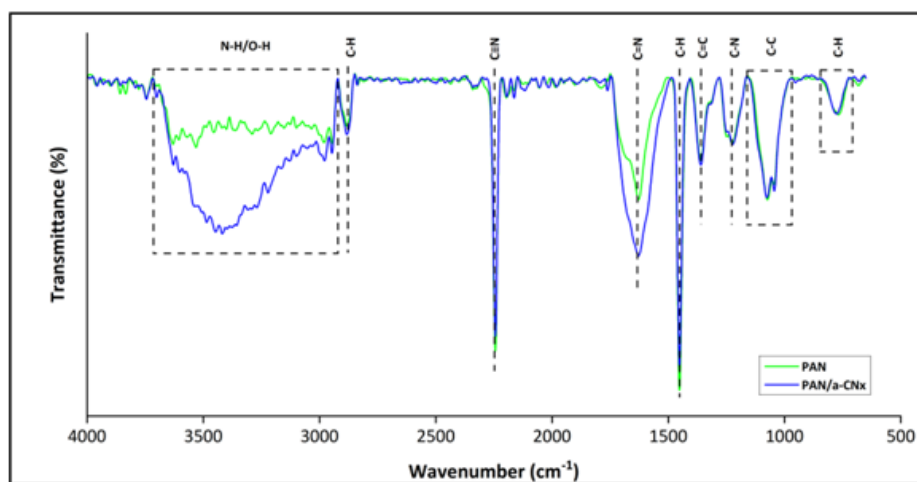
(c)

Fig. 4. (a) N₂ adsorption-desorption isotherm, and Langmuir plot of (b) PAN and (c) PAN/a-CN_x membranes

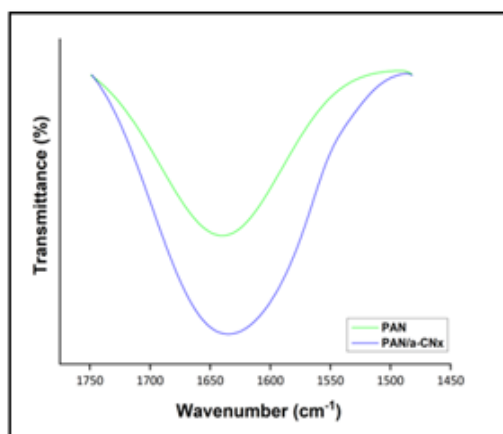
3.3 Chemical Bond Analysis

The surface chemistry and interaction between a-CN_x 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.

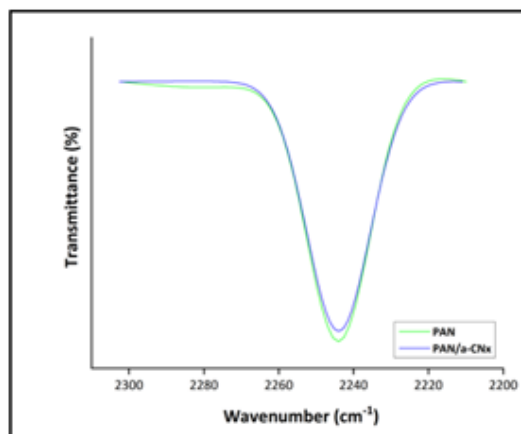
The FTIR spectra of the composite membrane also displayed peaks characteristic of a-CN_x, including C–N, C=C, C=N, C–H, and N–H/O–H bonds [56–58], indicating successful deposition and adhesion of the a-CN_x selective layer. The deposition of a-CN_x selective layer retained the characteristic peaks of the PAN matrix in the composite membrane but with different intensity. Specifically, the PAN/a-CN_x 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-CN_x deposition increases the presence of nitrogen-containing functional groups on the membrane surface.



(a)



(b)



(c)

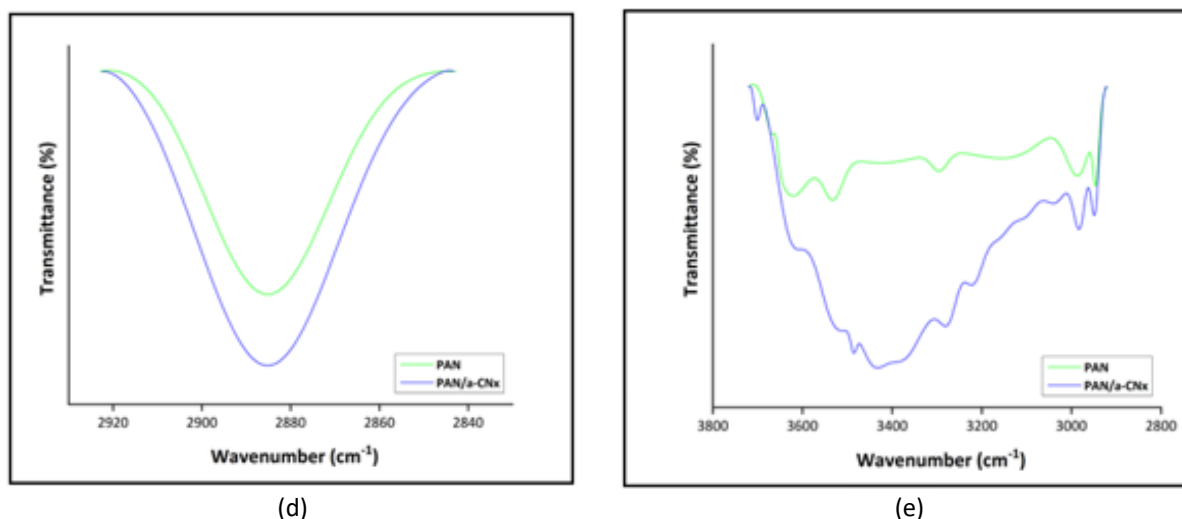


Fig. 5. FTIR Spectral showing: (a) Characteristic peaks of pristine PAN and PAN/a-CN_x membrane, (b) enhanced C=N Bond Intensity, (c) reduced C≡N bond intensity, (d) strengthened C–H stretching, and (e) increased N–H Bond intensity of the composite membrane

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-CN_x. The reduced intensity of the C≡N bond shown in Figure 5(c) influenced by the elevated temperature from the a-CN_x deposition further supports the breakdown and partial conversion of acrylonitrile groups into imino (C=NH) groups in the PAN/a-CN_x 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-CN_x, 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-CN_x due to the hydrogen bonding between N-H groups in the a-CN_x layer and the -OH groups in the PAN matrix. The hydrogen bonding facilitates the interaction between PAN and the a-CN_x selective layer and promotes the adhesion of a-CN_x to the PAN matrix [53]. The N-H and O-H groups play important roles in increasing surface activity and effectively interacting with CO₂ molecules which potentially increase CO₂ permeability [37]. The increase in nitrogen functionalities observed in the composite membrane modifies the membrane's surface chemistry and functionality for CO₂ 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 CO₂ molecules through Lewis interactions between CO₂ 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 CO₂ separation membranes. Future studies are required with focus on quantifying CO₂ 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-CN_x thin film onto PAN membrane using RF-PECVD technique. FESEM images showed a textured surface indicating a layer of a-CN_x on the PAN membrane. The integration of the a-CN_x thin film led to structural and chemical modifications in the PAN membrane. The Langmuir surface area increased (from 89.94 m²/g to 97.08

m²/g), suggesting the creation of more uniform adsorption sites. The BET analysis showed a slight reduction in the BET surface area (from 49.84 m²/g to 48.13 m²/g) due to partial pore coverage by the a-CN_x thin film. BJH analysis revealed an increase in cumulative mesopore volume (from 0.0994 cm³/g to 0.1073 cm³/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-CN_x into the PAN matrix increases nitrogen functionalities (e.g., N-H, C=N, and aromatic C-N stretching). This study demonstrates that a-CN_x deposition on PAN membranes introduces variety of nitrogen functionalities that are theoretically favorable for CO₂ separation. While promising, further research is necessary to validate these findings through direct CO₂ separation testing, including permeability and selectivity measurements. Future studies will address these aspects, completing the evaluation of a-CN_x/PAN membranes for CO₂ capture applications.

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