

Application and Progress of Praphitic Carbon Nitride in Proton Exchange Membranes

Ying Bi, Tianyuan Han, Ming Song, and Penghua Qian*

School of Materials and Chemical Engineering, Xuzhou University of Technology, Xuzhou, 221018, China

Abstract

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is a visible-responsive organic polymer semiconductor catalytic material, which is used in many fields due to its superior chemical and thermal stability, optical and electrical properties. In addition, its unique nanosheet structure and triangular nanopore are conducive to the construction of stable carrier transport channels, making it become a hot spot in the field of proton exchange membranes (PEMs). The amino ($-\text{NH}_2$) and imino ($-\text{NH}-$) groups on $g\text{-C}_3\text{N}_4$ can form acid-base pairs with sulfonic acid groups in the polymer matrix, promoting the dissociation of sulfonic acid groups and proton transfer through the Grotthuss mechanism. The interaction between $g\text{-C}_3\text{N}_4$ fillers and polymers can also improve the mechanical properties of composite membranes. Therefore, this paper reviews the preparation, modification, and application of $g\text{-C}_3\text{N}_4$ in PEMs, and evaluates the challenges and potential future research directions it faces in the field of PEMs.

Keywords

Graphitic Carbon Nitride; Covalent Modification; Non-covalent Modification; Proton Exchange Membranes.

1. Introduction

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is a visible-responsive organic polymer semiconductor catalytic material with a nanosheet structure [1]. In 1834, Berzelius and Liebig discovered $g\text{-C}_3\text{N}_4$ and carried out active exploration. After that, scientists began more research on carbon nitride and found that carbon nitride has two basic structures, as shown in Fig. 1. One is the C_6N_7 heptazine ring, and the other is the C_3N_3 triazine ring as the structural unit. The C and N atoms in each structural unit undergo sp^2 hybridization and are connected to each other by tertiary amines to form large π bonds similar to benzene rings, thus forming a highly delocalized conjugated system. The ends of each triazine ring or heptazine ring are connected by N atoms to form a planar extended structure [2,3]. Carbon nitride has a variety of allotropes, of which $g\text{-C}_3\text{N}_4$ with a graphene-like two-dimensional lamellar structure is the most stable. $g\text{-C}_3\text{N}_4$ is metal-free, non-toxic, abundant in the earth, easy to synthesize, and has good chemical and thermal stability. By theoretical calculation (DFT), it is proved that $g\text{-C}_3\text{N}_4$ composed of heptazine rings is more stable in chemical properties [4], and more research are also mainly focus on $g\text{-C}_3\text{N}_4$ composed of heptazine ring units.

The $g\text{-C}_3\text{N}_4$ has the characteristics of graphene-like lamellar structure, good stability and low cost, and has been widely used in many fields. In previous studies, the composite membrane prepared with $g\text{-C}_3\text{N}_4$ as a doping filler has shown good performance in all-vanadium flow batteries (VRFBs) and fuel cells. This is because the $-\text{NH}_2$ group in $g\text{-C}_3\text{N}_4$ can form acid-base pairs with the $-\text{SO}_3\text{H}$ groups in membrane matrix, improving proton conductivity. In addition, the Donnan effect of the $-\text{NH}_2$ group can effectively inhibit the permeation of active ions. Therefore, the Sulfonated poly (ether ether ketone)/ $g\text{-C}_3\text{N}_4$ (SPEEK/ $g\text{-C}_3\text{N}_4$) nanocomposite membrane prepared with $g\text{-C}_3\text{N}_4$ doping reduced

vanadium ion permeation while maintaining good stability. Compared with Nafion 117 membrane (CE: 90%, EE: 73.8%) and SPEEK membrane (CE: 89.9%, EE: 76.1%), the SPEEK/g-C₃N₄-1.5 membrane showed higher coulombic efficiency (CE: 97%) and energy efficiency (EE: 83.6%) at 30 mA/cm² [5]. However, the proton conductivity of the prepared composite membrane is still low, and the high content of g-C₃N₄ will cause the aggregation of fillers and poor compatibility with the matrix, resulting in a decrease in the mechanical properties and proton conductivity of the composite membrane. Therefore, it is necessary to modify g-C₃N₄ to improve its compatibility with the matrix and proton conductivity.

The surface modification of g-C₃N₄ is easy due to the presence of a large number of amino groups on its surface, the aromatic conjugated π bond skeleton and hydrogen bond inside, which provide sufficient possibilities for controlling its molecular structure and properties, enabling it to meet certain specific applications. Wang et al. [6] doped oxidized g-C₃N₄ nanosheets into sulfonated polyether ether ketone (SPEEK) based membranes and applied them to vanadium redox flow batteries (VRFBs), resulting in improved performance of the nanocomposite membranes. However, directly incorporating hydrophobic g-C₃N₄ into hydrophilic PEM always encounters incompatibility issues. Therefore, the hydrophilic functionalized g-C₃N₄ will offer better potential for PEM applications. The commonly used methods for surface modification of inorganic nanoparticles include covalent modification [7,8] and non covalent modification [9]. In the past few years, g-C₃N₄ and its modified derivatives have been prepared and applied to PEM with good results. It is necessary to systematically analyze the development of g-C₃N₄ nanomaterials. Therefore, in this paper, the preparation and modification methods of g-C₃N₄ nanomaterials are systematically reviewed, and their roles in the construction of proton transport channels and the promotion of proton selective transport were summarized and analyzed.

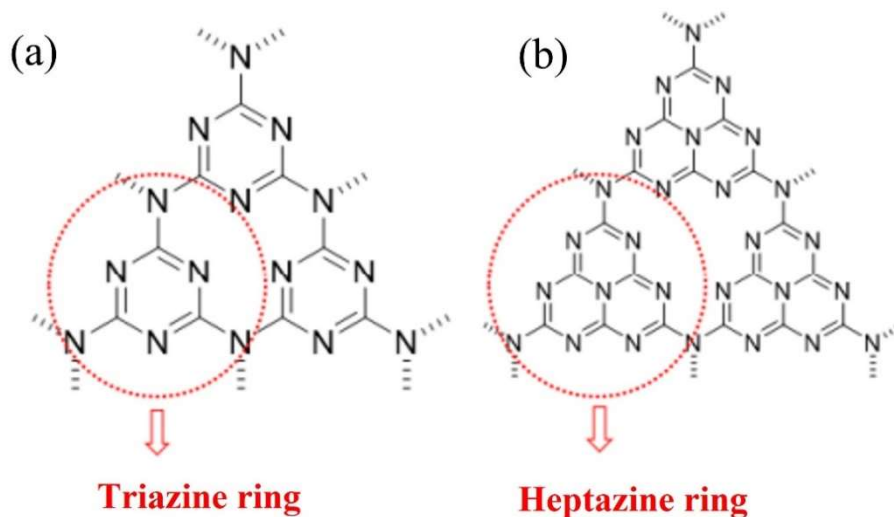


Fig. 1 Two structural units of g-C₃N₄ (a) triazine and (b) heptazine ring.

2. Preparation of g-C₃N₄

At present, the methods for preparing g-C₃N₄ include physical and chemical vapor deposition, solvent thermal method (hydrothermal method), and high-temperature thermal polymerization. Among them, the commonly used method is high-temperature thermal polymerization. The yield and properties of g-C₃N₄ prepared by different precursor systems are also different under the same high temperature roasting conditions. For example, Wan et al. [10] used urea as a raw material to prepare porous g-C₃N₄ at high temperature, but the carbon nitride prepared from urea has a small yield, which cannot meet the needs of mass production in industry. Therefore, dicyandiamide or melamine is now commonly used as a precursor to synthesize g-C₃N₄ at high temperature. Mo et al. [11] used melamine

as a precursor, loaded melamine into a covered crucible, and then placed it in a muffle furnace to directly synthesize g-C₃N₄ with high activity for visible light catalytic degradation of methyl orange by thermal condensation method at a heating rate of 20 °C min⁻¹. In the experiment, the degradation effect of g-C₃N₄ synthesized at different calcination temperatures on methyl orange was also compared, and it was found that the photocatalytic activity was highest when the calcination temperature reached 550 °C. As shown in Fig. 2, precursors commonly used for the synthesis of g-C₃N₄ include monocyan diamide, urea, thiourea, dicyandiamide [12], etc. They found that g-C₃N₄ was completely formed at a calcination temperature of 500 °C, whereas at 450 °C, the specimen displayed an X-ray diffraction (XRD) diffractogram assigned to melem-like derivatives. On the other hand, the increase in the calcination temperature (higher than 500 °C) led to the destruction of the g-C₃N₄ morphology. Niu et al. [5] dried 5 g of melamine at 60 °C for 12 hours, then placed it in a crucible and placed it in a box furnace. The mixture was heated from room temperature to 550 °C at a rate of 4 °C/min in an air atmosphere, and kept at 550 °C for 3 hours. After cooling to room temperature, the resulting product was ground and added to a certain amount of deionized water. After ultrasonic treatment for 5 hours, the resulting mixed solution was centrifuged and separated. The separated product was repeatedly washed with anhydrous ethanol, Dry at 60 °C for 24 hours to obtain g-C₃N₄ nanosheets. This is the most commonly used method for preparing g-C₃N₄.

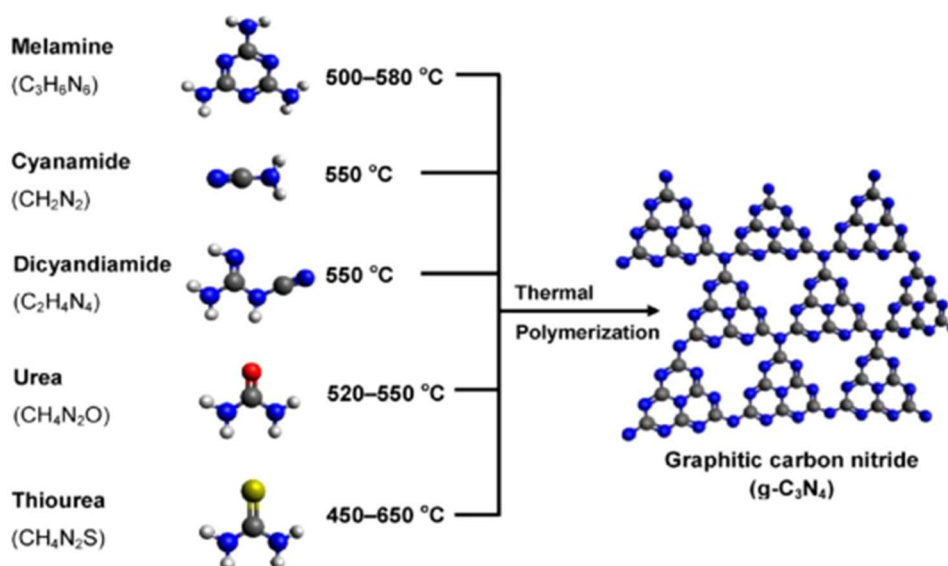


Fig. 2 Illustrative representation of g-C₃N₄ synthesis using thermal polymerization of C and N containing precursors.

3. Modification of g-C₃N₄

The g-C₃N₄ has superior electronic structure, good thermal and chemical stability performance, and is applied in various aspects of life. However, with the increasing research on g-C₃N₄, its disadvantages such as narrow visible light response range, small specific surface area, low carrier separation rate, difficult recovery and reuse, and low reuse rate have become apparent. Therefore, researchers have improved its performance through various modification methods. Many scholars have studied how to improve the various properties of g-C₃N₄. The methods of g-C₃N₄ modification generally include nano exfoliation, covalent modification, and non-covalent modification.

3.1 Nano Exfoliation

Nano exfoliation is the process of preparing bulk g-C₃N₄ into nano thin layers or even single-layer structures through exfoliation, similar to the preparation of graphene by exfoliating graphite. The commonly used methods for preparing g-C₃N₄ nano thin films include solvent exfoliation and thermal exfoliation. Solvent exfoliation refers to the process of exfoliating in solvents such as water, methanol,

and isopropanol. Yang et al. [13] performed liquid-phase exfoliation of bulk $g\text{-C}_3\text{N}_4$ in isopropanol, resulting in a $g\text{-C}_3\text{N}_4$ nano thin layer with a thickness of only 2 nm. And thermal exfoliation is the thermal oxidation and corrosion treatment of $g\text{-C}_3\text{N}_4$ in air, which can break the weak van der Waals forces between the layers of bulk $g\text{-C}_3\text{N}_4$, thereby obtaining nanoscale nano thin layers with larger specific surface area, smaller size, and enhanced redox ability [14]. However, hot stripping technology has the problem of relatively low product yield and is not suitable for large-scale production.

3.2 Covalent Modification

Introducing new functional groups into the framework of $g\text{-C}_3\text{N}_4$ is considered to be an effective way to modify the properties of $g\text{-C}_3\text{N}_4$. Similar to most carbon-based materials (such as carbon nanotubes, graphene, etc.), the functionalization of $g\text{-C}_3\text{N}_4$ is an effective way to adjust its surface chemistry by introducing a large number of functional groups on its surface. At present, the main chemical functionalization strategies include covalent methods and non-covalent methods. Covalent modification is the introduction of new functional groups through the formation of stable covalent bonds between $g\text{-C}_3\text{N}_4$ functional groups and chemical modifiers, such as oxidation, amidation, sulfonation, polymer grafting, etc. Wang et al. [15] briefly described the modification of carbon nitride using oxidation/carboxylation methods, which involves introducing covalent functional groups such as carboxyl and hydroxyl groups through oxidation reactions or doping oxygen into the network of $g\text{-C}_3\text{N}_4$. There are primary and secondary amine groups at the end edge of $g\text{-C}_3\text{N}_4$, which can be modified by acylation reaction with chemical modifiers. For example, Guo et al. [16] reported a simple strategy to functionalize the $g\text{-C}_3\text{N}_4$ framework through acylation reaction between the free -NH_2 group of $g\text{-C}_3\text{N}_4$ and 1,2,4,5-phenylenedicarboxylic anhydride. In another work, Zhao et al. [17] reported that pre carboxylated carbon nanotubes (CNTs) were bound to $g\text{-C}_3\text{N}_4$ through acylation reaction in the presence of formic acid (Fig. 3a). Furthermore, Pramoda et al. [18] prepared nanocomposites by covalently combining $g\text{-C}_3\text{N}_4$ with MoS_2 or NRGO nanosheets (Fig. 3b). The preparation process was based on the amide covalent crosslinking strategy, and a layer by layer assembly form was prepared.

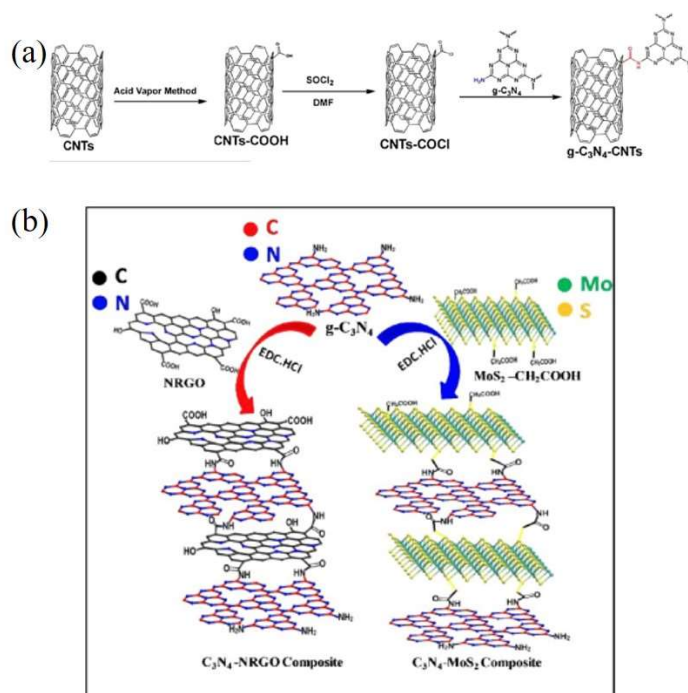


Fig. 3 Synthetic strategy for $g\text{-C}_3\text{N}_4$ -CNT (a) and covalently bonded $g\text{-C}_3\text{N}_4$ -NRGO or $g\text{-C}_3\text{N}_4$ - MoS_2 nanocomposites (b).

In addition, the surface of g-C₃N₄ can be functionalized with sulfonic acid and phosphoric acid groups. This modification is a powerful strategy to extend its application to other fields. Chhabra et al. [19] prepared g-C₃N₄ material by thermal polymerization of dicyanamide at 550 °C, and the obtained material was sulfonated with chlorosulfonic acid in dichloromethane medium (FIG. 35e) to prepare sulfonated g-C₃N₄. In another report, Lu et al. [20] synthesized g-C₃N₄ by thermal polymerization of a mixture of melamine and NH₄Cl at 550 °C. NH₄Cl was used as blowing agent to decompose into volatile gases such as ammonia and hydrogen chloride to disturb the polymerization process. Therefore, the obtained product has more terminal amino groups, which are reacted with 1, 4-butanolactone to obtain sulfonated g-C₃N₄ nanosheets with flexible butanolactone grafted.

By covalently modifying g-C₃N₄ with polymers, monomers can be directly polymerized in situ from the surface of g-C₃N₄, allowing for controlled polymerization and propagation on the surface of g-C₃N₄. Alternatively, the active end groups of the pre-synthesized polymer can be reacted with the active functional groups on the surface of g-C₃N₄. For example, Jiang et al. [21] reported the in-situ polymerization of aniline on g-C₃N₄ nanolayers using ammonium persulfate (APS) as an initiator to produce polyaniline fiber (PANI) intercalated g-C₃N₄ nanolayers. This strategy can prevent the aggregation/restacking of g-C₃N₄ nanosheets. In addition, g-C₃N₄ was functionalized by olefin molecules through grafting method [22], while retaining its inherent properties and changing its affinity to different solvents. For example, the hydrophilicity of functionalized g-C₃N₄ is enhanced by grafting 3-allyloxy-2-hydroxy-1-propanesulfonic acid sodium salt (AHPA) onto the surface of g-C₃N₄.

3.3 Non-covalent Modification

Non-covalent modification mainly involves physical bonding and intermolecular interactions, such as van der Waals interactions, electrostatic interactions, π - π interactions, etc. Non-covalent modification is formed by the interaction between delocalized π bonds (hybridized with π bond sp^2) on the carbon wall and the hexagonal ring structure or electrostatic attraction of functional molecules. The non-covalent interaction between g-C₃N₄ and organic/inorganic materials may be weak, leading to poor sustained stability. However, using non-covalent synthesis strategies can combine the characteristics of each molecule while preserving the inherent properties of both parts. Lv and collaborators proposed the preparation of g-C₃N₄ nanosheets modified with 1-pyrenebutyrate acid (Py-COOH) through non-covalent modification through π - π stacking interactions. This process is based on the delocalized π -electron conjugation of Py-COOH, which can be bound to the aromatic skeleton of g-C₃N₄ through π - π interactions. The XRD results confirmed that due to the π - π interaction between Py-COOH and g-C₃N₄ nanosheets, the (002) diffraction peak of graphite nitride carbon slightly shifted from 27.35° to 27.63° [23]. Wu et al. prepared a series of membrane composite based graphene oxide (GO) and g-C₃N₄ for nanofiltration, and used glycine as a molecular linker to enhance their interaction. The experimental and characterization results show that the difference of ζ potential between GO and g-C₃N₄ indicates that their dispersions are negatively and positively charged, respectively. Therefore, the interaction between graphene oxide and g-C₃N₄ in the composite film is mainly electrostatic force and π - π stacking interaction [24].

4. Application of g-C₃N₄ in Proton Exchange Membranes

Doping two-dimensional nanomaterials can regulate the microstructure of proton exchange membranes, resulting in better continuity of ion clusters and the formation of continuous proton transport channels. The doped nanofillers can also serve as barriers, effectively reducing the penetration of active substances. And graphite like carbon nitride is a two-dimensional nanomaterial that meets the requirements. The amino (-NH₂) and imine (-NH-) groups on g-C₃N₄ can form acid-base pairs with sulfonic acid groups in the polymer matrix, promoting the dissociation of sulfonic acid groups and improving the Grotthuss transfer of protons. Zhang et al. [25] prepared a composite proton exchange membrane using g-C₃N₄ nanosheets as nanofillers and sulfonated polysulfone (SPSF) as membrane matrix through a simple solution casting method. Due to the formation of acid-base

pairs between the $-NH_2$ groups of $g-C_3N_4$ and the $-SO_3H$ groups of SPSF, energy efficiency is improved. Based on the Donnan effect and acid-base interaction, placing $g-C_3N_4$ nanosheets into the SPSF matrix (SPSF/ $g-C_3N_4$) can effectively reduce ion permeability. The chemical stability and VRFB performance of the SPSF/ $g-C_3N_4$ composite membrane have also been significantly improved. The interaction between $g-C_3N_4$ nanolayers is strong, easy to agglomerate, and has poor compatibility with polymers. Its dispersion performance in polymer matrix is poor, which is not conducive to proton conduction in composite membranes. Lu et al. [26] prepared fluorinated poly (aryl ether) copolymer (SPFAE) nanocomposite membranes using two-dimensional sulfonated $g-C_3N_4$ (SCN) nanosheets as nanofillers (Fig. 4a). In this composite system, the acid-base pair effect between SCN and SPFAE promotes the dissociation of sulfonic groups and the formation of hydrogen bonding networks. Meanwhile, the ideal interface interaction acts as a "zipper", promoting the formation of nanophase separation morphology and significantly constructing remote ion channels at the interface (Fig. 4b and d). Therefore, the obtained nanocomposite membrane showed significant improvement in proton conductivity. When the SCN content was 0.5 wt%, the proton conductivity of SPFAE/SCN-0.5 membrane at 90 °C was 204 mS cm^{-1} , which is 26% higher than that of the pristine membrane. Song [27] successfully prepared carbon nitride-phosphotungstic acid (C_3N_4 -HPW) nanofiller by hydrothermal method, which fixed the HPW while improving the proton conductivity of the SPEEK base composite membranes. When the content of C_3N_4 -HPW nanofiller was 10 wt%, the vanadium resistance of the prepared composite membrane was basically the same as that of pristine SPEEK, but its impedance was greatly reduced. In the experiment of single cell in VRFB, excellent battery performance was demonstrated, that is, when the current density was 120 mA/ cm^2 , the coulombic efficiency of the composite membrane reached 98.4%, and the energy efficiency reached 87.4%, far higher than the pure SPEEK energy efficiency (84.6%). These all reflect the widespread application of $g-C_3N_4$ in the field of proton exchange membranes.

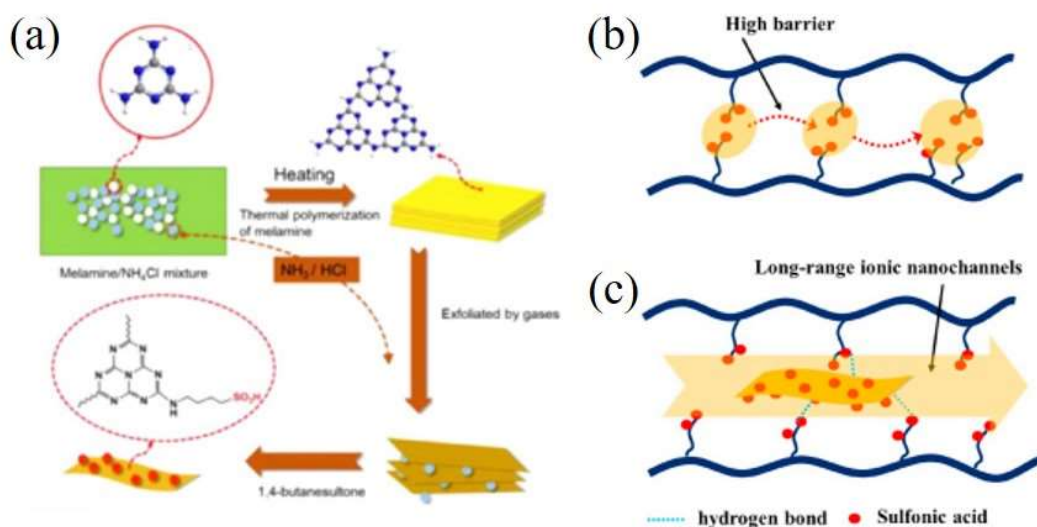


Fig. 4 Schematic illustration of CN and SCN nanosheets (a) and the proton transport process of (b) SPFAE and (c) SPFAE/SCN nanocomposite membrane.

The modified $g-C_3N_4$ is applied to SPEEK for the preparation of PEMs to expand its application field [28]. The $g-C_3N_4$ was modified with polydopamine (PDA) and SDBS (with hydrophobic alkyl backbone and hydrophilic sulfonic acid groups). The modified $g-C_3N_4$ with polydopamine can improve the hydrophilicity of $g-C_3N_4$. The structure of pyroquinol and amino functional groups in PDA can form covalent and non-covalent interactions with the surface of $g-C_3N_4$. The hydroxyl groups in $g-C_3N_4$ modified by PDA interacted with the hydrophilic groups of SPEEK, which strengthened the interface interaction and improved the dispersion of the PEM. The SDBS was

adsorbed between g-C₃N₄ nanosheets, thickened the nanosheets, interacted with sulfonic acid groups on the side-chains of SPEEK, improving interface compatibility, and the hydrophobic part of SDBS interacted with the main-chain of SPEEK, which can also improved the dispersion of nanofillers and the interaction between interfaces, facilitating proton conduction. As the content of g-C₃N₄ in SPEEK/g-C₃N₄ increases, the conductivity of the proton exchange membrane gradually increases, and reached maximum value at a content of 0.5 wt%. When the amount of nanofiller was small, the low content of g-C₃N₄ has better dispersion in the SPEEK matrix, and the two-dimensional nanosheet structure will reconstruct the SPEEK structure. The connectivity of ion clusters is better, which is conducive to proton conduction. Meanwhile, acid-base interactions can effectively promoted proton conduction through the Vehicular mechanism, thereby forming a more effective proton transition transport pathway and improving proton conductivity. In addition, -NH₂ and -NH- on g-C₃N₄ can induced the dissociation of sulfonate groups, creating a proton transport website, increasing ion cluster density and proton mobility, which can improve the proton conductivity of the membrane. When the content of g-C₃N₄ exceeded 1 wt%, the proton conductivity decreased. This is because excessive g-C₃N₄ nanosheets can disrupt acid-base balance and reduce the effective proton transport sites.

5. Summary

This paper focuses on g-C₃N₄ and briefly introduces the development of g-C₃N₄, common preparation methods, and modification methods such as nano-exfoliation, covalent modification, and non-covalent modification. Due to its superior performance, a low-cost and high-performance modified g-C₃N₄ can be obtained after modification. Its layered structure and triangular nanopores provide stable carrier transport channels, accelerating carrier transport efficiency. The nanopore structure can also increase the adsorption capacity of acid/base, further improving proton conductivity and enhancing the performance of composite proton exchange membranes. This article will provide new ideas for the modification research of g-C₃N₄ and its application in proton exchange membranes, laying the foundation for its large-scale application.

Acknowledgments

This work was supported by the Jiangsu Province 2023 College Student Innovation and Entrepreneurship Training Program Project [202311998048Y].

References

- [1] Xiao K., Kumru B., Chen L., et al. A biomimetic nanofluidic diode based on surface-modified polymeric carbon nitride nanotubes. *Beilstein Journal of Nanotechnology*, Vol. 10 (2019) No. 1, p. 1316-1323.
- [2] Xiao, K.; Tu, B.; Chen, L.; et al. Photo-driven ion transport for A photodetector based on an asymmetric carbon nitride nanotube membrane. *Angewandte Chemie*. Vol. 58 (2019), p. 12574–12579.
- [3] Chen, Y.; Ding, F.; Khaing, A.; et al. Acetic Acid Assisted Supramolecular Assembly Synthesis of Porous g-C₃N₄ Hexagonal Prism with Excellent Photocatalytic Activity. *Applied Surface Science*. Vol. 479 (2019), p. 757–764.
- [4] Zheng Y., Lin L. H., Wang B., et al. Graphitic carbon nitride polymers toward sustainable Photoredox catalysis. *Angewandte Chemie-International Edition*, Vol. 54 (2015) No. 44, p. 12868-12884.
- [5] Niu R., Kong L., Zheng L., et al. Novel graphitic carbon nitride nanosheets/sulfonated poly(ether ether ketone) acid-base hybrid membrane for vanadium redox flow battery. *Journal of Membrane Science*, Vol. 525 (2017), p. 220–228.
- [6] Gang M., He G., Li Z., et al. Graphitic carbon nitride nanosheets/sulfonated poly(ether ether ketone) nanocomposite membrane for direct methanol fuel cell application. *Journal of Membrane Science*, Vol. 507 (2016), p. 1-11.
- [7] Jiang Z-J, Jiang Z., Tian X., et al. Sulfonated holey graphene oxide (SHGO) filled sulfonated poly(ether ether ketone) membrane: the role of holes in the SHGO in improving its performance as proton exchange

- membrane for direct methanol fuel cells [J]. *ACS Applied Materials & Interfaces*, Vol. 9 (2017) No. 23, p. 20046-20056.
- [8] Li J., Zhang B., Wu H., et al. Incorporating imidazolium-functionalized graphene oxide into imidazolium-functionalized poly(ether ether ketone) for enhanced hydroxide conductivity [J]. *Journal of Membrane Science*, Vol. 565 (2018), p. 233-240.
- [9] Lu S., Xu X., Zhang J., et al. A self-anchored phosphotungstic acid hybrid proton exchange membrane achieved via one-step synthesis. *Advanced Energy Materials*, Vol. 4 (2014) No. 17, p. 1400842.
- [10] Wan S., Ou M., Zhong Q., et al. Haloid acid induced carbon nitride semi-conductors for enhanced photocatalytic H₂ evolution and reduction of CO₂ under visible light, *Carbon*. Vol. 138 (2018), p. 465–474.
- [11] Mo Z., Xu H., Chen Z., et al. Self-assembled synthesis of defect-engineered graphitic carbon nitride nanotubes for efficient conversion of solar energy. *Applied Catalysis B: Environmental*. Vol. 225 (2018) No. 154-161.
- [12] Ong W-J, Tan L-L, Yun H., et al. Graphitic carbon nitride (g-C₃N₄)-based photocatalysts for artificial photo-synthesis and environmental remediation: are we a step closer to achieving sustainability? *Chemical Reviews*. Vol. 116 (2016), p. 7159–7329.
- [13] Yang S, Gong Y, Zhang J, et al. Exfoliated graphitic carbon nitride nanosheets as efficient catalysts for hydrogen evolution under visible light. *Advanced Materials*. Vol. 25 (2013) No. 17, p. 2452-2456.
- [14] Pawar R. C., Kang S., Han H. K., et al. In situ reduction and exfoliation of g- C₃N₄ nanosheets with copious active sites via a thermal approach for effective water splitting. *Catalysis Science & Technology*. Vol. 9 (2019), p. 1004-1012.
- [15] Wang, B., Zhong, X., Chai, Y., et al. Ultrasensitive electrochemiluminescence biosensor for organophosphate pesticides detection based on carboxylated graphitic carbon nitride-poly-(ethylenimine) and acetylcholinesterase. *Electrochim. Acta*. Vol. 224 (2017), p. 194–200.
- [16] Guo, Y., Chu, S., Yan, S., et al. Developing a polymeric semiconductor photocatalyst with visible light response. *Chemical Communication*. Vol. 46 (2010), p. 7325–7327.
- [17] Zhao, S., Guo, T., Li, X., et al. Carbon nanotubes covalent combined with graphitic carbon nitride for photocatalytic hydrogen peroxide production under visible light. *Applied Catalysis B: Environmental*. Vol. 224 (2018), p. 725–732.
- [18] Pramoda, K., Gupta, U., Chhetri, M., et al. Nanocomposites of C₃N₄ with layers of MoS₂ and nitrogenated RGO, obtained by covalent cross-linking: synthesis, characterization, and her activity. *ACS Applied Materials & Interfaces*. Vol. 9 (2017), p. 10664–10672.
- [19] Chhabra, T., Bahuguna, A., Dhankhar, S. S., et al. Sulfonated graphitic carbon nitride as a highly selective and efficient heterogeneous catalyst for the conversion of biomass-derived saccharides to 5-hydroxymethylfurfural in green solvents. *Green Chemistry*. Vol. 21 (2019), p. 6012–6026.
- [20] Lu, Y., Liu, Y., Li, N., et al. Sulfonated graphitic carbon nitride nanosheets as proton conductor for constructing long-range ionic channels proton exchange membrane. *Journal of Membrane Science*. Vol. 601 (2020), p. 117908.
- [21] Jiang, W., Luo, W., Zong, R., et al. Polyaniline/carbon nitride nanosheets composite hydrogel: a separation-free and high-efficient photocatalyst with 3d hierarchical structure. *Small* Vol. 12 (2016), p. 4370–4378.
- [22] Kumru, B., Antonietti, M., Schmidt, B. V. K. J. Enhanced dispersibility of graphitic carbon nitride particles in aqueous and organic media via a one-pot grafting approach. *Langmuir*. Vol. 33 (2017), p. 9897–9906.
- [23] Lv, Z., Cheng, X., Liu, B., et al. Py-COOH modified g- C₃N₄ nanosheets with enhanced visible-light photo-catalytic H₂ production. *Applied Surface Science*. Vol. 504 (2020), p. 144486.
- [24] Wu, Z., Gao, L., Wang, J., et al. Preparation of glycine mediated graphene oxide/g- C₃N₄ lamellar membranes for nano-filtration. *Journal of Membrane Science*. Vol. 601 (2020), p. 117948.
- [25] Liu, B., Zhang, Y. Jiang, Y., et al. High performance acid-base composite membranes from sulfonated polysulfone containing graphitic carbon nitride nanosheets for vanadium redox flow battery, *Journal of Membrane Science*. Vol. 591 (2019), p. 117332.

- [26] Lu, Y., Liu, Y., Li, N., et al. Sulfonated graphitic carbon nitride nanosheets as proton conductor for constructing long-range ionic channels proton exchange membrane, *Journal of Membrane Science*. Vol. 601 (2020), p. 117908.
- [27] Song, Hao: Preparation and properties of proton exchange membranes for vanadium redox flow batteries (Master of Engineering, North China Electric Power University, China 2021).
- [28] Jia Huina: Preparation and properties of proton exchange membranes based on sulfonated poly(ether ether ketone) and its nanocomposites (Master of Engineering, North China Electric Power University, China 2017).