Research Progress in the Polymeric Nitrogen with High Energy Density

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Polymeric nitrogen is a potential high-energy-density material with the advantages of high energy density, easy availability of raw materials, and non-pollution. The design and synthesis of polymeric nitrogen are important in the research field of energetic materials. The cubic gauche nitrogen was successfully synthesized at high pressure in the diamond anvil cell, which stimulated the theoretical and experimental investigations. To date, several hundred kinds of polymeric nitrogen have been reported. This review introduces the progressive development of polymeric nitrogen with high energy density, the challenges faced by the synthesized polymeric nitrogen under high-pressure, and the importance to improve the stability of polymeric nitrogen at ambient pressure. Furthermore, alternative methods for synthesizing polymeric nitrogen under moderate conditions are also presented. In this field, more efforts are needed to develop strategies for stabilizing more polymeric nitrogen to ambient conditions, especially the stability of free surfaces.

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1. Introduction. High energy density materials (HEDMs) have significant applications, particularly as explosives and rocket propellants. One of the key objectives in studying HEDMs is to design and synthesize new materials with higher energy density and higher stability. Among the new generation of HEDMs, polymeric nitrogen has garnered considerable attention due to its significantly higher energy density compared to traditional energetic materials like TNT, RDX, and HMX. In polymeric nitrogen, nitrogen atoms are connected through N-N single bonds (160 kJ/mol) and N=N double bonds (418 kJ/mol). Consequently, upon decomposition into nitrogen gas, which features N≡N triple bonds (954 kJ/mol), the significant difference in bond energies contributes to a high energy density of polymeric nitrogen. Additionally, the decomposition product is nitrogen gas, making it an environmentally friendly energetic material. Nevertheless, the synthesis and practical application of polymeric nitrogen present considerable challenges that require ongoing research and innovation.

Nitrogen gas is the most abundant in the atmosphere, since the N≡N triple bond is one of the strongest chemical bonds, resulting in its high stability and low reactivity with other substances. Therefore, breaking triple bonds to synthesize polymeric nitrogen has long been a significant challenge. In 1890, the linear azide anion (N_3^-) characterized by double bonds was synthesized,[1] which is the first identified form of polynitrogen species. Since that time, extensive research has been dedicated to the discovery and synthesis of novel polymeric nitrogen forms. Noteworthy advancements include the synthesis of a V-shaped polynitrogen cation (N_5^+) within the compound N_5AsF_6 in 1999,[2] followed by the creation of a cyclo-N_5^- ring within bulk materials in 2017.[3,4] These developments signify significant progress in the field of nitrogen-based energetic materials. Each of these polynitrogen species contains a greater number of nitrogen atoms than the diatomic N_2 molecule, resulting in bonding configurations that differ from the N≡N triple bond characteristic of N_2. Furthermore, these species are synthesized through chemical methods and exhibit stability under ambient conditions. Despite more than a century of research into polymeric nitrogen, the synthesized species remain limited, underscoring the inherent difficulties associated with the creation of such polymeric nitrogen by chemical methods. In light of these difficulties, other techniques, including high-pressure synthesis and plasma-enhanced chemical vapor deposition (PECVD), have been developed to facilitate the synthesis of the polymeric nitrogen. These approaches utilize mechanical pressure, temperature effects, and plasma treatment to promote the dissociation of nitrogen's N≡N triple bonds and the subsequent recombination of nitrogen atoms into polymeric configurations.

In the past few decades, theoretical simulations and high-pressure experiments have jointly promoted the synthesis of various polymeric nitrogen forms. In 1992, cubic gauche nitrogen (cg-N) with the network of N-N single bonds was first predicted to be stable under high pressure,[5] followed by the discovery of other nitrogen allotropes like layered polymeric nitrogen (LP-N)[6] and hexagonal layered polymeric nitrogen (HLP-N).[7] Similarly, nitrogen-rich compounds featuring cyclic N_5 and N_6

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have been proposed.[8–16] In 2004, the advancements in high-pressure technology led to the successful synthesis of three-dimensional cg-N,[17] the first pure polymeric nitrogen. After this breakthrough, various forms of polymeric nitrogen were developed in pure nitrogen and nitrogen-rich compounds, including polynitrogen ions (N_4,[18] N_5,[19–21] N_6,[22–24] N-chains,[18,25–27] layered nitrogen,[28–34] and three-dimensional (3D) networks.[17] These examples have greatly increased confidence in synthesizing nitrogen-based HEDMs. However, with the exception of LiN_5,[19] the polymeric nitrogen synthesized at high pressure cannot be quenched to the ambient pressure. Thus, practical applications remain a challenge due to several key issues: (1) the low proportion of polymeric nitrogen within the synthesized compounds, resulting in lower energy density, and (2) the instability of polymeric nitrogen under ambient conditions. Illustrating decomposition mechanism of polymeric nitrogen and exploring method to enhance their stability are essential. For instance, insights into cg-N decomposition facilitate research on its synthesis under ambient conditions via the PECVD method. Therefore, ongoing research about polymeric nitrogen is vital for its design and synthesis aimed at improving performance in practical applications.

In this review, we present the significant research advancements in polymeric nitrogen, drawing insights from both theoretical predictions and experimental investigations. The current state of research on pure nitrogen, metal-nitrogen, and nonmetal-nitrogen systems will be examined, with a focus on analyzing the effects of various elements about the formation of polymeric nitrogen. Furthermore, the decomposition mechanisms and strategies for improving its stability are discussed, and recently developed methods for synthesizing polymeric nitrogen at moderate conditions are also presented.

2. Methods.

2.1. Theoretical Methods. Pressure causes a reduction in the interatomic distances, accompanied by microscopic changes such as variations in interatomic interactions and electronic configurations. This phenomenon is illustrated by phase transitions at high pressure, where structural forms differ from those found at ambient pressure. The determination of structure is fundamental for further investigations, which promotes the development of crystal structure prediction. Although the difficulty of identifying the ground states arising from a complex energy landscape filled with numerous local minima, crystal structure prediction has become increasingly important in the quest to discover new materials. Structures can be predicted by various methods, such as random search,[35] minima hopping,[36] genetic algorithm,[37,38] and particle swarm optimization.[39] Among these methods, computational efficiency is hindered by reliance on first-principles calculations, especially for complex and larger systems. Machine learning and large language models can effectively address this issue, where additional factors can be incorporated. For example, the Hubbard U correction for transition metal-nitrogen compounds with strongly correlated interactions can be quickly determined using machine learning.[40]

The performance of energetic materials is crucial for their applications, which is evaluated by parameters such as energy density (E_d), detonation velocity (V_d), and detonation pressure (P_d). Theoretically, the energy density is derived by the formation energy, which represents the energy difference of the reactants and the products. Additionally, detonation velocity and detonation pressure of polymeric nitrogen are generally estimated using the Kamlet–Jacobs (K–J) empirical formula,[41] which is originally developed for C-H-O-N systems. Actually, new method for simulating the explosive performance of polymeric nitrogen is also needed.

2.2. Experimental Methods. Conducting high-pressure in-situ research on polymeric nitrogen or nitrogen-rich materials is extremely challenging due to the demanding conditions required, including high-pressure and high-temperatures, as well as the environmental factors within the sample chamber, the reaction pathway, and the reaction zone. Diamond anvil cells create the high-pressure environment, while an insulating layer that does not react with the sample is necessary to achieve high temperatures.[42] Auxiliary light-absorbing substances may be needed for insulating samples that do not couple well with lasers. Different reaction pathways can affect the phase transition kinetics, leading to the synthesis of materials with varying structures. Thus, significant difficulties remain in experimental synthesis, and preparing nitrogen-rich materials at lower pressures requires collaboration among physics, chemistry, and materials science.

PECVD technology is a plasma-assisted chemical vapor deposition method widely used for preparing materials and thin films. In this process, the desired gaseous precursors like nitrogen and argon are introduced into the reaction chamber under vacuum. A high-frequency electric field generated plasma, causing charged particles collide with precursor gas molecules, leading to gas decomposition and production of numerous positive and negative ions, free radicals, and reactive atoms. As long as the temperature in the reaction chamber is properly controlled, the reaction gases will react with the surface of the raw material, facilitating material synthesis. This method has been successfully used to synthesize the polymeric nitrogen.[43]

The DAC approach requires high pressures to enable the formation of unique phases, but is limited by small reaction volumes and phase destabilization at ambient conditions. In contrast, PECVD, operating at moderate vacuum with plasma activation, enables large-area deposition and can realize surface modification more easily. Furthermore, both approaches face challenges with mixed-phases formation due to incomplete precursors dissociation and complex reaction dynamics.

3. Research Progress.

3.1. The Theoretical Research Progress.

3.1.1. The Pure Nitrogen System. Theoretically, monatomic nitrogen is proposed as early as 1985,[44] fol-

lowing by the prediction of cg-N.[5] These findings indicate that high pressure can break the strong triple bond in the N_2 molecule. Significant advancements in computational methods have greatly improved the ability to predict the structures of pure nitrogen under high pressure. The crystal structures of predicted typical polymeric nitrogen are shown in Fig. 1. For nitrogen, a diverse array of polymeric nitrogen forms has been identified, including armchair chain,[5] zigzag chain,[45] layered structures,[5–7] and 3D networks,[5] where the latter two types of polymeric nitrogen have been synthesized at high pressure. Additionally, special forms have been reported, such as molecular crystal with N_8[46] at ambient pressure and metallic salts with $(N_2^{\delta+}N_5^{\delta-})_2$[47] at ultra-high pressure. Analysis of these structures indicate a preference of chain-like structures at lower pressure, followed by cg-N, which transforms into layered polymeric nitrogen, then evolve into cagelike polymeric nitrogen,[7] and finally into metallic salts.

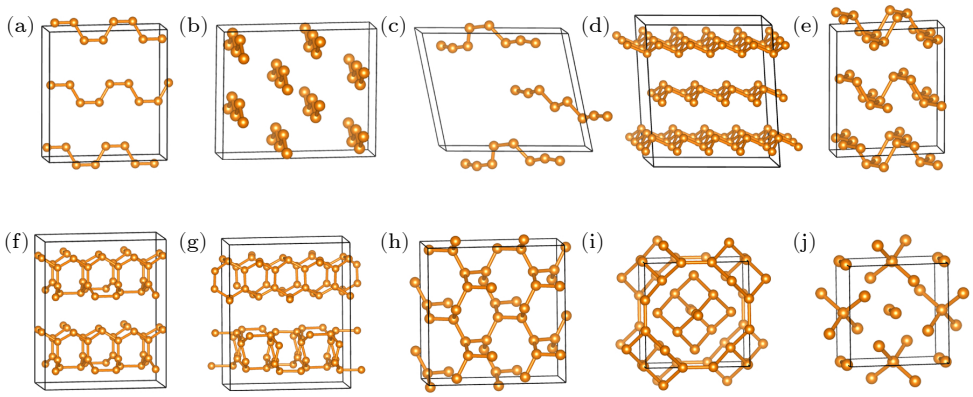

Fig. 1. The crystal structures of predicted typical polymeric nitrogen. (a) The crystal structure with armchair N-chains, (b) the crystal structure with zigzag N-chains, (c) the crystal structure with N_8 molecules, (d) A7 structure, (e) BP-N, (f) LP-N, (g) HLP-N, (h) cg-N, (i) the cagelike nitrogen and (j) the metallic nitrogen salt.

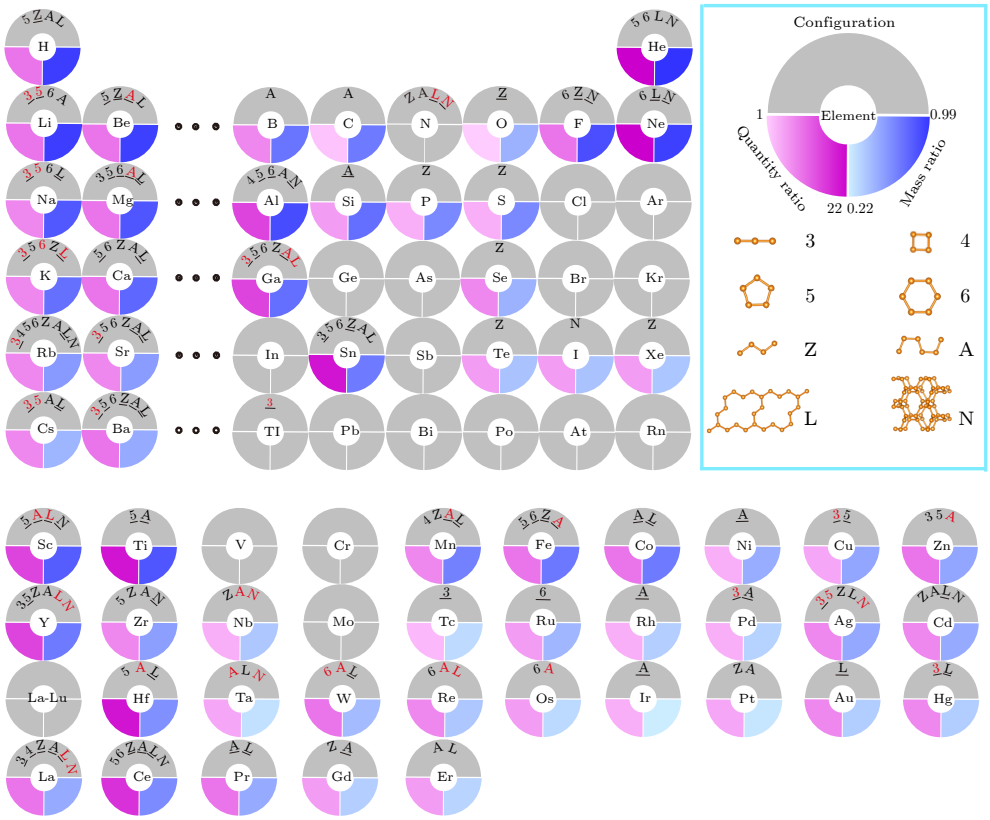

Fig. 2. The information of polymeric nitrogen in binary nitrogen-based compounds. The circles are divided into three parts, which represent configurations of polymeric nitrogen, quantity ratio of nitrogen and mass ratio of nitrogen. Typical configurations of polymeric nitrogen are listed in the legend, where numbers represent N_3 azide, N_4 unit, N_5 ring, and N_6 ring, while Z, A, L, and N denote zigzag chain, armchair chain, layered nitrogen and 3D networks. Red labels in the gray region indicate experimentally synthesized polymeric nitrogen, while underlined characters denote polymeric nitrogen predicted to be dynamically stable at 0 GPa. The magenta region represents the maximum quantity ratio of nitrogen, and the blue region represents the maximum mass ratio of nitrogen in binary nitrogen-based compounds.

In addition, there exists a unique category of elements known as noble gases. Due to the fully occupied electron configurations in the outermost shells, these gases generally exhibit an inability to participate in chemical bonding with other elements at ambient pressure. Nonetheless, under high pressure, noble gases are capable of forming compounds with nitrogen.[48–51] It is noteworthy that the charge transfer between noble gases and nitrogen atoms is minimal, indicating weak interaction between them. This characteristic allows a strategic approach to removing noble gases while maintaining polymeric nitrogen. In Fig. 2, as the best of our knowledges, the information of predicted and synthesized polymeric nitrogen are summarized.[5,7–27,29,30,32–34,44–196] We can find that the polymeric nitrogen,[48–50,113,114] such as N_5, N_6, layered structures, and 3D networks, can be obtained by introducing noble gases, which contains nitrogen rings different from the types reported in pure nitrogen. Furthermore, this may be possible for the elements with similar electronegativity to nitrogen. These findings suggest a potential pathway for synthesizing a novel type of polymeric nitrogen, which can be preserved even upon the removal of the noble gases.

3.1.2. The Metal-Nitrogen System. In addition to the behavior of pure nitrogen under high pressure, alkali metal azides represent one of the earliest classes of nitrogen-rich compounds to garner interest. Since the N=N double bonds in the azide ion are weaker than the N≡N triple bond in pure nitrogen, they are believed to polymerize more easily than nitrogen at lower pressures. For instance, in alkali metal azides, azide ions evolve into N_6 rings at pressure ranging from 30 to 60 GPa,[8,10,11,13,15,16,117,118,128] which is lower than the pressures required for the polymerization of pure nitrogen. Furthermore, as illustrated in Fig. 3(a),

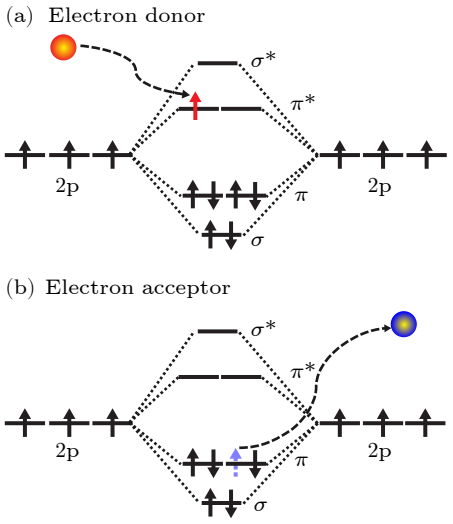

Fig. 3. The mechanism of weakening the triple bond. (a) When the metals are introduced, the electrons are transferred into the antibonding orbitals of nitrogen molecules. (b) When elements with higher electronegativities than nitrogen are introduced, the electrons in bonding orbitals of nitrogen molecules are lost.

the incorporation of metals promotes charge transfer from metal atoms to the antibonding orbitals of nitrogen molecules, thereby weakening the triple bond, decreasing the synthesis pressure, and facilitating the formation of new polymeric nitrogen at high pressure.

As shown in Fig. 2, polymeric nitrogen patterns are most abundant in alkali metal-nitrogen systems among the periodic table, including N_3,[8,10,11,13,99,128,158] N_4,[11] N_5,[8–12,19,21,123–125,160] N_6,[8,10,11,15,23,24,118,128] zigzag N-chain,[10,11] armchair N-chain,[8,9,12,15,23,99] layered nitrogen,[10,15,34,60] and 3D nitrogen networks.[15] Alkali earth metals also exhibit a diversity of polymeric nitrogen structures, but no 3D-networks are reported. The chain-like structure is common when introducing metals. Notably, compared to the pure nitrogen, the nitrogen rings are identified in the polymeric nitrogen hybridized with metals. The types of polymeric nitrogen show a decreasing trend from left to right across the periodic table. Each element possesses its own unique properties, including electronegativity, ionic radius, and electron configurations, which directly influence the types of polymeric nitrogen formed. However, elements within the same group exhibit certain similarities in these characteristics, resulting in the similar structures when forming polymeric nitrogen. Considering the dynamical stability at 0 GPa, the layered structure shows good stability among most of elements. In addition to these structural features, nitrogen content in binary compounds also exhibits correlations with metal characteristics.

While metals with higher valence states can form compounds with higher quantity ratio of nitrogen, their higher atomic mass depresses mass ratio of nitrogen in these compounds. In contrast, alkali-nitrogen and alkaline-earth-nitrogen systems achieve higher mass ratio of nitrogen, even with lower quantity ratio of nitrogen compared to some transition-metal-nitrogen systems. This balance between quantity and mass ratio of nitrogen is crucial for optimizing the properties of HEDMs. In reported metal-nitrogen systems, the chemical bonds between metals and polymerized nitrogen are ionic type, due to the charge transfer from metal to nitrogen. Unlike gaining electrons from metals, the non-metallic elements tend to form covalent bonds with nitrogen, which provides new roads to design and synthesize polymeric nitrogen.

3.1.3. The Nonmetal-Nitrogen System. Non-metallic elements with electronegativities similar to that of nitrogen tend to form covalent bonds with nitrogen atoms, as seen in compounds like NH_3 and HN_3. New nitrogen-rich compounds are formed at high pressure by introducing the non-metallic elements, accompanied by the emergence of polymeric nitrogen. Different from the cases of metallic elements, the polymeric nitrogen forms with non-metallic elements are scarce. N_5[56] and N_6[106,107] ring can only be observed in N-H and N-F system, respectively, while polymeric nitrogen chains are dominated in the cases of non-metallic elements. In total, both quantity and mass ratio of nitrogen in these compounds are lower compared to metal-nitrogen systems.

In previously discussed nonmetal-nitrogen compounds, it has been established that non-metallic elements such as H,[56] B,[84] C,[94] S,[178] O,[162] and Se[176] typically form covalent bonds with nitrogen. However, a change in bonding behavior may occur when elements with higher electronegativities than nitrogen are introduced. This suggests that nitrogen atoms can also undergo polymerization with an alternative pathway. The presence of more electronegative elements can prompt nitrogen to lose electrons from its occupied bonding orbitals, effectively destabilizing the triple bond [see Fig. 3(b)]. Consequently, the incorporation of highly electronegative elements opens new route for the formation of polymeric nitrogen species, for example, fluorine, which is the most electronegative element in the periodic table. The predicted novel one-dimensional NF chain exhibits stability at ambient condition, indicating its potential for experimental realization.[107] If reductor is added, the one-dimensional NF chain can act as an excellent high energy density material, since the energies of both breaking N-N single bonds and reacting between F and reductor are released. This insight broadens the horizon for the exploration and synthesis of polymeric nitrogen with potentially high performance.

3.2. The Experimental Research Progress.

3.2.1. The Pure Nitrogen System. At low-temperature and high-pressure, nitrogen gas can solidify into a molecular crystal. As shown in Fig. 4, several molecular phases of nitrogen have been reported, such as α, β, γ, δ, and ε phases. With increasing pressure, molecular nitrogen transforms to polymeric nitrogen.[197] This transition is accompanied by changes in the crystal structure, atomic positions, and bonding patterns. Advancements in high-pressure technology have indeed facilitated the experimental synthesis of polymeric nitrogen.

In 2000, a transition from molecular nitrogen into a non-molecular phase was experimentally reported at pressures above 150 GPa.[198] Subsequently, an insulator-semiconductor transition in nitrogen was detected at 140 GPa, with the non-molecular semiconductor phase persisting up to 240 GPa.[199] Until 2004, the cg-N was synthesized in a diamond anvil cell for the first time at 110 GPa and 2000 K, marking a milestone in the study of polymeric nitrogen.[17] It remains stable upon pressure reduction to 42 GPa, following a decomposition. In 2014, LP-N was synthesized in the pressure range of 120–180 GPa.[28] Heating LP-N resulted in its transformation to post layered polymeric nitrogen (PLP-N).[30] Furthermore, at 244 GPa and 3300 K, HLP-N was synthesized, representing another layered phase of polymeric nitrogen.[29] Additionally, black phosphorus-nitrogen (BP-N) was synthesized at approximately 140 GPa.[32] These phases exhibit three-coordinated crystal structures, where each nitrogen atom covalently bonds with three others through N-N single bond. Prior to their experimental synthesis, the structures and stabilities of cg-N, LP-N, HLP-N, and BP-N were theoretically investigated, underscoring the reliability and significance of theoretical prediction methods.

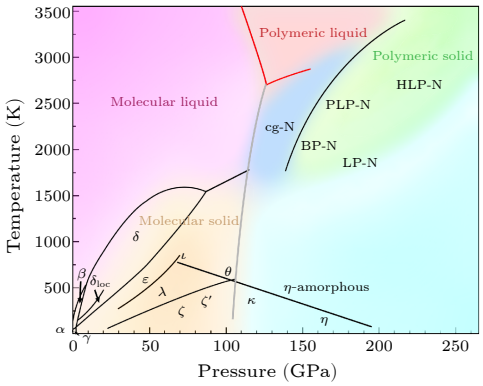

Fig. 4. The pressure-temperature phase diagram of nitrogen.

Although polymeric nitrogen has been successfully synthesized under high-pressure, it is not stable once the pressure is released, gradually dissociating as pressure decreases. Its instability at ambient conditions poses a challenge for practical applications. Therefore, capturing polymeric nitrogen at ambient conditions is a crucial goal, prompting further optimization of its design and synthesis methods. For example, the surface saturation and chemical dopants are effective approaches.

3.2.2. The Metal-Nitrogen System. In the metal-nitrogen system, experimental synthesis has yielded a variety of polymeric nitrogen patterns, including N_5 rings, N_6 rings, N chains, and layered nitrogen. The N_5 ring is the first polymeric nitrogen species synthesized in alkali metal-nitrogen systems. Generally, the N_5 ring in alkali metal-nitrogen systems carries one electron, such as LiN_5,[19,123–125] NaN_5,[21] and CsN_5.[20] Exceptionally, the N_5 ring with two electrons was synthesized in Na_2N_5.[21] In contrast, the subsequent synthesis of the N_6 ring has resulted in a more diverse array of configurations, such as boat-like N_6 in WN_6,[22] planar N_6^{2-} in K_2N_6,[23] and planar N_6^{4-} in K_9N_{56}.[24] Notably, the N_6 ring carrying 4 electrons adheres to Hückel's rule and is considered to be aromatic, conferring enhanced stability. The synthesis of zero-dimensional N_4 units includes compounds such as Mg_2N_4[18] and TaN_4,[182] as well as the N_8^{6-} in Sc_2N_8.[172] One-dimensional chain-like polymeric nitrogen is mainly found in transition metal-nitrogen systems.[25–27] Recently, layered forms of polymeric nitrogen containing N_{18} rings, such as K_2N_{16}, have been synthesized.[34]

In general, the pressure required for nitrogen polymerization is reduced upon the introduction of metals compared to the pressures needed for polymerization of pure nitrogen. As shown in Fig. 5, the polymerization in pure nitrogen requires a pressure of at least 110 GPa. However, in the alkali metal-nitrogen systems, the pressures for synthesizing N_5 and N_6 rings are approximately 50 GPa, demonstrating that charge transfer in alkali metal-nitrogen systems can effectively weaken the N≡N triple bond, thus facilitating the polymerization of nitrogen atoms. Additionally, the theoretically predicted pressures are lower than those required for experimental synthesis, primarily due to the fact that phase transitions must overcome

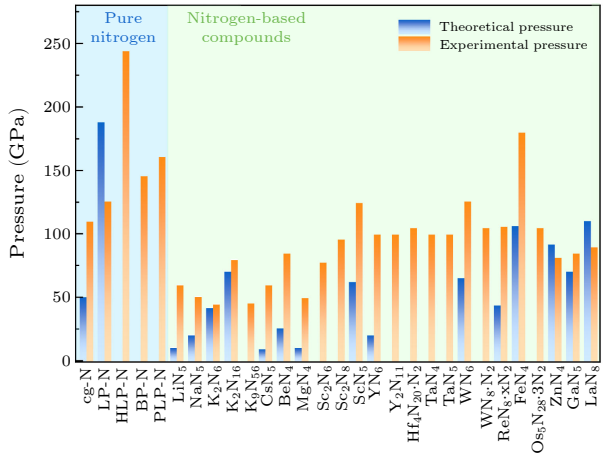

Fig. 5. The polymerization pressure in nitrogen and binary nitrogen-based compounds.

larger energy barriers, whereas theoretical calculations only account for the changes in enthalpy between the two phases. Consequently, high-temperature combined with high-pressure are used to synthesize new forms of polymeric nitrogen.

3.2.3. The Nonmetal-Nitrogen System. In metal-nitrogen compounds, a multitude of polymeric nitrogen configurations have been successfully synthesized. Conversely, for nonmetal-nitrogen compounds, there exist experimental investigations of N_2 reacting with H_2 under elevated pressures to form N-H bonds.[200] For B and C, they are known to create superhard materials in combination with nitrogen, such as cubic boron nitride (c-BN)[201] and C_3N_4.[202] However, the synthesis of polymeric nitrogen has not yet been reported in these systems. The absence of successful high-pressure synthesis of polymeric nitrogen with these elements may partially attributed to their moderate electronegativity. Theoretical simulations show that the polymerization in nonmetal-nitrogen compounds is realized in the future, for their high stability and high energy than metal-nitrogen compounds.[203]

Overall, the polymeric nitrogen species in nitrogen-rich compounds exhibit a wide variety and are synthesized at relatively low pressures. This renders them promising candidates for further exploration and applications. Achieving the polymerization of nitrogen through chemical doping is a viable approach.

3.2.4. The Ternary System. Compared to binary systems, current research on ternary systems is limited, primarily due to inherent challenges in structural prediction. For example, theoretical explorations of H-N-O[204] and C-N-O[205] systems did not indicate the presence of polymeric nitrogen at high pressure. While some ternary compounds, such as $LiBN_2$,[206] XN_5N_5F (X = Li, Na, K),[207] $NaClN_x$[208] and $KClN_x$,[209] have been predicted, their discovery relied on composition-constrained searches. This further underscores the computational complexity of predicting ternary configurations. These findings provide important information for designing polymeric nitrogen, suggesting that nitrogen-rich ternary phases deserve further investigations with advanced methodology.

Theoretical investigations on ternary polymeric nitrogen face lots of challenges, which may be solved with the assistance of artificial intelligence (AI) by exploring the energy landscape more efficiently. While current studies typically predict compositions and structures of polymeric nitrogen and then analyze their properties, challenges persist in achieving high energy density in metal-nitrogen systems and ensuring stability at ambient condition. An AI-driven reversal design approach could be employed to develop HEDMs with desired properties.

3.3. The Research Progress of Polymeric Nitrogen Under Ambient Conditions. In designing and synthesizing new forms of polymeric nitrogen, both experimental and theoretical studies have demonstrated abundant results through chemical doping. However, there are still significant challenges relating to the stability of polymeric nitrogen at ambient pressure, which is crucial for its practical applications. The main issue with high-pressure synthesis is the difficulty in maintaining the polymeric nitrogen to ambient conditions, which leads to extensive research into the destabilization processes of polymeric nitrogen and the search for stabilization strategies.

Previously, dynamical and thermodynamic stabilities were considered for judging the stability of polymeric nitrogen at 0 GPa. However, the stability of free surfaces should also be taken into account. For example, the cg-N surfaces saturated with hydrogen display robust stability at ambient pressure, with the capacity to remain stable at temperatures of at least 750 K.[210] Additionally, the nanoscale confinement effect has also been identified as a method to enhance the stability of polymeric nitrogen at ambient pressure. For instance, nitrogen chains can be encapsulated in carbon nanotubes or inserted between graphene layers to form composite materials, which have been observed to maintain their stability under ambient pressure.[141,211,212] Thus, saturation of dangling bonds and nano-confinement are effective approach to stabilize polymeric nitrogen. In addition to surface stability, defects are also common in the materials and are closely related to their stability.[45] This has been discussed in Zhong *et al.*'s review article.[213] Actually, existing simulated results shown that vacancy size can affect the stability of cg-N notably.[214] However, the relationship between defects and polymeric nitrogen remains unclear. Clarifying these relationships could enhance the stability of polymeric nitrogen at ambient conditions.

The synthesis of the N_8 anion using NaN_3 as a precursor on the sidewalls of multi-walled carbon nanotubes was achieved, indicating that carbon nanotubes may play a role in both the synthesis and stabilization of polymeric nitrogen.[215] In recent years, techniques such as radio frequency plasma have been utilized to synthesize cg-N from NaN_3 and N_8 precursors under near-ambient temperature and pressure conditions. This has made advances toward the practical application of cg-N. Recently, free-standing cg-N was synthesized by using PECVD method at ambient condition by using safer KN_3 as precursor, and the

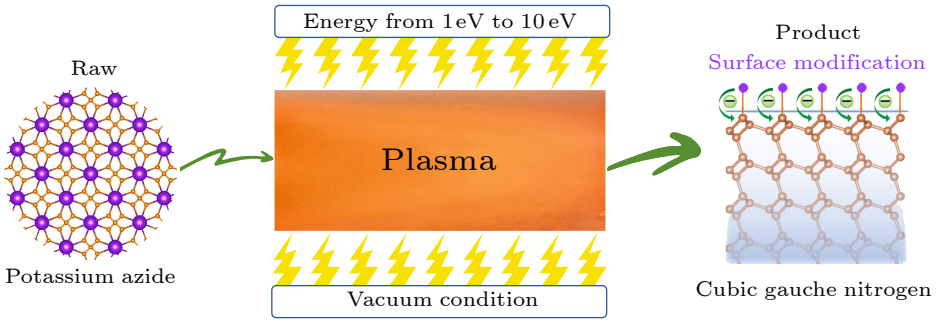

Fig. 6. The synthesis of cg-N from the precursor KN_3 by using PECVD method. The surface stability of polymeric nitrogen is enhanced by surface saturation and charge transfer.

explosion parameters are also measured using laser-induced plasma spectroscopy.[43] As shown in Fig. 6, the azide ions in the precursor KN_3 transformed into cg-N under plasma treatment. The charge transfer from metal can promote nitrogen polymerization and surface stability,[43,210] accounting for the successful storage of cg-N under ambient conditions. Notably, both high-pressure methods and PECVD, using azides as precursors, yield distinctly different products. For instance, N_6 rings form at high pressure,[23,24] while cg-N is obtained via PECVD.[43] These differences arise from variations in reaction kinetics. High-pressure methods favor thermodynamical control due to uniform thermal conditions, whereas PECVD is governed by chemical reaction in non-equilibrium plasma and rapid quenching.

Similar to successful sample synthesis, understanding energy release mechanisms is also critical for advancing polymeric nitrogen as HEDMs. The polymeric nitrogen fundamentally differs from traditional explosives in their energy release mechanisms,[216] offering significant research opportunities. While the released energy is commonly attributed to bond dissociation to form nitrogen gas, deeper analysis is lacking, such as bond dissociation pathways, exothermic decomposition kinetics, and decomposition process of various types of polymeric nitrogen. Addressing these aspects would provide a valuable foundation for designing HEDMs with optimized energy densities and controllable release characteristics.

4. Summary and Outlook. In polymeric nitrogen, nitrogen atoms form N-N single bonds, which are both the reason for polymeric nitrogen's high energy content and the key to its instability at ambient pressure. The emergence of polymeric nitrogen represents an opportunity to break through traditional energetic materials while also facing significant challenges. Synthesizing polymeric nitrogen by compressing nitrogen gas under high pressure requires high-temperature and high-pressure conditions, making the synthesis of polymeric nitrogen quite stringent. Introducing other elements to form compounds with nitrogen can effectively reduce the synthesis pressure of polymeric nitrogen, but the nitrogen content will affect the energy density of the material. In the nitrogen-based compounds hybridized with alkali metal and alkali earth metal, the theoretically predicted and experimentally synthesized structures are considered adequate. In contrast, the structural searches for nonmetal-nitrogen system need to be further explored, while no experimental synthesis is realized. Furthermore, techniques such as nanoscale confinement and surface saturation can enhance the stability of polymeric nitrogen. It is time to pay more efforts to the elucidation of the polymeric nitrogen decomposition mechanism at ambient conditions, and then new method to enhance its stability can be explored, which is very important for promoting the potential applications of polymeric nitrogen.

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