One Pot Synthesis of Cubic Gauche Polymeric Nitrogen

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The long sought cubic gauche polymeric nitrogen (cg-N) consisting of N-N single bonds has been synthesized by one pot route using sodium azide as a precursor at ambient conditions. The recrystallization process was designed to expose crystal faces with low activation energy that facilitates initiating the polymeric reaction at ambient conditions. The azide was considered as a precursor due to the low energy barrier in transforming double bonded N=N to single bonded cg-N. Raman spectrum measurements detected the emerging vibron peaks at 635 cm^{-1} for the polymerized sodium azide samples, demonstrating the formation of cg-N with N-N single bonds. Different from traditional high-pressure technique and recently developed plasma enhanced chemical vapor deposition method, the route achieves the quantitative synthesis of cg-N at ambient conditions. The one pot synthesis of cg-N offers potential for further scaling up production as well as practical applications of polymeric nitrogen based materials as high energy density materials.

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Introduction. The N≡N triple bond is one of the strongest chemical bonds, with a very high bond energy of 954 kJ/mol,[1] while the N-N single bond is much weaker, with a bond energy of 160 kJ/mol.[2,3] Due to the huge difference in energy between triply bonded dinitrogen and singly bonded nitrogen, the polymerized nitrogen materials with N-N single bonds are proposed as high energy density materials and expected to release a high amount of chemical energy while transforming into a triply bonded dinitrogen molecules. It was anticipated that the greatest utility of fully single-bonded nitrogen would produce a ten-fold improvement in detonation pressure over HMX[4] and therefore polymerized nitrogen is highly sought as a high energy density material.

It was predicted in 1985 that molecular nitrogen would polymerize into atomic solid at high pressure.[5] Later, the cubic gauche (cg-N) lattice with a single bond diamond like structure was proposed.[6] Subsequently, large amounts of theoretical work reported on the high pressure approach to polymerized nitrogen with N-N single bonded forms.[7–23] It was not until 2004 that Eremets *et al.* prepared cg-N directly from molecular nitrogen at pressures above 110 GPa (1 GPa≈10,000 atmospheric pressure) and temperatures above 2000 K using laser heated diamond cell technique.[24] The cubic gauche structure was confirmed by growing the single crystal in 2007.[25] However synthesis pressures above 110 GPa are highly required. Later on, polymerized nitrogen with layered structure (LP-N),[26] hexagonal layered structure (HLP-N),[27] black phosphorus nitrogen (BP-N),[28] and Panda nitrogen[29] were successfully prepared at 120 GPa, 244 GPa, 146 GPa, and 161 GPa, respectively. Nevertheless, the high pressure is commonly regarded as a necessary route to synthesize polymerized nitrogen. All these polymerized nitrogen samples decomposed in the process of releasing pressure. Some strategies, such as chemical doping, were attempted at high pressure by introducing metals in order to stabilize the polymerized nitrogen lattice at lower pressure,[30–34] but it remains challenging to recover the polymerized nitrogen samples at ambient pressure. In addition, introducing non-energetic element, especially the heavy metal seriously decreases energetic density of polymerized nitrogen materials, detrimental to the natural applications.

In the past few years, plasma enhanced chemical vapor deposition (PECVD) technique has been developed to take advantage of the non-equilibrium plasma environment to synthesize polymerized nitrogen materials. The relative thermodynamic instability of polymerized nitrogen can be overcome by kinetic stability provided through energy band hybridization by a charge transfer mechanism, which makes the high energy lattice gain stability and avoid the highly energetic conversion to molecular N_2.[35] The cg-N and N_8 cluster were successfully prepared with or without the assistance of carbon nanotube using sodium azide as precursor.[35–40] However, the plasma generally can only penetrate several nanometers into the solid surface,[41] leading to limited quantity of cg-N. Besides, high energy plasma particles also could dissociate the cg-N produced in the experiment, which is backed up by the fact that the optimized synthesis time is demanded for a

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very small amount of cg-N sample prepared by the PECVD method.[38]

Theory proposes that the transition path to polymerized nitrogen might pass through different molecular structures with limited thermodynamic stability fields.[42] Additionally, earlier experiments aimed at synthesizing polymerized nitrogen only reached the amorphous state at ambient temperature compression, indicating that increasing reaction temperature to activate the precursor might play a crucial role in the formation of the atomic structures.[43,44] For example, LiN_5 and K_2N_6 were synthesized at lower pressures[30,32,33] with the assistance of laser heating.

We here for the first time report one pot synthesis of cg-N by using sodium azide as a precursor. The cg-N was successfully obtained through recrystallization reaction, followed by transforming azide ions with N=N double bonds into single bonded cg-N that can stabilize at ambient pressure conditions. To date, it is the simplest synthesis route to realize cg-N that can be further developed for scaling up production and potential practical applications.

Materials and Methods. High pure sodium azide (NaN_3) (⩾99.9%) was chosen as nitrogen source to synthesize cg-N. The recrystallization process was performed first. A solution of NaN_3 (2 mol/L) was pre-prepared and dropped into a crucible. Then the crucible was transferred into a tubular furnace. The vacuum operation was performed to realize the recrystallization of the NaN_3 powder. The reaction temperatures and times within the 200–300 ℃ and up to 10 hours were tried in the synthesis processes. The optimized synthesis condition with reaction temperature 240–260 ℃ and heating time 5 hours was employed to synthesize the cg-N. The sample was named as polymerized sodium azide (PSA) followed by synthesis temperature, time, such as PSA-240℃-5h. According to aforementioned conditions, heating NaN_3 without recrystallization process to prepare cg-N was tried and it was named as unpolymerized sodium azide (UPSA).

The Raman spectra were recorded in range of 100–1500 cm^{-1} with a spectral resolution of 1 cm^{-1} using an integrated laser Raman system (Renishaw) with a confocal microscope and multichannel air cooled CCD detector. The excitation source is an Ar ion laser ($\lambda_0 = 532$ nm).

Results. The cg-N was proposed to adopt a body centered cubic Bravais lattice, belonging to $I2_13$ space group with a lattice constant of 3.773 Å. The N-N bond length is predicted to be 1.40 Å and the bond angle is 114.0° at ambient pressure conditions.[6,45] Figure 1 shows the crystal structure of cg-N, in which each nitrogen atom bonds to three nearest neighbors with N-N single bonds at equal distances and the remaining p orbital is occupied by the lone pair electrons. Thus, cg-N exhibits a near tetrahedral structure similar to that in diamond (left panel in Fig. 1). The single bonded nitrogen atoms form fused rings, which connect with others forming a three-dimensional network structure,[46] as shown in the right panel of Fig. 1. The theoretical work on cg-N did not show imaginary frequency in phonon spectrum calculation,[12] indicating that the entire covalent network of cg-structure is metastable at ambient pressure.

The azide ion is composed of N=N double bonds that can be used as an ideal precursor for synthesizing the cg-N due to the low energy barriers for transforming into single bonded cg-N. In this work, the sodium azide is used in present one pot synthesis experiments. The recrystallization process is expected to expose the crystal faces with low activation energy. Then the polymeric reaction can be initiated at mild conditions. To date, the amount of cg-N obtained experimentally at ambient pressure is still not sufficient to obtain ideal X-ray diffraction patterns. Therefore, the Raman spectrum was adopted to characterize the chemical bond transformation in the present work that is commonly used for experimental detections of polymerized nitrogen.

Figure 2 shows the Raman spectra of polymerized NaN_3 (PSA) synthesized at 200–300 °C with a reaction

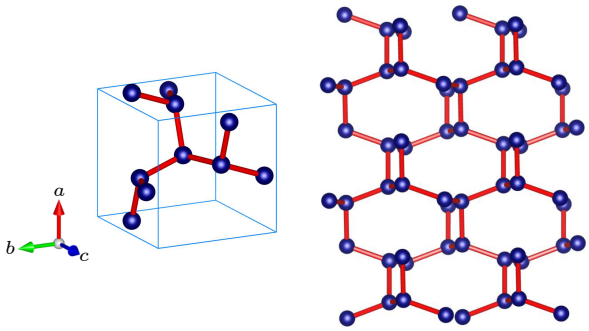

Fig. 1. The schematic view of cg-N crystal structure.

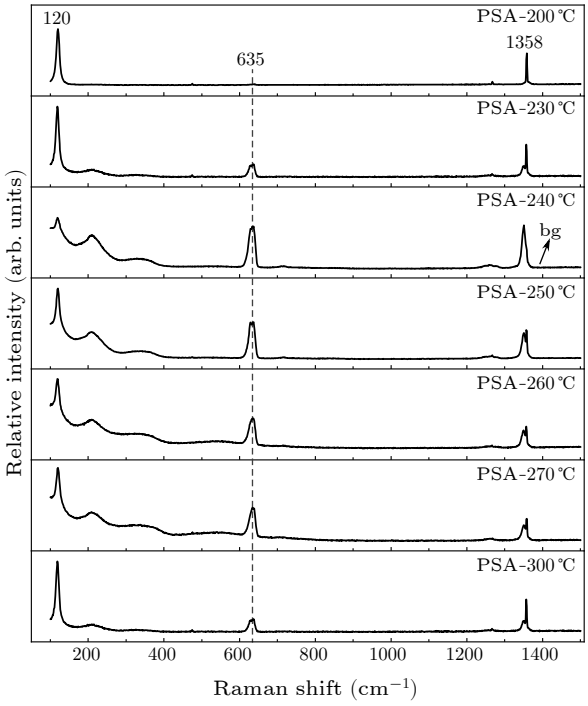

Fig. 2. The Raman spectra of PSA synthesized at 200–300 °C with a reaction time of 3 hours, where the fingerprint peak at 635 cm^{-1} for cg-N is detected. The vibron intensity of cg-N shows optimized synthesis temperature between 240–260 °C.

time of 3 hours. The sharp peaks of NaN_3 near 120, 1267, and 1358 cm^{-1} are assigned to the vibrational lattice mode, the first overtone of the IR active bending $\nu 2$ mode and the symmetric stretching $\nu 1$ mode of the azide ion, respectively, which matches well with the Raman spectra of free standing NaN_3.[39] For comparison, the NaN_3 raw material and a sample heated only at 250 °C for 3 hours without the recrystallization process were characterized and showed same Raman vibron profiles without any signals at 635 cm^{-1} (see Fig. S1 in Supplementary Materials). The lines at 635 cm^{-1} for PSA sample are comparable to the theoretical results extrapolated to ambient pressure because the Raman modes tend to soften with decreasing pressure.[24,45,47] It also agrees with our recent work on polymerized cg-N based on potassium azide.[48] Therefore, the emerging intense vibron at 635 cm^{-1} is assigned to the pore breathing A symmetry and is regarded as the finger print peak of cg-N, which unambiguously indicates the successful synthesis of cg-N.[45]

The synthesis conditions of cg-N were first systematically investigated by controlling the reaction temperature with a fixed reaction time of 3 hours. As shown in Fig. 2, the vibron intensity of cg-N increases as the reaction temperature rises from 200 °C to 240 °C compared to that at 1358 cm^{-1} for the unreacted or remnant NaN_3 in the PSA samples. As temperature increases up to 270 °C, the Raman intensity of cg-N remains comparable, but decreases clearly at 300 °C. Additionally, it is worth noting that the intensity of vibrational lattice mode at 120 cm^{-1} for the unreacted NaN_3 in PSA-240 sample dramatically decreases compared to those prepared at other temperatures. The PSA sample exhibits uniformly dark blue color and should be related to the by product formed during the synthesis of cg-N and will be discussed below. Therefore, the optimized temperature range of 240–260 °C was adopted for cg-N preparation.

Table 1. The main Raman peak intensity for sodium azide (NaN_3) raw material (SA-R), NaN_3 heated only (UPSA) and polymerized NaN_3 (PSA) samples at 200–300 °C for 3 hours.

Sample	I_{bg}	I_{120}	I_{635}	I_{1358}	$(I_{120}\text{-}I_{bg})/(I_{1358}\text{-}I_{bg})$	$(I_{635}\text{-}I_{bg})/(I_{120}\text{-}I_{bg})$	$(I_{635}\text{-}I_{bg})/(I_{1358}\text{-}I_{bg})$
SA-R	1401	61101	/	23411	2.71	/	/
UPSA-250 °C	505	18324	/	8093	2.35	/	/
PSA-200 °C	189	3019	/	1192	2.82	/	/
PSA-230 °C	225	4800	964	2298	2.21	0.16	0.36
PSA-240 °C	503	8325	5185	4231	2.10	0.60	1.26
PSA-250 °C	3382	48310	26556	21578	2.47	0.52	1.27
PSA-260 °C	1100	12360	5834	4509	3.30	0.42	1.39
PSA-270 °C	4952	46283	17281	15951	3.76	0.30	1.12
PSA-300 °C	1996	49297	3205	20430	2.57	0.03	0.07

Notes: Table 1 shows the intensities (I) of Raman vibrons at 120, 635, and 1358 cm^{-1}. Background is defined by the intensity of linear part at 1400 cm^{-1} marked in Fig. 2.

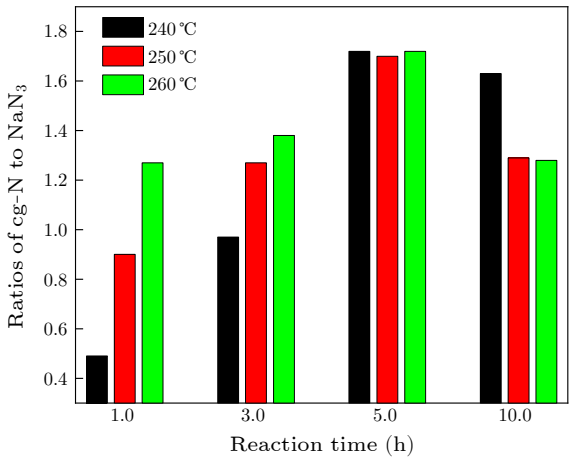

Fig. 3. The reaction time dependence of the conversion ratios of NaN_3 for the PSA samples prepared at 240, 250, and 260 °C. The optimized synthesis conditions for the PSA samples are 240–260 °C with a reaction time of 5 hours.

A quantitative comparison was made by calculating the intensity ratios of the characteristic Raman peaks to measure the abundance of cg-N phase in the PSA samples. Table 1 summarizes the partial line intensities of NaN_3 and cg-N. The amount of cg-N synthesized is reflected by the peak intensity at 635 cm^{-1}, while those at 120 and 1358 cm^{-1} represent the unreacted NaN_3. Herein, a simplified conversion degree from NaN_3 to cg-N is defined by the peak intensity ratio. The intensities of NaN_3 at 120 and 1358 cm^{-1}, calculated by $(I_{120}\text{-}I_{bg})/(I_{1358}\text{-}I_{bg})$ for the NaN_3 raw material (SA-R), NaN_3 heated only (UPSA) and polymerized NaN_3 (PSA) samples at different temperatures are between 2 and 3 and remain little changed. For the SA-R and UPSA samples no trace of cg-N is detected. After recrystallization process the vibron intensity of cg-N enhances dramatically for PSA samples and the ratio of cg-N to NaN_3 is 1.26–1.39 calculated by $(I_{635}\text{-}I_{bg})/(I_{1358}\text{-}I_{bg})$, and 0.42–0.60 calculated by $(I_{635}\text{-}I_{bg})/(I_{120}\text{-}I_{bg})$ for the PSA samples synthesized at 240–260°C. Therefore, it indicates that the recrystallization process strongly promotes the formation of cg-N and the optimized synthesis temperature range is 240–260 °C.

Further the preparation conditions were explored by synthesizing PSA samples at 240–260 °C with variable reaction time. The Raman vibron intensity of cg-N in the PSA-240 samples increases gradually as the reaction time extends up to 5 hours and then decreases, which is shown in Fig. S2. Samples prepared at 250 and 260 °C show the same results (Fig. S3). For comparison, the intensity ratios of the cg-N to unreacted NaN_3 in these PSA samples

were calculated in Table SI. The reaction time dependence of the ratios of cg-N to NaN_3 at 240–260 °C was plotted in Fig. 3. All samples show consistent trends: the PSA samples with a reaction time of 5 hours show the highest conversion degree. Therefore, the optimized preparation conditions for polymerized sodium azide samples are a temperature range of 240–260 °C and a reaction time of 5 hours.

Discussion. To date for cg-N preparation the high pressure technique and PECVD method have been proposed, which suffer from the challenge that samples could not be recovered to ambient pressure and enhancing yield is difficult. Here one pot synthesis route was designed for synthesizing cg-N under atmospheric conditions considering the thermodynamic barriers related to transforming to N-N single bonds and activation energy of precursor. In our experiments it was found that recrystallization process played a crucial role to form cg-N. For azides the crystal face with low activation energy may facilitate initiating the transformation of the double bonds N=N in azide ions to single bonded cg-N. The optimized temperatures for cg-N preparation by NaN_3 are primarily restricted by the melting point of NaN_3 (∼275 °C). These results align well with the fact that the cg-N forms on the crystal face with lower activation energy of azides precursors oriented by the recrystallization process. Regarding the formation mechanism of cg-N it was observed that the polymerized sodium azide turned dark blue in our experiments that should be related to the formation of by-product Na_3N during the synthesis of cg-N. This is consistent with the reported results that pH value of the solution increases after synthesis reaction as Na_3N displays alkalinity when dissolved in water.[38] A more detailed conversion mechanism is currently at investigation.

Conclusion. The polymeric nitrogen with cubic gauche structure was successfully prepared by one pot synthesis route using sodium azide as a precursor. A high yield may be obtained by separating the by products formed on the surface of the produced cg-N. The route is promising for further scaling up and can be applied to synthesize other metastable polymerized nitride materials.

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