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Nitrogen-Rich Molybdenum Nitride Synthesized in a Crucible under Air

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Abstract

The triple bond in N₂ is significantly stronger than the double bond in O₂, meaning that synthesizing nitrogen-rich nitrides typically requires activated nitrogen precursors, such as ammonia, plasma-cracked atomic nitrogen, or high pressure N₂. Here, we report a surprising synthesis of nitrogen-rich nitrides under ambient pressure and atmosphere. Using Na₂MoO₄ and dicyandiamide precursors, we synthesized nitrogen-rich γ -Mo₂N₃ in an alumina crucible under ambient atmosphere, heated in a box furnace between 500 and 600 °C. Byproducts of this metathesis reaction include volatile gases and solid Na(OCN), which can be washed away with water. X-ray diffraction and neutron diffraction showed Mo₂N₃ with a rocksalt structure having cation vacancies, with no oxygen incorporation, in contrast to the more common nitrogen-poor rocksalt Mo₂N with anion vacancies. Moreover, an increase in temperature to 700 °C resulted in molybdenum oxynitride, Mo_{0.84}N_{0.72}O_{0.27}. This work illustrates the potential for dicyandiamide as an ambient-temperature metathesis precursor for increased effective nitrogen chemical potential under ambient conditions. The classical experimental setting often used for solid-state oxide synthesis, therefore, has the potential to expand nitride chemistry.

Introduction

The nitride anion (N^{3-}) has unique solid-state bonding characteristics that span covalent, ionic, and metallic bonds, which have made nitrides useful for applications ranging from superconductors¹, electrides², phosphors^{3,4}, pigments^{5,6}, magnets⁷ and catalysts^{8,9}. Exploration of new nitrides has the potential to expand chemical space and reveal new materials with emergent functionality. Recent highlights of nitride chemistry include the computational screening of new nitrides¹⁰, thin film synthesis of nitrogen-rich nitrides¹¹, high-pressure synthesis of ternary nitrides¹², as well as ferroelectricity¹³ and high catalytic activities¹⁴.

Nitride synthesis is generally still very constrained compared to the synthesis of the corresponding oxides. The high stability of the N_2 molecule, arising from its triple bond, is the main reason for the difficulty of forming nitrides in ambient air. Transition metal nitrides therefore tend to be nitrogen poor. High-pressure synthesis is a route to activate nitrogen and achieve nitrogen-rich nitrides^{15,16}, for instance, Zr_3N_4 and LaReN_3 are synthesized above 8 GPa in a diamond anvil cell¹⁷ and 1000-ton large volume press¹⁸, respectively.

Alternatively, the use of activated nitrogen sources, which includes Radiofrequency (RF) nitrogen plasma, nitrogen radicals, NH_3 , and urea, produces a variety of nitrides^{19–22}. As a physical approach, by using magnetron sputtering, ZrN_x ($x \sim 1.35$)²³ and MgZrN_2 are synthesized by nitrogen radicals²⁴. To develop an alternative chemical synthesis route of nitrides, nitridation of oxides under an ammonia flow is a typical strategy, where NH_3

decomposes into N_2 and H_2 and the removal of H_2O byproduct by an ammonia flow facilitates the formation of nitrides. We previously developed a low-temperature nitridation process of oxides using $NaNH_2$ as a solid nitrogen source^{25,26}. Although this process uses no ammonia gas, $NaNH_2$ should be handled inside a glove box because it can react with moisture and ignite in the air. In other words, even though nitrides can be synthesized at ambient pressure, the precursors can often be toxic, explosive or corrosive, which necessitates cumbersome safety equipment and low p_{O_2} gloveboxes for producing nitrides.

Among nitrides, molybdenum nitride is known to have various physical and chemical properties such as superconductivity, super hardness, and catalytic activity^{27–29}. The experimental phase diagram of the Mo-N system at ambient pressure shows α , β , γ - Mo_2N , and δ - MoN , but nitrogen-rich molybdenum nitride with a rocksalt structure has not been reported³⁰. Under high pressure of 3.5 GPa, layered 3R- MoN_2 can be synthesized by the metathesis reaction of Na_2MoO_4 and BN in a closed system³¹. Molybdenum vacancies could expand a variety of nitrogen-rich molybdenum nitrides—for example, layered nitrides of Mo_5N_6 stoichiometry with ordered molybdenum vacancies are synthesized by the reaction of MoS_2 and NH_3 ³². Computational calculations show the possibility of other nitrogen-rich nitrides, $Mo_{15}N_{16}$ ³³ and cubic σ - Mo_2N_3 ³⁴ as metastable polymorphs, but these compounds have not been experimentally synthesized. Pandey *et al.* reported that thermal ammonolysis of MoO_3 produces a rocksalt structure with molybdenum vacancies, in contrast to γ - Mo_2N with nitrogen vacancies³⁵. Neutron diffraction reveals that the resulting rocksalt phase is an oxynitride with molybdenum

vacancies and hydrogen incorporation, represented as $\text{Mo}_{1-x}(\text{N}_{1-y}\text{O}_y)\text{H}_z$. This suggests that oxygen incorporation is likely what stabilizes the anion-rich chemistry. Therefore, the synthesis of nitrogen-rich nitrides without oxygen incorporation under ambient pressure serves as a great synthesis challenge.

Dicyandiamide, represented by $\text{H}_2\text{N}-\text{CNH}-\text{NH}-\text{CN}$, is a stable organic substance used in fertilizers and curing agents^{36,37}. Since it acts both as a reducing agent and as a nitriding agent, it has been studied as a nitriding agent for oxides under non-atmospheric conditions³⁸. In 2021, Chen *et al.* reported the synthesis of rocksalt-type molybdenum nitride by reacting $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and dicyandiamide in a crucible under atmospheric conditions³⁹. This discovery is a breakthrough of nitride synthesis because this synthesis method does not use a gas cylinder or glove box to keep low p_{O_2} non-atmospheric conditions. TEM observation showed that the particle size of the synthesized molybdenum nitrides is 3-10 nm. However, the intensity ratio of the XRD peaks of the rocksalt structure was largely different from the previously reported $\gamma\text{-Mo}_2\text{N}$, and the elemental analysis was performed only by XPS. Thus, the product may not be $\gamma\text{-Mo}_2\text{N}$, as previously reported by Chen *et al.*

Herein, we show that this reaction between $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and dicyandiamide in an alumina crucible under an ambient atmosphere in fact does not yield nitrogen-poor $\gamma\text{-Mo}_2\text{N}$, but rather forms a new nitrogen-rich molybdenum nitride, $\gamma\text{-Mo}_2\text{N}_3$, which has a rocksalt structure with molybdenum vacancies, no internal oxygen, and a fully occupied anion lattice. Detailed XRD and neutron diffraction together with chemical and physical analyses revealed that this nitrogen-rich $\gamma\text{-Mo}_2\text{N}_3$ can be synthesized by a traditional

setting used for oxide synthesis.

Experimental

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (FUJIFILM Wako Pure Chemical co. >99.0 %) and dicyandiamide (FUJIFILM Wako Pure Chemical co.) were weighed in a molar ratio of 3:5. The total mass was 24 g. MoO_3 (KANTO CHEMICAL CO., INC. >99.5 %) and dicyandiamide was similarly weighed. After mixing the sample by a mortar and pestle for approximately 5 minutes, it was set in a 50 ml alumina crucible with a lid. The crucible was heated in a furnace, which is settled in a fume hood, preheated to 500, 550, 600, 650, and 700 °C for 30 minutes. CAUTION: TOXIC GAS IS LIKELY GENERATED. After the furnace cooled to room temperature, black powder was obtained in a crucible. The product was crushed in a mortar and pestle, washed with water and/or a weak acid, and centrifuged. The resulting precipitates was dried at room temperature to obtain the final product.

The crystalline phase of the final product was investigated by XRD on an X-ray diffractometer with $\text{CuK}\alpha$ radiation (Rigaku, Miniflex600). Powder neutron diffraction (ND) measurements were performed in air with a neutron beam of wavelengths of 1.34171(5) and 1.62124(4) Å. The neutron diffraction measurements were carried out on an angle-dispersive-type neutron diffractometer, HERMES at JRR3 at the Japan Atomic Energy Agency, or Echidna, at the Open Pool Australian Light water reactor (OPAL) at the Australian Nuclear Science and Technology Organisation (ANSTO). Two different combustion analyses performed the elemental analyses. The amounts of hydrogen and carbon were determined by heating the samples in an oxygen atmosphere at ~800 °C

using JSL MicroCorder (MT-5). The amounts of oxygen and nitrogen were determined by heating with Sn flux in a carbon crucible in He atmosphere by oxygen/nitrogen analyzer (Horiba, EMGA-620W). As another elemental analysis, ICP analysis (SHIMADZU, ICP-AES, ICPS-8100) was performed. The valence of molybdenum in the product was evaluated by the absorption edge of Mo-K edge (XANES). The measurement of the spectra can be conducted in a transmission mode at the BL14B2 beamline at SPring-8 with the approved number of 2022B1585. Mo₂N (Kojundo Chemical Laboratory Co., Ltd.) and MoO₃ (KANTO CHEMICAL CO., INC. >99.5 %) were used as standard substances at XANES. The Rietveld analysis of this Mo₂N powder with the ratio of anion and cation is in Figure S4. The surface state of the product was evaluated by XPS (JEOL, JPS-9200). Magnetic properties were measured at 100 Oe using a vibrating sample magnetometer using a physical property measurement system (Quantum Design PPMS DynaCool).

Results



Figure 1. Photo of the crucible and black powder synthesized from $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and dicyandiamide at 600 °C heating.

Figure 1 shows a photo of the product synthesized from $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and dicyandiamide after heating a crucible at 600 °C in a furnace, as a typical example. After washing the product above, the black product of 5-6 grams was obtained, which is enough to perform the analysis including neutron diffraction.

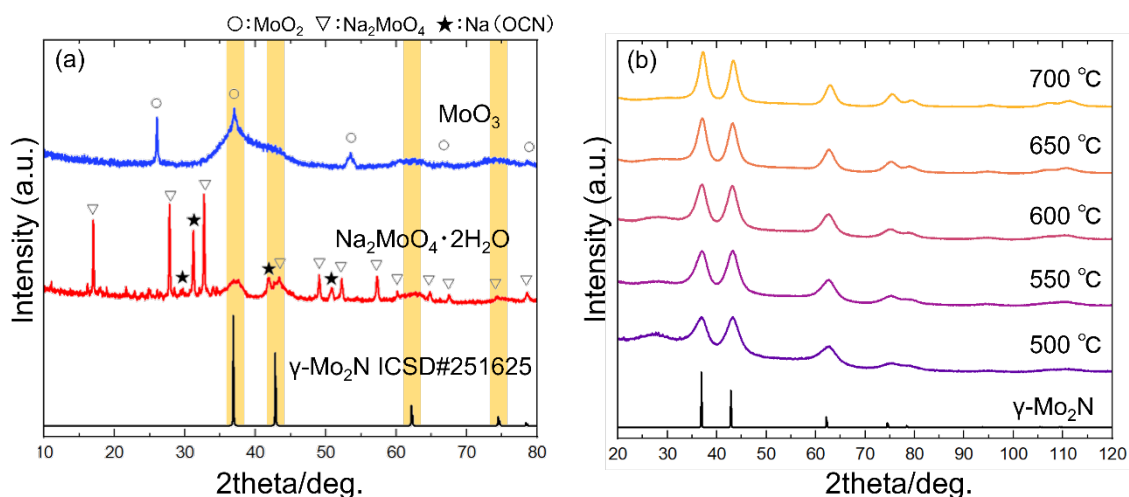


Figure 2. XRD patterns of the mixture of (a) MoO_3 -dicyandiamide and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ -dicyandiamide after heating at 600 °C before washing, (b) $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and dicyandiamide after washing.

To investigate the effect of the presence of sodium in the precursor, the nitridation of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and MoO_3 with dicyandiamide were compared (Figure 2(a)). The

reaction with MoO_3 brought about a broad halo at $\sim 40^\circ$ with the sharp peaks assigned to MoO_2 . The reaction with $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ exhibited broad peaks at ~ 37 and $\sim 43^\circ$ close to the γ - Mo_2N together with the peaks of $\text{Na}(\text{OCN})$ and unreacted Na_2MoO_4 . Thus, Na_2MoO_4 is an effective precursor for producing rocksalt structures. Weak peaks could not be indexed but these peaks disappeared after washing, as shown in Figure 2(b).

Figure 2(b) shows the XRD patterns of the synthesized nitrides from $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ after washing with water. Major diffraction peaks were indexed as a cubic rock-salt structure, similar to the reported γ - Mo_2N (ICSD#251625). However, the intensity ratios of the first and second most intense peaks at ~ 37 and $\sim 43^\circ$ of the products are different from those of γ - Mo_2N reported in the ICSD#251625.²⁹ The crystallite size determined from the 111 peak ($\sim 37^\circ$) was in the range between 3 and 4 nm, which increased with increasing the heating temperature (Figure S2). A halo pattern at $\sim 28^\circ$ indicates the amorphous phase, of which intensity decreases with increasing temperature.

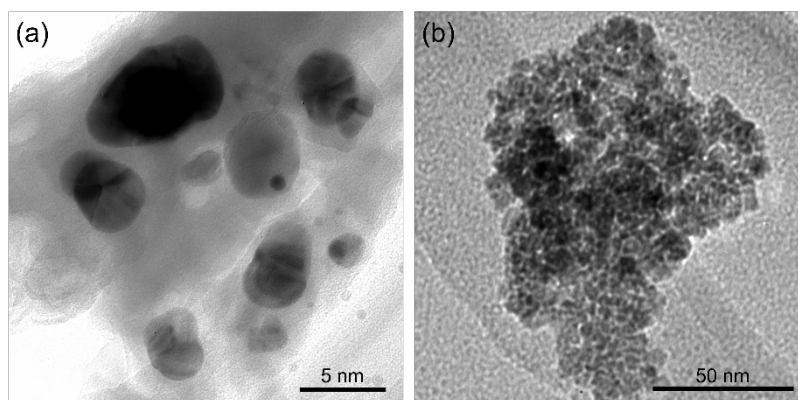


Figure 3. TEM images of the molybdenum nitrides/oxynitrides synthesized at (a) 600 and (b) 700 °C.

Figure 3 shows the TEM images of the products at 600 and 700 °C. The particles synthesized at 600 °C are 2-10 nm in size and are embedded in an amorphous matrix. On the other hand, the particles synthesized at 700 °C are aggregated, and no thick amorphous layer is seen. The particle size is close to the crystalline size determined by Scherrer equation and agrees with the previous report³⁹.

Table 1. Elemental analysis of the products. The amounts of hydrogen and carbon are measured by CHN analysis, and nitrogen and oxygen are measured by combustion analysis.

Synthesis temp/°C	H /wt%	C /wt%	N /wt%	O /wt%
500	0.76	4.14	15.42	18.32
550	0.67	0.68	10.15	17.10
600	0.69	0.46	9.70	16.89
650	0.51	0.00	9.56	15.64
700	0.48	0.00	9.32	13.11

Table 1 shows the elemental (hydrogen, carbon, nitrogen, and oxygen) analysis results. The amounts of H and C were determined by CHN analysis, and those of N and O were determined by ON combustion analysis. The difference between the nitrogen amount acquired by CHN analysis and ON analysis was ~1 %. Approximately 4% of carbon was detected in the sample obtained by heating at 500 °C, suggesting that a large

amount of carbon source remains. The carbon amount became significantly less in 550 and 600 °C samples and was not detected in 650 and 700 °C samples. Dicyandiamide has been reported to completely undergo combustion at approximately 600 °C⁴⁰, consistent with the present experimental results. The amount of hydrogen, nitrogen, and oxygen decreases with increasing heat-treatment temperatures. A large amount of oxygen/hydrogen suggests the surface of nitrides would be covered by amorphous oxide/oxy-nitride/hydroxide, adsorbed water/gas, or oxynitride crystal phase³⁵, as described later. The amount of sodium was also determined by ICP analysis of the product synthesized at 600 °C. The amount was 3.37 wt%. Washing with hot water and citric acid did not change the diffraction peaks of the XRD pattern but decreased the Na content to 0.58%. Therefore, we presumed the amorphous phase was partially composed of Na.

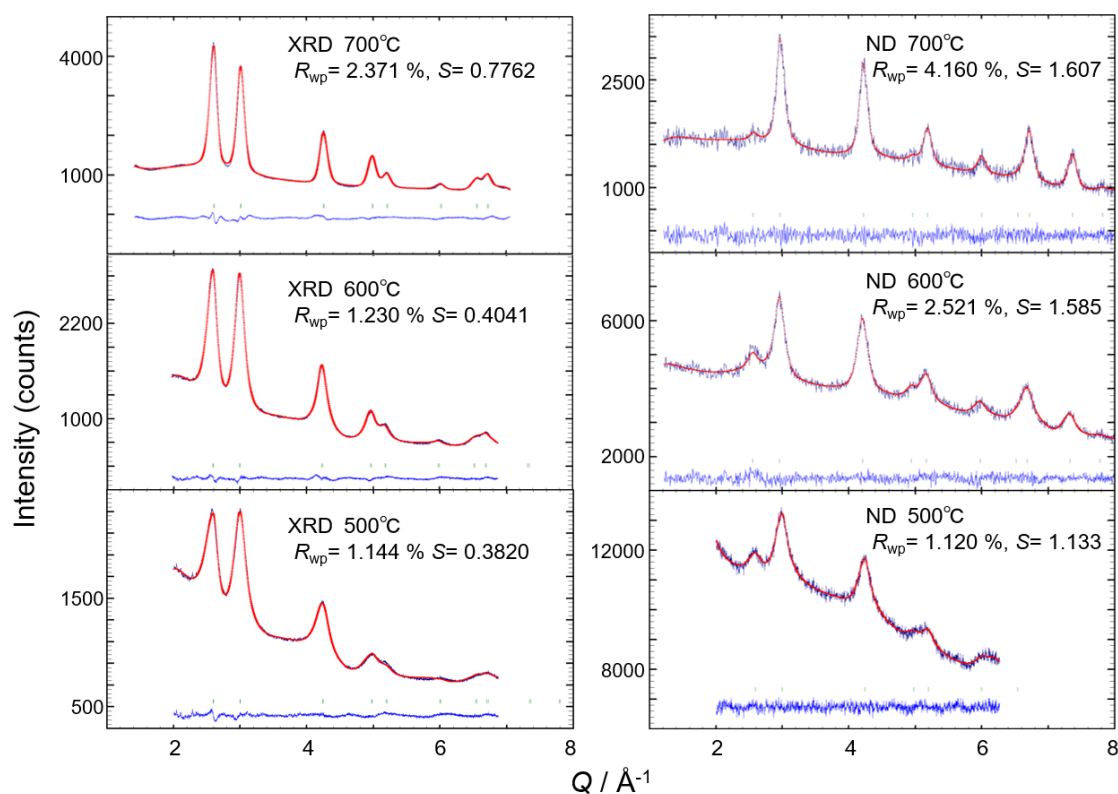


Figure 4. Rietveld profiles of XRD and neutron diffraction patterns. Measured data are shown in the purple line, pattern position in the green bar, calculation in the red line, and difference in the blue line.

In order to investigate the crystalline phase of the rock-salt structure, Rietveld refinement of XRD and ND using the rock-salt structure model was performed. The ratio of molybdenum to the total of anions (O^{2-} , N^{3-}) was acquired by XRD, and the ratio of O^{2-} to N^{3-} was from ND. Rietveld profiles are shown in Figure 4, and the lattice parameters and the occupancies are shown in Table 2. The initial refinement was performed with the rock-salt structure of Mo_2N where anion was partially occupied, but the fitting was not good. The proposed crystal structure models here are rocksalt where the anion site is fully occupied but the molybdenum site is partially occupied, suggesting an anion-rich compound. By using this anion-rich crystal model, XRD results show that the anion occupancies when synthesized at 500 and 600 °C are almost the same, but the occupancy of anions decreases at 700 °C. To determine the N/O ratio, the refinement of ND was performed with the constraints on the cation/anion ratio acquired by XRD. The refinement of ND shows that the anion sites are fully occupied by nitrogen at 500 and 600 °C, while nitrogen and oxygen are occupied at 700 °C. Because the scattering length of nitrogen is approximately 1.5 times larger than that of oxygen and carbon, the incorporation of carbon is also ruled out. Accordingly, the crystalline phase was cubic nitrogen rich γ - Mo_2N_3 at 500 and 600 °C, and $Mo_{0.84}N_{0.72}O_{0.27}$ oxynitride at 700 °C. To further confirm analysis, we performed the simultaneous analysis of XRD and ND that

converged with the slightly more nitrogen-rich and no oxygen: $\text{MoN}_{1.73(2)}$ (Figure S3. Table S2). Therefore, this analysis provides plausibility that the product is nitrogen-rich $\gamma\text{-Mo}_2\text{N}_3$.

Elemental analysis suggests the possibility of Na incorporation into the Mo site. However, this substitution is unlikely because of the significant difference in ionic radii between $\text{Mo}^{4+}/\text{Mo}^{5+}$ and Na^+ ; 6-coordinated molybdenum is about 0.650-0.69 Å, and the ionic radius of sodium is about 1.02 Å⁴¹. Moreover, the structural factors derived by Rietveld refinement also support no or little substitution of Na, even though Na substitution causes little change in the refinements of XRD, Na substitution significantly degrades the refinements of ND (Table S3).

Table 2. Lattice constants and occupancies of 500, 600, and 700 °C products obtained from Rietveld analysis of X-ray and neutron powder diffraction data.

	XRD			ND		
	500°C	600°C	700°C	500°C	600°C	700°C
<i>a</i> /Å	4.1889(5)	4.1991(3)	4.1765(3)	4.1889	4.1991	4.1765
Occ. Mo	0.642(5)	0.672(19)	0.842(3)	0.642	0.672	0.842
Occ. N	1	1	1	1	1	0.72(9)
Occ. O				0	0	0.27(9)
<i>R_{wp}</i> /%	1.144	1.230	2.371	1.120	2.51	4.160

<i>S</i>	0.3820	0.4041	0.7762	1.1331	1.5848	1.6068
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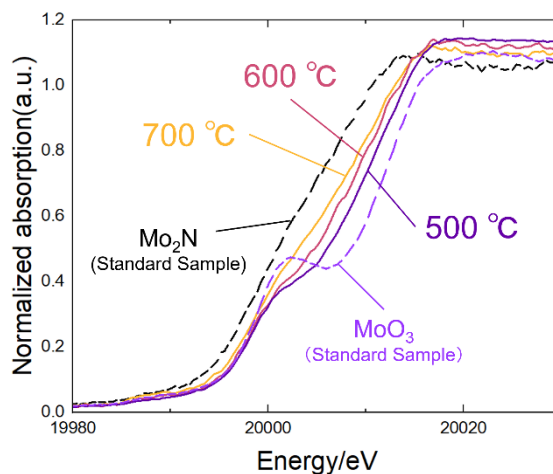


Figure 5. XANES spectra of the synthesized products at 500, 600, and 700 °C.

Figure 5 represents the XANES spectra of the synthesized product. The energy of the absorption edge is located between those of Mo_2N and MoO_3 , indicating the valence of molybdenum is less than Mo^{6+} but higher than $\text{Mo}^{1.5+}$. Assuming that the shift of edge is linearly changed with the valence of Mo, the valence is higher than three at 500-600 °C. The synthesized product does not contain the reported Mo_2N as an impurity because the onset of X-ray absorption is clearly higher than that of Mo_2N . As the heat-treatment temperature increases to 500, 600, and 700 °C, the absorption edge shifts to the low energy side, suggesting a decrease in the Mo valence. This shift is attributed to the reduction of molybdenum in both crystalline and amorphous phases.

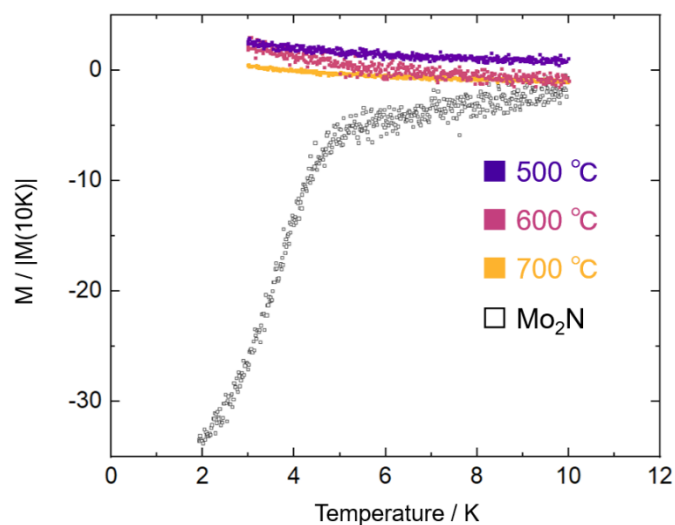


Figure 6. Temperature dependence of magnetic moment for 500 °C (purple), 600 °C(pink), 700 °C(orange), Mo₂N(black). That of Mo₂N refers to the literature ²⁵. Reproduced from ref²⁵. Copyright 2019 American Chemical Society.”

Figure 6 shows the magnetic properties of synthesized products. In contrast to the diamagnetic signal of Mo₂N with the superconducting transition temperature of ~ 5K, the synthesized product shows no diamagnetic signals. This is further evidence that the rock-salt phase found here does not contain reported γ -Mo₂N.

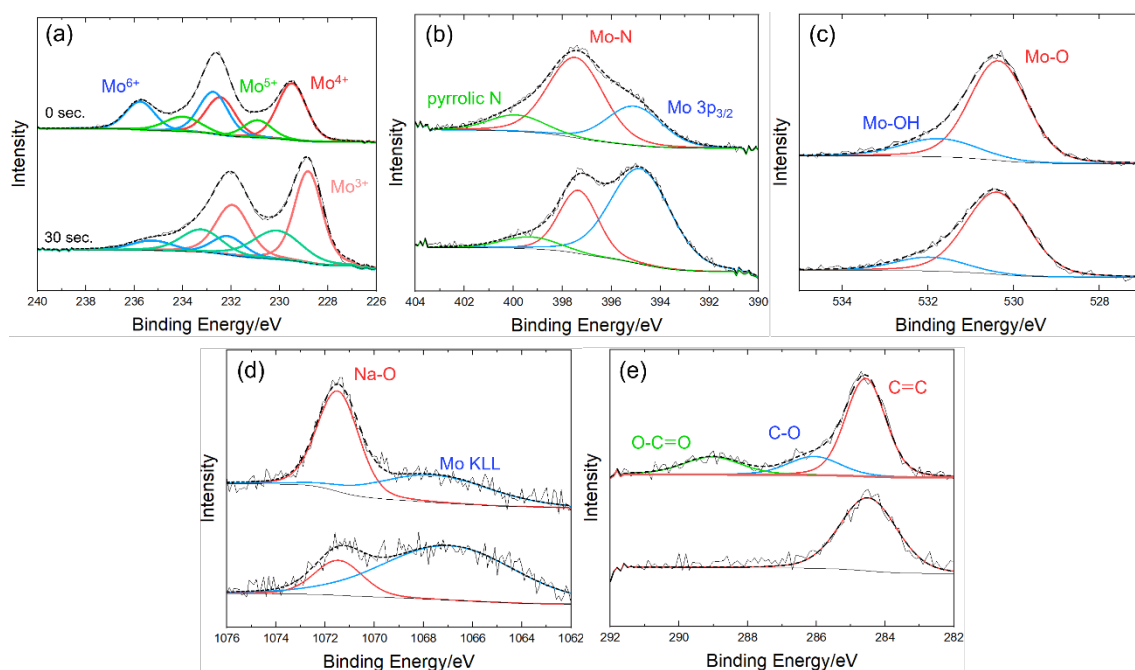


Figure 7. XPS spectra for the product synthesized at 600 °C. (a) Mo 3d (b) N 1s, Mo 3p (c) O 1s (d) Na 1s (e) C 1s. The figure shows XPS data after Ar⁺ ion etching for 0 and 30 seconds.

Figure 7 shows the XPS measurement results to clarify the surface state of the product synthesized at 600 °C. From the XPS data of Mo 3d (Figure 7 (a)), peaks attributed to Mo⁶⁺(232.7, 235.8 eV), Mo⁵⁺(231.0, 234.2 eV), and Mo⁴⁺(229.5, 232.6 eV) were observed⁴². The Mo⁶⁺ peak decreased with etching, while the Mo⁵⁺ and Mo⁴⁺ peaks shifted to lower energies after etching. The reason for the peak shift is presumed to be the reduction of molybdenum by Ar⁺ ion etching. N 1s pattern (Figure 7 (b)) was assigned to pyrrolic N (399.8 eV)⁴³, Mo-N (397.4 eV), Mo 3p_{3/2} (395.0 eV) are present⁴⁴⁻⁴⁶. Pyrrolic N disappears upon etching, suggesting its presence only on the surface. O 1s spectrum (Figure 7 (c)) displays two peaks at about 530.4, and 531.9 eV, indexed to Mo-O and Mo-

OH^{47,48}, suggesting the presence of amorphous molybdenum oxide and adsorption of hydroxyl groups on the surface. The Na 1s XPS spectrum of the 600 °C product is shown in Figure 7(d). There are two peaks, 1071.5 eV and 1066.7 eV, which are attributed to the Na-O bond and the Mo KLL⁴⁹. Figure 7(e) shows the XPS spectrum of C 1s. There are C=C (284.6 eV), C-O (286.1 eV), and O-C=O (289.0 eV), and it is assumed that O-C=O originates from CO₂ and CO adsorbed on the surface, and C=C and C-O derives from organic matter^{43,50}. The peaks of O-C=O and C-O have disappeared by etching, indicating that the surface includes these chemical species.

Discussion

Our elemental analysis suggests that the molar ratio of N/Mo was 1.72 in the product heat-treated at 500 °C and 0.828-0.973 from 550 °C to 700 °C. The large amount of nitrogen in the sample heat-treated at 500 °C is presumably attributed to the organic compounds derived from dicyandiamide; the decomposition of dicyandiamide via melamine, tri-s-triazine, and g-C₃N₄ is reported above 500 °C⁴⁰. Above 500 °C, a large amount of oxygen suggests the co-existence of γ -Mo₂N₃ with a surface amorphous phase, the surface layer of oxides/oxyhydroxides and absorbed oxygen/water⁵¹, which is also consistent with the XPS results, as illustrated in Figure 8.

From the XRD and ND patterns of the products synthesized at 500 and 600 °C, we propose the structural model of the rock-salt structure with fully occupied nitride anion and approximately two-third of occupied molybdenum cation, i.e., the composition may be also presented at γ -Mo₂N₃. This rock-salt structure is different from the

computationally predicted structure from the literature³⁴. The XANES shows that Mo in the synthesized molybdenum nitride has a higher valence than that in Mo₂N. Moreover, the magnetic properties also confirm that this synthesis nitride does not contain γ -Mo₂N. XANES also shows that the Mo valence decreases with increasing heating temperature, which is consistent with the anion-less molybdenum nitride synthesized at 700 °C, as characterized by XRD and ND. XPS has also revealed the existence of molybdenum with high valence, but also suggests the surface is covered by high-valence oxides, hydroxides, carbonates, and organic compounds. Therefore, we propose a core-shell model, as illustrated in Figure 8.

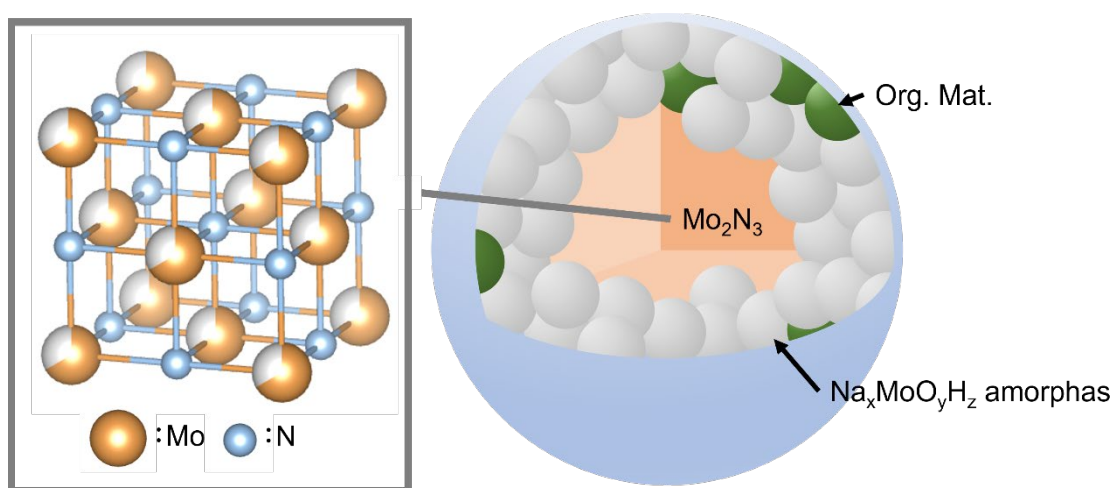


Figure 8. Proposed crystal structural model and surface structure of synthesized γ -Mo₂N₃.

γ -Mo₂N₃ with a rocksalt structure is calculated to be thermodynamically metastable^{33,34}. Because Na(OCN), which is the byproduct of the reaction shown in Figure 2(a), is a stable substance with standard enthalpy of formation $-405.39 \text{ kJ mol}^{-1}$ ⁵²,

it is speculated that the formation of metastable nitrogen-rich nitrides is driven by the formation of stable by-products, similar to other nitride syntheses^{25,26}. Moreover, the formation of gases, such as CO, H₂O and CO₂, which are thermodynamically stable byproducts, contribute to the entropy of the process. According to the formation mechanism of metastable nitrides proposed by computationally-predicted reaction energies⁵³, the formation of γ -Mo₂N₃ from Na₂MoO₄ but not from MoO₃ suggests that Na⁺ in Na₂MoO₄ and dicyandiamide together increase the effective chemical potential of nitrogen, which leads to the formation of metastable nitrides.

We consider that the low partial pressure of oxygen in a crucible is another factor the formation of nitrogen-rich oxynitride/nitrides. Nitrides that are oxygen-free in the lattice were obtained if the residual carbon remains (500 and 600 °C). Oxynitride was formed in the sample heat-treated at 700 °C, and no residual carbon was detected. Generally, nitrides are known to be oxidized when heated in air. However, in this system, the reaction with residual carbon would consume oxygen. Thus, carbon residual should be a requirement for producing nitrides that are oxygen-free in the lattice under ambient atmosphere, as the oxygen gas reacts with carbon to form carbon monoxide. In other words, the oxygen partial pressure should increase when carbon disappears, resulting in the formation of oxynitrides at 700 °C. Further analysis, such as in-situ XRD and/or TG-mass analysis, are necessary for understanding more detailed mechanism.

Conclusion

A simple setting of an aluminum crucible and box furnace enabled us to produce a

nitrogen-rich nitride, γ -Mo₂N₃, from Na₂MoO₄ · 2H₂O and dicyandiamide, which are mixed using a mortar and a pestle. XRD and ND showed the formation of nitrogen-rich molybdenum nitride, γ -Mo₂N₃. It crystallizes in the rocksalt structure with fully occupied nitride anion without incorporating oxide anion and cation vacancies. XANES and magnetic measurements also support that the product does not include γ -Mo₂N phase. Furthermore, Mo_{0.84}N_{0.72}O_{0.27} was produced by increasing the heating temperature. We proposed that the combination of Na₂MoO₄ and dicyandiamide increases the driving force to form metastable nitrides by forming thermodynamically stable byproducts, such as Na(OCN). We demonstrated that the classical setting used for oxide synthesis, box furnace, and aluminum crucible without nitrogen gas can be used to prepare new metastable molybdenum nitrides, and we believe that this method would further contribute to exploring nitride chemistry. Based on the superior catalytic activity of catalysts with different nitrogen contents^{54–57}, we believe that the synthesis of nitrogen-rich nitrides opens the door for inspiring new catalysts for highly efficient chemical and energy conversions.

Supporting Information

Additional Information regarding experimental data, details and materials including table and figure (PDF)

ASSOCIATED CONTENT

Summary of Rietveld refinements with different Na incorporation.

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Author Contributions

The manuscript was written with contributions from all authors. All the authors have approved the final version of the manuscript.

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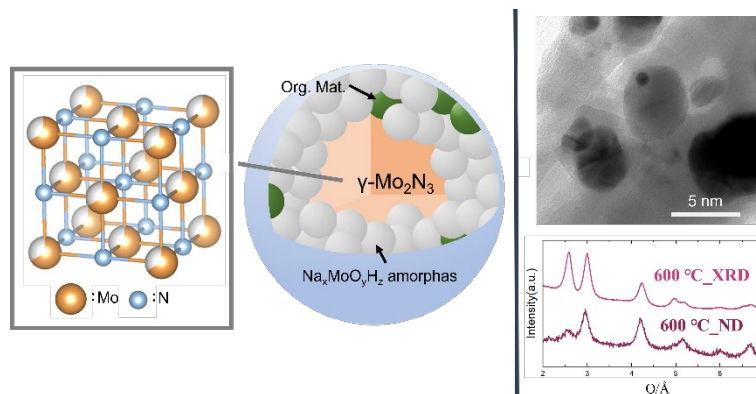
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TOC



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The classical apparatus, an aluminum crucible and a box furnace, produced nitrogen-rich molybdenum nitride with cationic vacancies, $\gamma\text{-Mo}_2\text{N}_3$ from Na_2MoO_4 and $\text{C}_2\text{N}_4\text{H}_4$.

The obtained nitride was found to have a core-shell structure covered with an amorphous oxide.