**Supporting Information**

# Nitrogen-Rich Molybdenum Nitride Synthesized in a Crucible under Air

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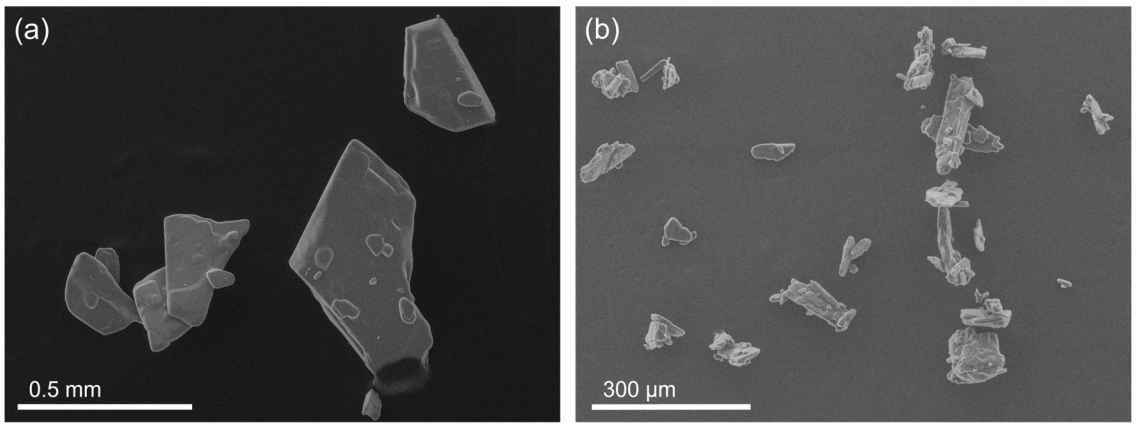


**Figure S1. SEM image of starting materials, (a)$Na_2MoO_4 \cdot 2H_2O$, (b) dicyandiamide ($C_2N_4H_4$).**

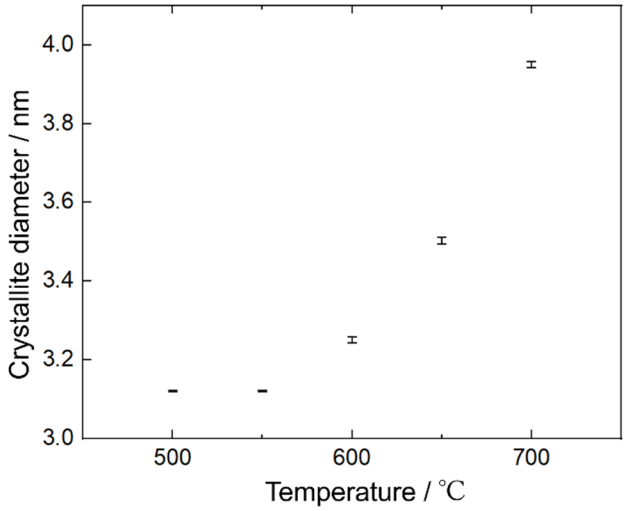


**Figure S2. Dependence of synthesis temperature and crystalline size of $Mo_2N_3$ determined by Scherrer equation.**

**Table S1. Simultaneous analysis results of XRD and neutron diffraction of the product synthesized at 600 °C.**

| | |
|---|---|
| **Lattice / Å** | 4.186(13) |
| **Occ. Mo** | 0.577(6) |
| **Occ. N** | 0.996(5) |
| **$R_{wp}$/%** | 3.4678 |

**Figure S3. Simultaneous analysis profile of XRD and neutron diffraction of the product synthesized at 600 °C**

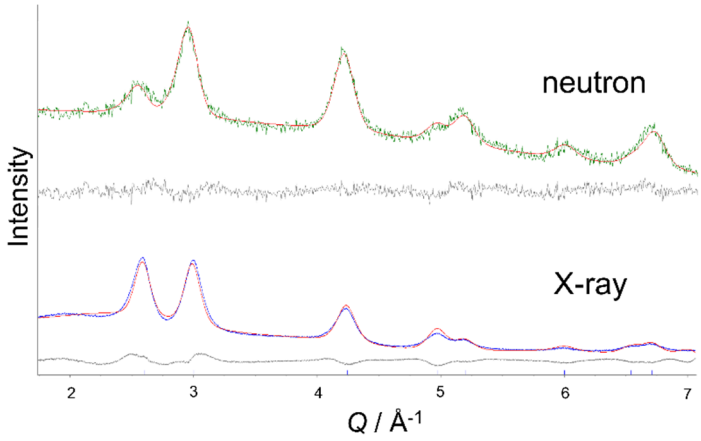

**Table S2. Hypothetical Na substitution effect on the lattice constants and occupancies of the product synthesized at 600 ℃.**

**XRD**

| | **Na 0** | **Na 0.1** | **Na 0.2** |
|---|---|---|---|
| **Lattice / Å** | 4.1991(3) | 4.1991(3) | 4.1991(3) |
| **Occ. Mo** | 0.672(19) | 0.645(2) | 0.620(2) |
| **Occ. N** | 1 | 1 | 1 |
| **Occ. Na** | 0 | 0.1 | 0.2 |
| $R_{wp}$**/%** | 1.230 | 1.226 | 1.229 |
| ***S*** | 0.4041 | 0.4031 | 0.4039 |

**ND**

| | **Na 0** | **Na 0.1** | **Na 0.2** |
|---|---|---|---|
| **Lattice / Å** | 4.1991 | 4.1991 | 4.1991 |
| **Occ. Mo** | 0.672 | 0.645 | 0.620 |
| **Occ. N** | 1 | 1 | 0.3934 |
| **Occ. O** | 0 | 0 | 0.6066 |
| **Occ. Na** | 0 | 0.1 | 0.2 |
| $R_{wp}$**/%** | 2.51 | 2.715 | 4.264 |
| ***S*** | 1.5848 | 1.7065 | 1.6465 |

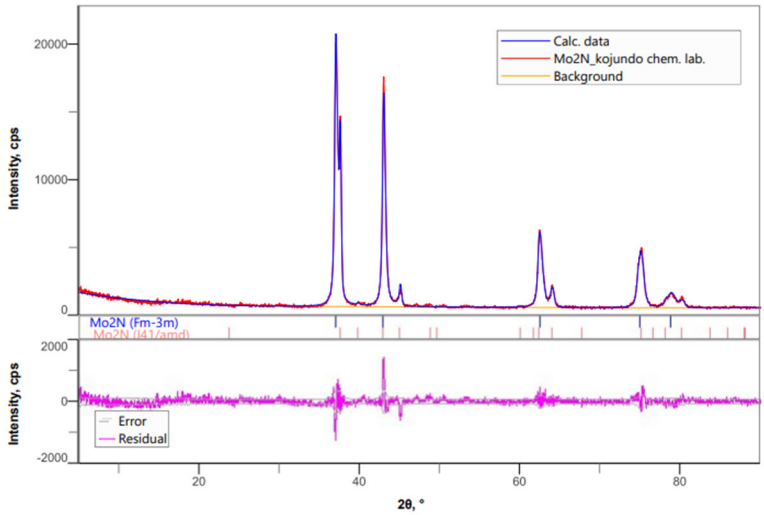


**Figure S4. Rietveld refinement of $Mo_2N$ used as a standard of XANES analysis. Brack line is experimental value, red one is calculated date, and blue one is residual value.**

**Table S3. Rietveld analysis results of $Mo_2N$ used in XANES.**

| | **$Mo_2N$ ($Fm\bar{3}m$)** | **$Mo_2N$($I4_1/amd$)** |
|---|---|---|
| ***a*/Å** | 4.2051(4) | 4.2102(6) |
| ***b*/Å** | 4.2051(4) | 4.2102(6) |
| ***c*/Å** | 4.2051(4) | 8.0445(11) |
| **Occ. Mo** | 1 | 1 |
| **Occ. N** | 0.734(13) | 0.54(5) |
| **Mass %** | 74.4(2) | 25.6(2) |

**Figure S4. Details of the $Ar^+$ etching channel used.**

| | |
|---|---|
| **Beam energy (eV)** | 3000 |
| **Emis current (mA)** | 20 |
| **Gas Pressure (Pa/$10^2$)** | 9.5 |
| **Etching rate (nm $min^{-1}$)** | 6.0 |