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Supporting Information

Nitrogen-Rich Molybdenum Nitride Synthesized in a Crucible under Air

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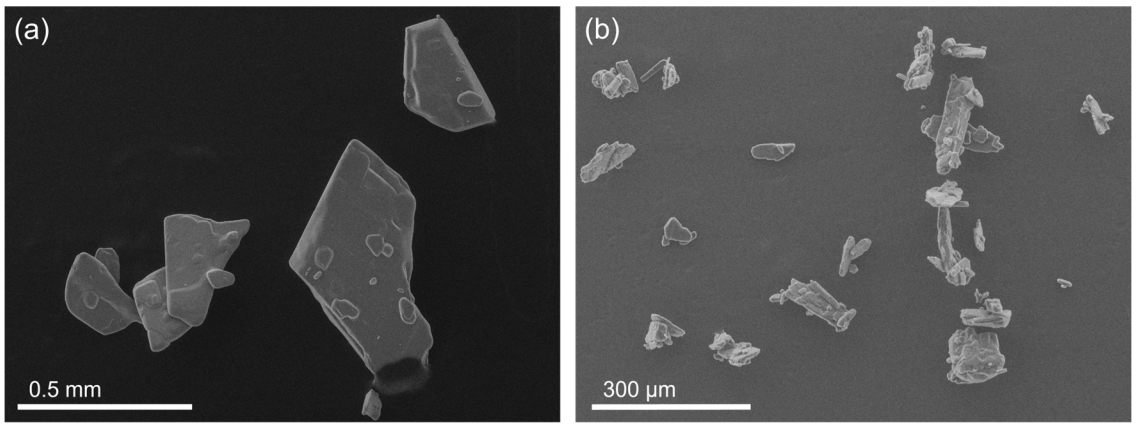

Figure S1. SEM image of starting materials, (a)$Na_2MoO_4 \cdot 2H_2O$, (b) dicyandiamide ($C_2N_4H_4$).

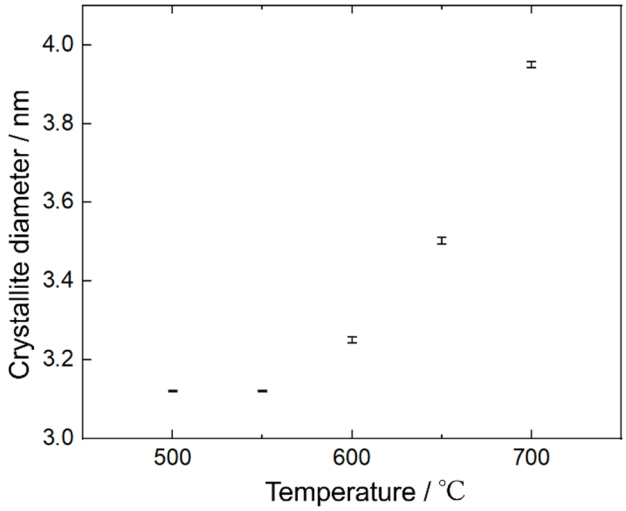

Figure S2. Dependence of synthesis temperature and crystalline size of Mo_2N_3 determined by Scherrer equation.

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

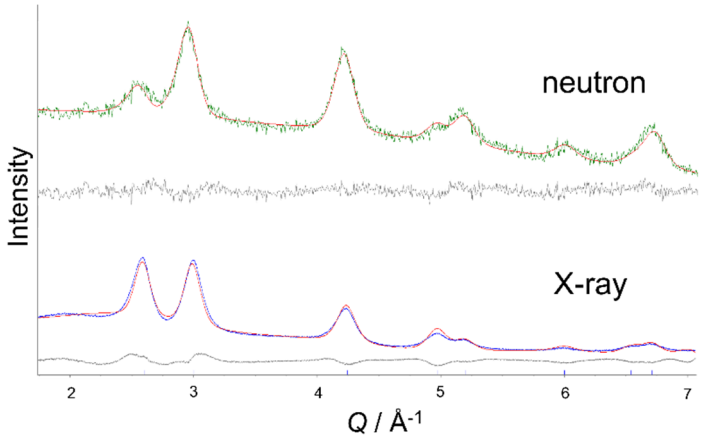

Table S2. Hypothetical Na substitution effect on the lattice constants and occupancies of the product synthesized at 600 ℃.

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

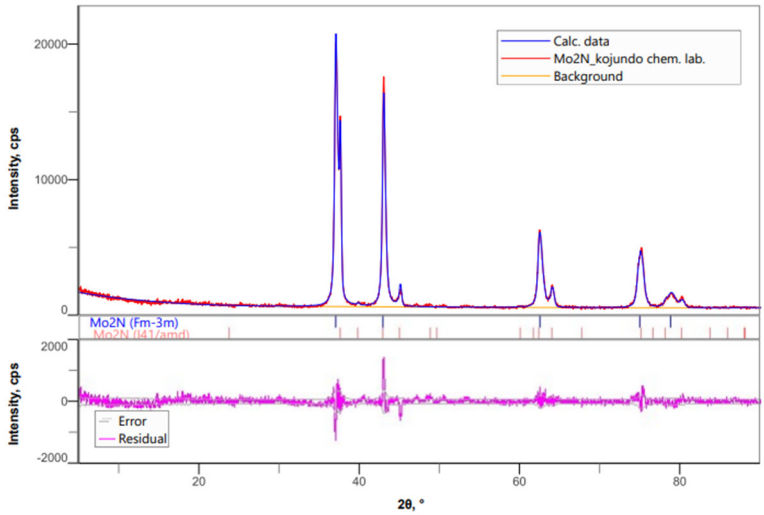

Figure S4. Rietveld refinement of Mo_2N used as a standard of XANES analysis. Brack line is experimental value, red one is calculated date, and blue one is residual value.

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