



Title	Rapid In Situ Investigation of Nitride Synthesis: Ambient Atmospheric Nitridation of 3d Metal Oxides Using Dicyandiamide
Author(s)	Demura, Momoka; Ono, Keigo; Nagao, Masanori et al.
Citation	Chemistry of Materials, 36(23), 11490-11498 https://doi.org/10.1021/acs.chemmater.4c02137
Issue Date	2024-11-12
Doc URL	https://hdl.handle.net/2115/97308
Rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in Chemistry of materials, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://pubs.acs.org/doi/full/10.1021/acs.chemmater.4c02137 .
Type	journal article
File Information	cm4c02137_si_001 (1).pdf



Supporting Information: Rapid In Situ Investigation of Nitride Synthesis: Ambient Atmospheric Nitridation of 3d Metal Oxides Using Dicyandiamide

Momoka Demura¹, Keigo Ono², Masanori Nagao³, Takafumi Yamamoto⁴, Chul-Ho

Lee², Aichi Yamashita⁵, Chikako Moriyoshi⁶, Shohei Tada⁷, Yuji Masubuchi⁷, Yuta

Fujii⁷, Kiyoharu Tadanaga⁷, Akira Miura^{7*}

¹Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13, Nishi 8, Sapporo, Hokkaido, 060-8628, Japan

² National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, 305-8568, Japan

³Center for Crystal Science and Technology, University of Yamanashi, Kofu, 400-0021, Japan

⁴Department of Chemistry, Graduate School of Science, Kyoto university, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

⁵Department of Physics, Tokyo Metropolitan University, 1-1, Minami-osawa, Hachioji 192-0397, Japan

⁶Graduate School of Advanced Science and Engineering, Hiroshima University, 1-3-1 Kagamiyama, Higashihiroshima, 739-8526, Hiroshima, Japan

⁷Faculty of Engineering, Hokkaido University, Kita13 Nishi8 Sapporo, 060-8628, Japan

Email: amiura@eng.hokudai.ac.jp

Table S1. The mixing ratio of the sample before heating and volume of alumina crucible used

Metal precursor: dicyandiamide	Molar ratio	Sum of mixed sample/g	Crucible capacity/ml
NaVO ₃ : dicyandiamide	3:5	24	60
NH ₄ VO ₃ : NaHCO ₃ : dicyandiamide	1.5:1.5:5	6	-
V ₂ O ₅ : dicyandiamide	3:5	6	-
NaCrO ₂ : dicyandiamide	3:5	6	40
NaFeO ₂ : dicyandiamide	3:5	6	40
NaMnO ₂ : dicyandiamide	3:5	6	40

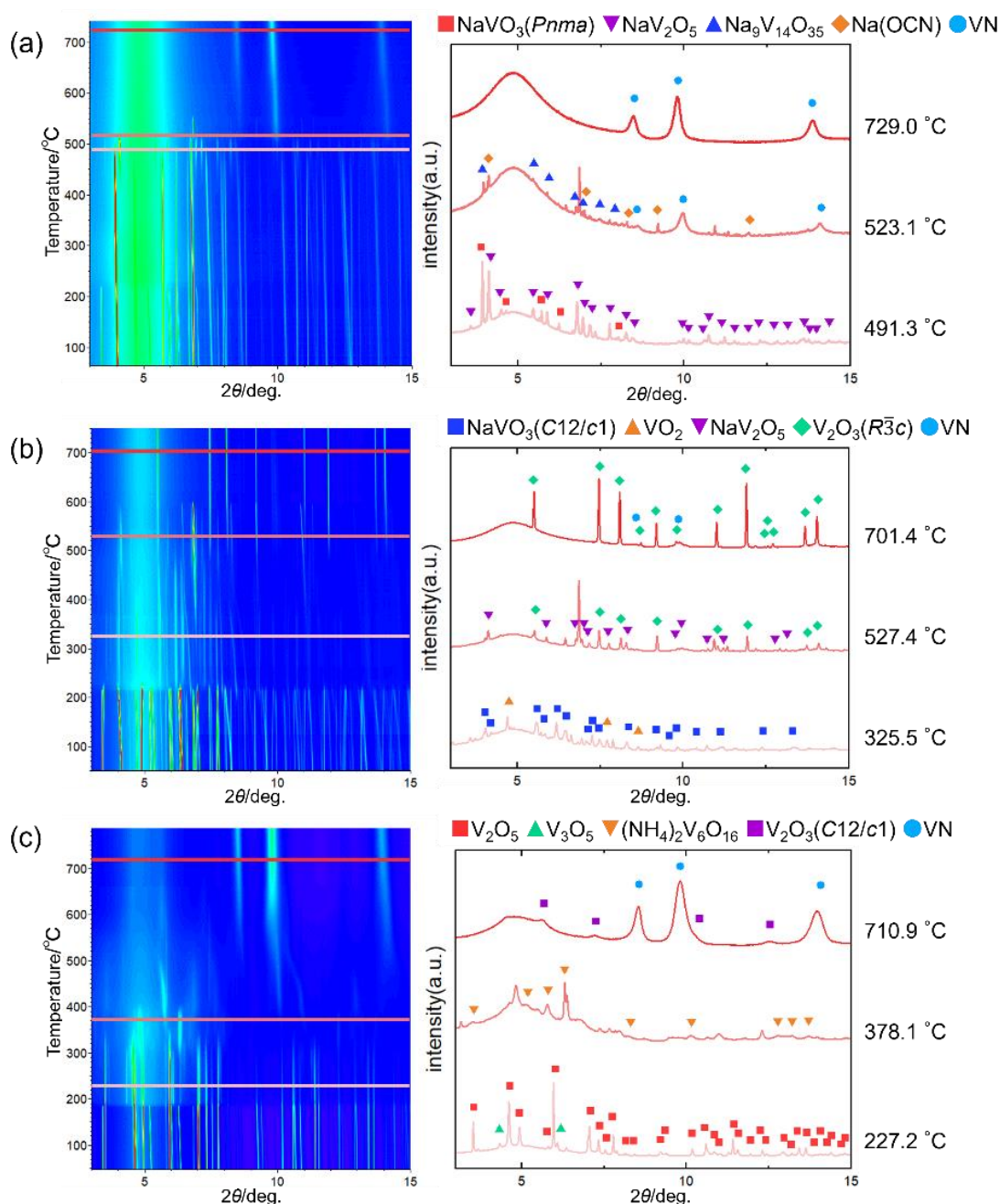


Figure S1. 2D plots of an in-situ synchrotron XRD patterns and 1D XRD patterns of (a) $\text{NaVO}_3 + \text{C}_2\text{H}_4\text{N}_4$ ($\lambda=0.354050 \text{ \AA}$), (b) $\text{NH}_4\text{VO}_3 + \text{NaHCO}_3 + \text{C}_2\text{H}_4\text{N}_4$ ($\lambda=0.354050 \text{ \AA}$), and (c) $\text{V}_2\text{O}_5 + \text{C}_2\text{H}_4\text{N}_4$ ($\lambda=0.35769 \text{ \AA}$) at selected heating temperatures. The horizontal lines on the 2D plots correspond to the selected 1D XRD patterns. Peaks on the XRD profiles are assigned symbols corresponding to each crystalline phase, and peaks without symbols are peaks for which no crystalline phase could be identified and indexed.

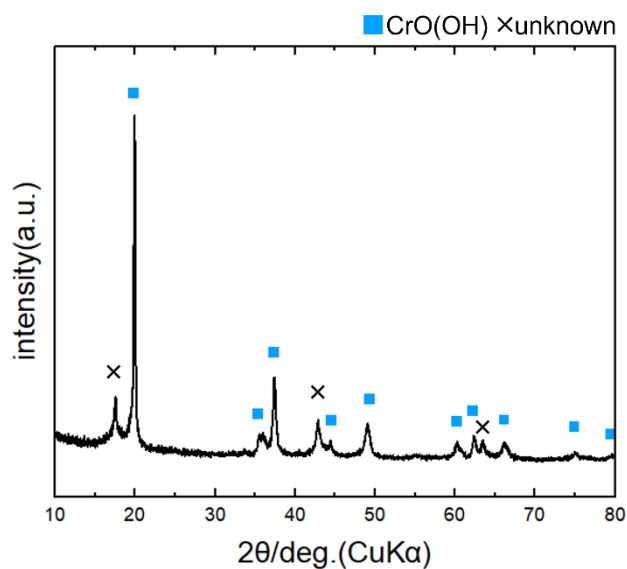


Figure S2. XRD pattern of the final products of NaCrO_2 and dicyandiamide heated at atmospheric pressure. NaCrO_2 and dicyandiamide were mixed in molar ratio 3:5 to a total weight of 6 g, and heated to 580°C for 10 minutes, washed with water, centrifuged and dried.

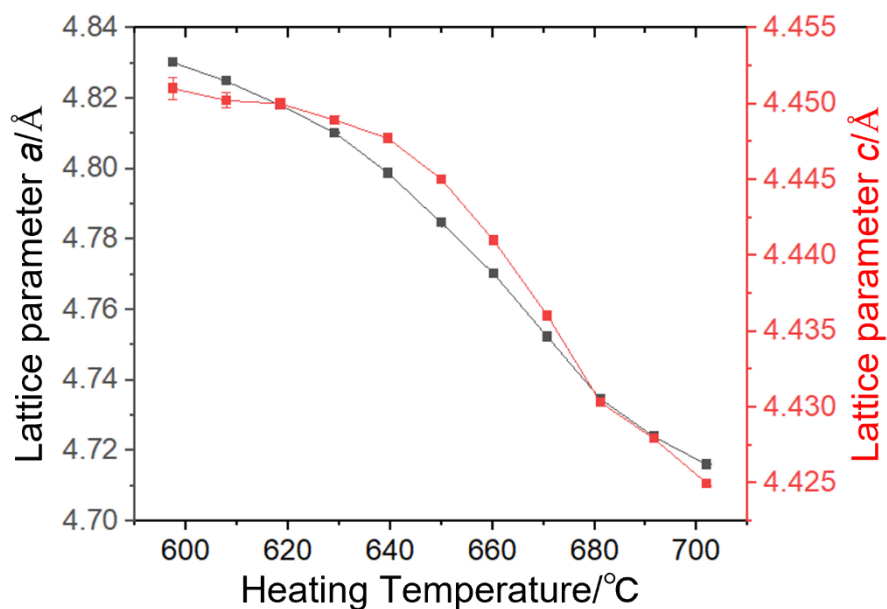


Figure S3. Lattice constant of Fe_3N_x with increasing heating temperature.

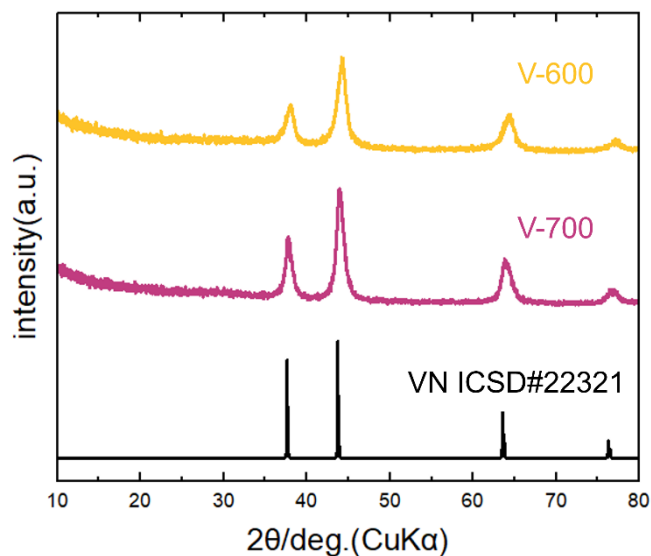


Figure S4. XRD patterns of vanadium nitride synthesized in air. The yellow and purple XRD pattern shows the product heated at 600 and 700 °C for 30 minutes respectively. The vanadium nitride reference pattern (ICSD#22321) is shown at the bottom.

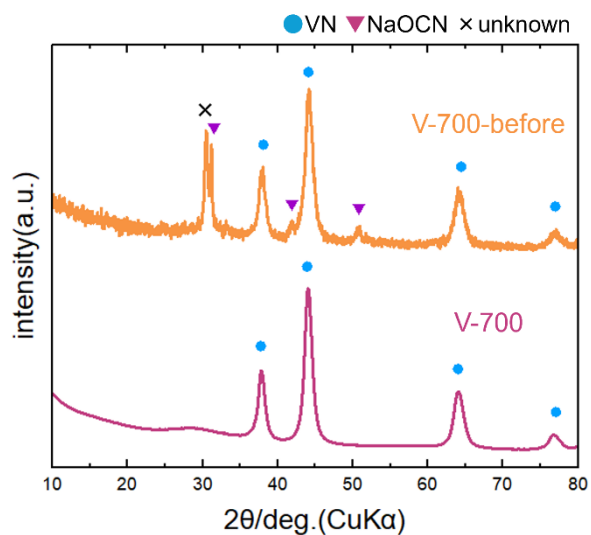


Figure S5. XRD patterns of vanadium nitride synthesized in air before washing. Both XRD patterns are from products heated at 700 °C for 30 min, while the yellow and purple patterns are before and after cleaning, respectively.

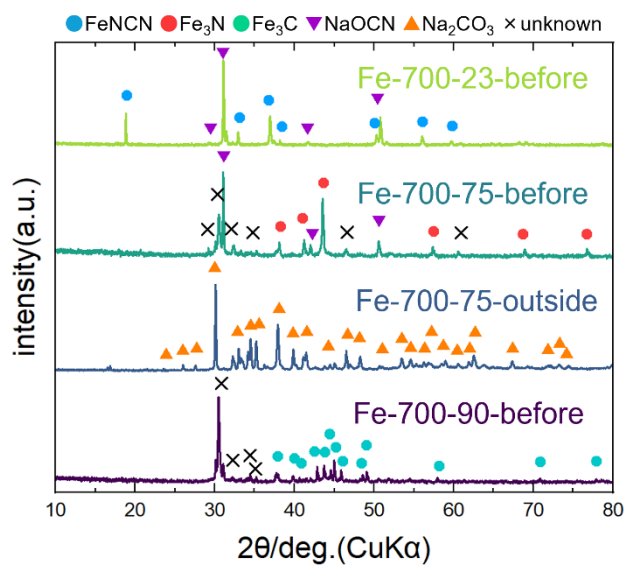


Figure S6. XRD patterns of NaFeO₂ and dicyandiamide heated at 700 °C before washing, and XRD patterns of the white powder on the outside of the crucible after heating for 75 minutes.



Figure S7. Photo of Fe-700-75 crucible after heating.

Table S2. Elemental analysis for C, H, N, and O of vanadium nitride.

	V-600	V-700
C / wt %	2.42	0.66
H / wt %	0.82	0.92
N / wt %	19.63	14.63
O / wt %	-	14.59

Table S3. Lattice parameters of iron compounds synthesized under an atmospheric condition

	Fe-700-23 (FeNCN)	Fe-700-75 (Fe ₃ N)	Fe-700-90 (Fe ₃ C)
<i>a</i> /Å	3.27913(11)	4.71886(15)	5.0909(4)
<i>b</i> /Å	= <i>a</i>	= <i>a</i>	6.7424(5)
<i>c</i> /Å	9.4177(5)	4.3782(3)	4.5269(3)

Table S4. CHN analysis results for Fe-based products

	Fe-700-23 (FeNCN)	Fe-700-75 (Fe ₃ N)	Fe-700-90 (Fe ₃ C)
C / wt%	12.35	0.00	6.43
H / wt%	0.17	0.28	0.36
N / wt%	29.15	4.91	0.33

Table S5. CHN analysis results of Mn-700-10

	C / wt%	H / wt%	N / wt%
Mn-700-10	11.25	0.08	26.14